RADIUM DISTRIBUTION IN SOILS, ANALYSED WITH SEQUENTIAL EXTRACTION, AND ITS EFFECT ON RADON EMANATION

Cecilia Edsfeldt

Royal Institute of Technology, Division of Engineering Geology, SE-100 44 Stockholm, Sweden.
Phone: +46 8 790 68 07; Fax: +46 8 790 68 10; e-mail: ceciliae@ce.kth.se

The radium distribution of the soil is one important parameter governing radon emanation. The present study’s main objective is to investigate radium distribution in different Swedish soils, using chemical selective sequential extraction, and to compare the outcome with the radon emanation of the sampled soil types. Investigated samples were unconsolidated sediments (till, sand and clay) from the Stockholm area. In the developed selective sequential extraction procedure, ammonium chloride and hydrochloric acid were used to extract an exchangeable and an oxide-bound fraction from grain-size separated samples. The soil residues were digested after extractions. Radium-226, uranium, iron, manganese, calcium and barium were analysed from the extractant solutions and the digested samples. Radon emanation was measured on unleached samples. In pedogenic soil phases concentrations of all elements, as well as Rn emanation, increased with decreasing grain size and increasing specific surface area. Radium was very well correlated with Ca and Ba, implicating an association between these elements in the sampled soils. A major portion of the Ra was bound on the surfaces of grains. Radium in oxide bound phase was the primary source of emanating radon, although exchangeable radium was also important. Radium in the oxide bound was very well correlated with iron, which indicates that this Ra was adsorbed to or co-precipitated with iron oxides. However, since iron in soils can be well correlated with organic matter, it can not be ruled out that this Ra was partly associated with organic matter that was leached in the same extraction. Radium bound in the crystal lattice of minerals did not seem to contribute to the radon emanation. The sequential extraction method for characterising radium distribution is promising. With the sequential extraction method, it is possible to identify in which soil phase radium resides, and to gain information about the complicated soil system that controls the emanation of radon.

Keywords: $^{222}$Rn, $^{226}$Ra, radium, radium distribution, radon emanation, radon risk, radon, sequential extraction, soil, soil geochemistry

INTRODUCTION

Radon in indoor air is a recognised health-risk, which has led to extensive research in the area of radon emanation. The actual mechanisms that control radon emanation are not totally understood. The radium distribution of the soil is one important parameter governing radon emanation. Several workers have presented theoretical calculations of how the radium distribution affects radon, e.g. Morawska and Phillips, (1993). According to their formulae, the theoretical radon emanation coefficient would be 0.00006 for a spherical sand-sized grain (0.5 mm) without inner porosity, with a recoil range of 40 nm ($^{222}$Rn) and a homogeneous Ra distribution, whereas it would be 0.5 for the same grain assuming a surface radium distribution. Knowledge of the radium distribution is thus of key importance in characterising emanation processes in different materials. Not many have studied this in practice.

One approach towards characterising radium distribution is to use selective sequential extraction. The same soil sample is extracted with a sequence of selective extractants, removing different soil phases in each step, thus differentiating soil phases. The method has been used for characterisation of uranium and radium distributions, e.g. on uranium mine tailings (Landa, 1984) and on natural soils (Greeman and Rose, 1996; Greeman, et al., 1990). The aim of this study is to determine the
radium-226 distribution in soils, and its effect on radon-222 emanation, using selective sequential extraction. The major differences between this and previous work (e.g. Greeman and Rose 1990; Greeman et al., 1999) is a different extraction procedure and the fact that the soil samples in the present study were sieved prior to extractions. This was done in order to establish the influence of grain-size on Ra adsorption and distribution.

MATERIALS

The stratigraphy of the sampling area (NV of Stockholm, Sweden) consists of basement Precambrian migmatite-gneiss and granite-gneiss with pegmatite and aplite dikes, and younger granites (Stålhös, 1969), overlain by Quaternary deposits; till, glaciofluvium, glacial and postglacial clay (Möller and Stålhös, 1965). The granites (granite-gneisses) are enriched in uranium, why samples collected in this area were expected to have a radium content that was somewhat higher than normal. Soil Rn measurements close (~50 m) to the till sampling gave a Rn content of 70 000 Bq/m$^3$ in till, and 150 000 Bq/m$^3$ in clay, which is considered to be high radon ground. Gamma spectrometry measurements at the same location gave a soil uranium content of 5-6 ppm.

