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Estimation of distribution coefficient of radium around a uranium mining site

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Abstract – The present study provides an estimation of the site-specific distribution coefficient for radium around a uranium mining site. The soil parameters which affect the K_d value of radium were also estimated. For the estimation of the distribution coefficient of radium the equilibration time was optimized. The distribution coefficient of radium was determined using the laboratory batch method. The distribution coefficient of radium varies from 796 ± 9 mL g^{-1} to $2,285 \pm 52$ mL g^{-1}. K_d values of radium were observed to be higher for one-meter-depth soil samples compared with top soil samples in all the sampling locations. It was found that the K_d of radium strongly depends on different soil parameters such as pH, organic matter (OM) and cation exchange capacity (CEC). With increasing soil pH, OM and CEC, the K_d of radium increases linearly.

1 Introduction

Naturally occurring radionuclides (NORM) that are present in uranium tailings may be leached into the soil and enter the groundwater. Migration of NORMs and other tailing constituents occurs through leaching and erosion. The degree of migration is related to numerous factors such as the permeability of the impoundment and liner (if present), the amount of precipitation, the nature of the underlying soils, and the proximity to both surface and groundwater. Predicting the transfer of radionuclides in the environment for normal release, and accidental, disposal or remediation scenarios in order to assess exposure requires the availability of a number of important generic parameter values. One of the key parameters in environmental assessment is the solid-liquid distribution coefficient, K_d, which is used to predict radionuclide–soil interaction and subsequent radionuclide transport in the soil column (Vandenhove *et al.*, 2009). The fate of contaminant transport is often estimated using the distribution (partition) coefficient, K_d. It is a measure of sorption of contaminants to soil (Maity and Pandit, 2014) and is defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of solid to the amount of the adsorbate remaining in a unit volume of solution at equilibrium. The radionuclides present can enter the food chain directly via the soil–plant–animal pathway, or indirectly by the use of groundwater or surface water for irrigation purposes or drinking water. To assess the uptake in the food chain and by biota in general and to predict human exposure, knowledge of the environmental parameters governing radionuclide mobility and uptake is indispensable. Distribution coefficients (K_d) of uranium daughter products are very important for migration studies around uranium mining sites. In the literature there is a large variation of K_d values of radium; therefore, for realistic prediction of contaminant migration, literature K_d values may not be very effective. So, site-specific experimental K_d values are required. Also, the distribution coefficient depends very much on the soil chemistry, therefore generation of site-specific K_d is very important.

Radium (Ra) is an alkaline earth element, and can exist in nature only in the +2 oxidation state. Relative to other alkaline earth elements, radium is the most strongly sorbed by ion exchange on clay minerals. The adsorption of radium is strongly dependent on ionic strength and concentrations of other competing ions. Radium is also strongly adsorbed to mineral oxides present in soils, especially in near-neutral and alkaline pH conditions. The results of some studies also suggest that radium may be strongly adsorbed by organic material in soils (Nathwani and Phillips, 1979a).

In the present study soil from top and one-meter-depth and groundwater samples were collected from seven different locations around a uranium mining site in India. Soil samples were chemically characterized and the distribution coefficient for radium was estimated in soil samples using the laboratory batch method. Since the distribution coefficient of radium is a strong function of soil parameters, the effect of these parameters on the K_d values of radium were also studied.

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Figure 1. Sampling location.

2 Experimental

2.1 Sampling location

Soil and groundwater samples were collected from seven different places, around the Turamdih uranium mining area, Jharkhand, India (Figure 1). Groundwater samples were collected in plastic carboys previously treated with one molar solution of hydrochloric acid and rinsed with distilled water. In India the first uranium mining and ore processing operations commenced in the mid-1960s in Jaduguda (E86° 20'; N22° 40') in the eastern part of the country. Jharkhand state has a long slender area called "East Singhbhum" which lies between West Bengal and Orissa. The other three uranium ore deposits in Turamdih, Narwapahar and Bhatin are all located in this area and taken up for underground mining. The position of the central part of Turamdih is E86° 11'; N22° 43'.