Samples of glacial till (2 samples), sand and clay (1 sample each) were obtained. Sample material was mainly granitic. Samples of till and sand were dried at room temperature and dry-sieved to obtain the fine fraction, consisting of silt and clay particles (<0.063 mm). The coarser portion of the samples were washed to remove remaining clay and silt particles, then dried at room temperature and sieved. The clay was not sieved. Sedimentation analysis of clay and fine material (silt and clay) of till and sand was performed according to Stål (1972). The clay sample consisted of 66 % clay-sized material (grain-size <0.002 mm) and negligible amounts of grains >0.06 mm.

METHODS

Sequential extractions, radon emanation measurements and chemical analysis of extraction fluids are outlined in Figure 1. There are no general standards sequential extraction procedures, thus a new procedure suitable for the goals of this project was developed after Landa (1984) and common sequential extraction procedures (e.g. Förstner, 1993; Nordic Council of Ministers, 1988). The usual sequential extraction scheme includes extraction agents for exchangeable cations, carbonates, organic material, oxides (of Fe, Mn and Al), and residual. The source material for the sampled soils was mainly granitic and the content of organic material was low; thus separate extractants for carbonates and organic matter were excluded.

All chemicals used in the procedure were at least pro analyti (p. a.) grade. After extraction samples were filtered through Munktells OOH paper filters. Filtrates and digested samples were acidified with nitric acid (0.5 ml conc. HNO$_3$ (suprapur)/100 ml solution) to ensure a low pH, in order to reduce adsorption onto flasks and stabilise the solution. Soil residues were air-dried between extractions. Sequential extractions were performed on three grain-sizes of sand (1-2 mm, 0.125-0.25 mm and <0.063 mm), on four grain-sizes of till (1-2 mm, 0.25-0.5 mm, 0.125-0.25 mm and <0.063 mm), and on unsieved clay (with the exception of the first extraction for dissolved elements).

Dissolved elements - This extraction step was performed on naturally moist clay and the air-dried fine fractions of sand and till (not on coarser grain sizes, since they were washed prior to sieving).
20 or 40 g of sample was equilibrated with 25 or 50 ml of deionised water for two hours, then centrifuged and filtered. The filtrate was diluted to 100 ml and acidified.

**Exchangeable elements** (cation exchangeable elements, including elements weakly bound to organic matter) – 25 g of air-dried sample was mixed with 100 ml of 1M NH₄Cl (ammonium chloride) and agitated on a shaker for two hours. If the leaching solution was cloudy after shaking, it was centrifuged before filtration. The sample was washed with 1M NH₄Cl to 100 ml of filtrate and acidified.

**Oxide bound elements** (elements coprecipitated with Fe/Mn/Al oxides and elements strongly bound to organic matter) - 2.5 g of soil residue was boiled with 100 ml of 1 M HCl (hydrochloric acid) for 15 minutes, then filtered. The sample was washed with deionised water until the filtrate volume added up to 100 ml.

**Residual** (elements bound in the crystal lattice of minerals) – Soil residues from the preceding leaching step were dried at 105 °C for 24 hours, ignited at 550 °C for 1 hour, and then ground in an opal mortar. The powdered sample (0.25 g) was mixed with lithium metaborate (LiBO₃, 0.75 g), and fused by heating at 1000 °C for 45 minutes; resulting in a “glass” bead that was dissolved in 25 ml of 5 % HNO₃ during shaking. The dissolution method is described by Potts (1987).

Radium in extractant solutions and digested samples was analysed with α-spectrometry by means of liquid scintillation counting (LSC). Sample solutions were pre-treated in order to isolate ²²⁶Ra, and analysed according to Suomela (1993). The procedure includes precipitation of Ra together with barium sulphate and dissolution of the precipitate in EDTA. Samples with obvious content of humic acids (yellow-brown colour) were digested with hydrogen peroxide (H₂O₂) prior to the pre-treatment. Standard deviations ranged from 7-22 % in the dissolved phase, from 1-9 % in the exchangeable phase (with the exception of Till 2 <0.063 mm: 25 %) and from 4-20 % in the oxide bound phase. The concentrations of Ra in the residual were under the detection limit, thus the exact Ra content in this phase is not known. The concentration can be estimated from the total concentration of Ra subtracted by the total concentration of Ra in surface-bound fractions.

Uranium was analysed by ICP-MS (Induced Coupled Plasma - Mass Spectrometry; Potts, 1987). Standard deviations were 0.2-5 % for the dissolved, oxide bound and residual phases and 4-12 % for the exchangeable phase. Iron, manganese, calcium and barium were analysed with ICP-AES (Induced Coupled Plasma - Atomic Emission Spectrometry). Standard deviations were generally less than 1 %. For both types of ICP analyses four consecutive measurements were made on each sample. Standard solutions with a matrix similar to the leachate matrix were used and potential contamination was checked by analysing method blanks. Samples were analysed in a random order to prevent false trends caused by instrument drift, which was checked by analysing control standards after every 7th or 8th sample.

Total radium content of sieved, unleached samples was determined by gamma spectrometry at the Kernfysisch Versneller Instituut (KVI), Netherlands. The analysis procedure is described in van der Graaf et al. (1998a). Radon exhalation measurements were performed at the KVI, Netherlands, in a sealed exhalation chamber, where nitrogen gas, flowing through the container, acted as a radon carrier. After passing the container, the gas mixture was passed through activated charcoal, which adsorbed the radon. The radon activity of the charcoal was then measured with a gamma spectrometer. The measurement procedure is carefully described in van der Graaf et al. (1998b).
The exhalation measurements were performed on dry samples, excluding the influence of soil moisture. The soil was arranged in layers with a thickness of about 0.3-3 cm, which is considerably less than the Rn diffusion length in these materials (≈2 m). All Rn that emanated from the soil can thus be assumed to have exhaled, and the Rn emanation coefficient can be calculated with the knowledge of the total Ra content in the samples according to: \( R_{\text{em}} = E/(R_{\text{a}} \cdot \lambda_{\text{Rn}}) \), where \( R_{\text{em}} \) = Rn emanation coefficient, \( E \) = Rn exhalation \([\text{Bq} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}]\), and \( \lambda_{\text{Rn}} \) = Rn decay constant \([2.0985 \cdot 10^{-6} \text{s}^{-1}]\).

RESULTS

Generally, concentrations of Fe, Mn, Ca, Ba, U and Ra in all surface-bound soil phases increased with decreasing grain-size (Figures 2 and 3). The maximum concentration was most often attained in the clay sample. Generally Ra correlated better with Ca than U did; and U correlated better with Fe than Ra did.

Dissolved elements - Generally low concentrations of all analysed elements.

Exchangeable elements - Calcium was clearly most predominating in the exchangeable fraction, with concentrations about two orders of magnitude greater than the other elements. More than 10 % of total Ra was found in the exchangeable fraction, 1-16 % of total Ca, and less than 1 % of the other elements (Figure 2).

Oxide bound elements - Iron predominated in the fraction that was extracted with hydrochloric acid. Fe and Mn had the highest relative occurrence, 20-70 %, with the highest number corresponding to the clay sample (Figure 3).

Residual - Regarding the residual fraction, the concentrations of elements were about equal in all fractions, and did not increase with decreasing grain-size.

Radon exhalation \( E \), radon emanation coefficients and total \(^{226}\text{Ra}\) concentrations of unleached samples are displayed in Table 1. The total Ra concentration corresponds closely to the sum of Ra in surface bound fractions (exchangeable + oxide bound), indicating a low Ra content in the residual. The Rn emanation increased with decreasing grain size. The Rn emanation coefficients are rather low, depending on the fact that the Rn exhalation was measured on completely dry samples.

DISCUSSION

Expected, obtained and an interpretation of results from sequential extractions are summarised in Table 2. Element concentrations in filtrates from all extractions were found to increase with decreasing grain-size. This is to be expected, due to the increased adsorption/precipitation onto smaller particles, resulting from the larger specific surface area (Megumi and Mamuro, 1974). In accordance with the results of Greeman et al. (1999), this study shows that Ra has a better overall correlation with Ca, while U correlates better with Fe. Ra was also well correlated with Ba, and it is thus concluded that Ra was associated with Ca and Ba in the investigated soils.

The element distribution in the ammonium chloride extraction, with relatively high concentrations of Ca and Ba, implies that cation-exchangeable elements were indeed extracted in this leaching
step. In the acid-leached fraction, all analysed elements correlated very well for all soil types and grain-size fractions. The iron concentrations were much higher than the concentrations of the other elements, indicating that the iron oxides were partly dissolved, liberating elements adsorbed to or co-precipitated with these. The even concentrations in the residual was expected since this phase is marginally affected by pedogenic processes.

That Rn emanation increases with decreasing grain size is explained partly by the recoil theory (e.g., Fleischer, 1980), but it primarily depends on the fact that the smaller grains tend to have a larger total concentration of Ra, due to the larger surface area (Figure 4). The Rn emanation (E) was very well correlated with Ra concentrations in the acid-leached fraction. The correlation was also good with Ra in the exchangeable, but the total amount of Ra in this phase was smaller. Results from multiple regression point to Ra in oxide bound phase as the variable that was most important with respect to the radon emanation. It can thus be assumed that the Ra contributing to Rn emanation was primarily associated with iron oxides (or strongly bound to organic matter) on the surface of soil grains. Ra in the exchangeable phase was also important, while radium in the crystal lattice of minerals seems to have been of minor importance.

Research results from Greeman et al. (1999) and Hogue et al. (1997) suggest that radium that contributes to radon emanation is primarily bound to organic matter and to the exchangeable fraction, while uranium, to a large extent, is bound to Fe oxides. Since the present study did not have a separate extractant for the organic phase, Ra bound to organic matter was leached at either the salt (weakly bound) or the acid extraction step (strongly bound). The very good correlation between Ra and Fe in the acid extraction step does not suggest that the organic phase contribute significantly to the result in this phase, thus the results of this study indicate a larger importance of the Fe oxide phase than does the results of Greeman et al. (1999). However, there is a possibility that the Ra is connected with Fe-organo-metallic complexes that also might have been leached in this extraction, rather than with Fe oxides, which would then be more in accordance with Greeman et al. (1999). This possibility is supported by the results of Karltun and Gustafsson (1993) that show a good correlation between Fe and Al oxides and organic matter in soils.

The developed sequential extraction method worked well, the intended soil phases were extracted in the extraction steps designed for them. However, an improved resolution would have been advantageous, and thus a separate extractant for organic matter would have been desirable. All the elements analysed from the extractant solutions gave valuable information. Ca is a typically exchangeable element, while Fe precipitates as iron oxides. They give essential information on what soil phase have really been extracted. Mn precipitates as oxides, as Fe does, and Ba is interesting because Ba\(^{2+}\) behaves similarly to Ra\(^{2+}\) in most environments. However, an analysis of silica (Si; possible dissolution of crystalline matter), aluminium (Al; presence of Al oxides), thorium (Th; comparison with other work) and organic carbon (C; extraction of organic matter) would also have been desirable. The method will be revised prior to further use. The present study is an initial study to test the sequential extraction method for different Swedish soil types. Further studies will be performed in order to establish if the method gives results that are representative of the investigated soils.
CONCLUSION

Determining radium distribution using sequential extraction gives information about the radon risk potential of a soil. The present and previous studies (e.g., Landa, 1984; Greeman and Rose, 1996; Greeman et al., 1999) show that Ra that can be extracted from soil by simple methods is the primary source of emanating radon. The sequential extraction method can be used to gain valuable knowledge concerning Ra geochemistry, which can be taken into account when radon risk models are developed.

ACKNOWLEDGEMENTS

I would like to thank Emiel van der Graaf and the others at the Kernfysisch Versneller Instituut, Groningen, Netherlands, for the opportunity to perform radon exhalation measurements at their laboratory. This work was funded by the Swedish Radiation Protection Institute, and the Royal Institute of Technology, Stockholm.

REFERENCES


Table 1: Radon exhalation (E), activity concentrations of $^{226}$Ra, and Rn emanation coefficients (Rn eman) of unleached soil samples.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Grain size [mm]</th>
<th>E [Bq/(kg s)]</th>
<th>$^{226}$Ra [Bq/kg]</th>
<th>Rn eman$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Till 1</td>
<td>&gt;1</td>
<td>1.2E-05</td>
<td>33.4</td>
<td>0.171</td>
</tr>
<tr>
<td></td>
<td>&gt;0.25</td>
<td></td>
<td>32.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;0.125</td>
<td>1.48E-05</td>
<td>36.7</td>
<td>0.192</td>
</tr>
<tr>
<td></td>
<td>&lt;0.063</td>
<td>5.76E-05</td>
<td>121.4</td>
<td>0.227</td>
</tr>
<tr>
<td>Till 2</td>
<td>&gt;1</td>
<td>8E-06</td>
<td>32.2</td>
<td>0.115</td>
</tr>
<tr>
<td></td>
<td>&gt;0.25</td>
<td></td>
<td>31.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;0.125</td>
<td>1.03E-05</td>
<td>32</td>
<td>0.153</td>
</tr>
<tr>
<td></td>
<td>&lt;0.063</td>
<td>4.05E-05</td>
<td>101.8</td>
<td>0.189</td>
</tr>
<tr>
<td>Sand</td>
<td>&gt;1</td>
<td>7E-06</td>
<td>32.7</td>
<td>0.099</td>
</tr>
<tr>
<td></td>
<td>&gt;0.125</td>
<td>1.05E-05</td>
<td>32.7</td>
<td>0.153</td>
</tr>
<tr>
<td></td>
<td>&lt;0.063</td>
<td>3.85E-05</td>
<td>167.1</td>
<td>0.108</td>
</tr>
<tr>
<td>Clay</td>
<td>&lt;0.063</td>
<td>4.7E-05</td>
<td>100.8</td>
<td>0.223</td>
</tr>
</tbody>
</table>

$^1$ Uncertainties due to counting statistics and variation in total efficiency (1 standard deviation) are 2-5 %. Systematical uncertainties in absolute calibration are at maximum 4 %.

$^2$ Uncertainties due to counting statistics (1 standard deviation) are 2-5 %. Systematical uncertainties in absolute calibration are at maximum 10 %.

$^3$ Uncertainties due to counting statistics and variation in total efficiency (1 standard deviation) are 3-5 %. Systematical uncertainties in absolute calibration are not included and are at maximum 11 %.

Table 2: Summary of expected outcome, results and interpretation of results from the sequential extraction procedure.

<table>
<thead>
<tr>
<th>Leaching agent</th>
<th>Expected outcome</th>
<th>Outcome</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M NH$_4$Cl</td>
<td>Cation exchangeable ions, e.g. Ca, Ba and Ra, and ions weakly bound to organic matter.</td>
<td>Ca predominated. Ra correlated well with Ca (and Ba). Very little Fe and U.</td>
<td>Cation exchangeable elements. Ra associated with Ca and Ba.</td>
</tr>
<tr>
<td>1M HCl</td>
<td>Elements coprecipitated with Fe/Mn/Al oxides and elements strongly bound to organic matter.</td>
<td>Fe predominated. Good correlation between all analysed elements. More Ra in this fraction than in the preceding one.</td>
<td>Fe oxides dissolved, elements bound to these liberated. Possibly also elements associated with organic matter.</td>
</tr>
<tr>
<td>Digestion of soil residues</td>
<td>Elements bound in the crystal lattice of minerals.</td>
<td>Concentrations did not vary much between samples. Ra analysis failed.</td>
<td>Elements bound in the crystal lattice of minerals. Marginal effects of soil formation processes.</td>
</tr>
</tbody>
</table>
Figure 1: Flow chart outlining sequential extractions, radon emanation measurements and chemical analysis of extraction fluids.
Figure 2: Concentrations in the exchangeable phase.
Figure 3: Concentrations in the oxide bound phase.
Figure 4: Scatter plots of radon exhalation vs. surface bound Ra and surface area.