2.2 Sample collection and processing

Groundwater samples were filtered through 0.45-μm filter paper and pH was determined by pH meter (DPH-500) and is shown in Table 1. All the soil samples (top and 1 meter depth) were collected with a wooden spatula and kept in polyethylene bags previously treated with one molar solution of hydrochloric acid and rinsed with distilled water. Soil samples were dried and sieved below 2 mm using an electromagnetic sieve shaker (EMS 8). The dry soil samples (<2 mm) were homogenized and used for chemical characterization as well as estimation of the distribution coefficient of radium. The same soil samples (<2 mm) were used for estimation of the pH, calcium carbonate ($CaCO_3$), cation exchange capacity (CEC) and organic matter. Groundwater samples were collected in plastic carboys previously treated with one molar solution of hydrochloric acid and rinsed with distilled water. All chemicals used were Merck, Suprapur, Analar or electronic grade.

2.3 Soil characterization

2.3.1 Particle size distribution in soil

Soil samples were air-dried and sieved using different mesh sieves (2-mm, 300-μm and 45-μm) in an electromagnetic sieve shaker (EMS 08) to find out the particle size distribution in order to know the soil type.

2.3.2 Estimation of pH in soil

The pH of soil was estimated using the methodology IS 2720, Part 26. For this, 30 g of soil (<2 mm) were taken in a 100-mL beaker and 75 mL of double-distilled water were added to it. The suspension was stirred for a few seconds, covered with a watch glass and allowed to stand for one hour with occasional stirring. The soil solution pH was estimated using a pH meter (DPH-500) which was calibrated using a standard buffer (pH 4, 7 and 9) before testing.

2.3.3 Estimation of calcium carbonate in soil

Calcium carbonate was estimated by using the methodology IS 2720, Part 23. Five grams of soil (<2 mm) were taken in a 150-mL beaker and 100 mL of 0.1 (N) HCl were added to it. The solution mixture was covered with a watch glass and vigorously stirred occasionally for one hour. After settling, 20 mL of the supernatant liquid were taken in a conical flask and 6–8 drops of bromothymol blue indicator were added to it and titrated against 0.1 (N) NaOH solution.

2.3.4 Estimation of cation exchange capacity (CEC) in soil

The values of the CEC were obtained by calculation from exchangeable cations. One gram of soil was taken in a 100-mL beaker, 18 mL CH_3COONH_4 (1N) was added, and kept for 1 hour under stirring conditions. Allowed to settle and filtered, the remaining soil was washed 3 times with 1(N) CH_3COONH_4. The soil was washed again with absolute alcohol (10 mL). The solution was evaporated and final volume was made up to 10 mL. Na^+, K^+, Ca^{++} and Mg^{++} were analyzed in this sample by using atomic absorption spectrometry (AAS) (GBC Avanta). The sum of the equivalent concentration of these ions give the CEC in soil.

2.3.5 Estimation of organic matter content in soil

Organic matter in the samples was estimated by the weight loss on ignition method. Ten grams of dry soil (95 °C) sample (<2 mm) were taken in a porcelain crucible covered with a watch glass. The soil was heated in a muffle furnace at 360 °C (Storer, 1984; Bianchi *et al.*, 2008) for 2 hours and after that the final weight was taken. Then, loss on ignition (LOI) was calculated by using the following equation

$$LOI\,(\%) = \frac{(weight\ at\ 95\,°C - weight\ at\ 360\,°C) \times 100}{weight\ at\ 95\,°C}.$$

Table 1. pH of groundwater samples collected from seven different locations across the Turamdih uranium mining area.

Sampling location	Location 1	Location 2	Location 3	Location 4	Location 5	Location 6	Location 7
pH	7.02	7.03	6.82	6.86	7.0	7.27	7.11

Ben-Dor and Banin (1989) showed that ignition temperatures in the range of 400–430 °C resulted in no significant bias from thermal breakdown of carbonates. Jackson (1958) and Ball (1964) both recommended ignition temperatures of <400 °C to minimize weight loss from carbonates, structural waters in clays and hydrated salts.

2.4 Sorption experiment for determination of equilibration time

The sorption experiment was carried out by the laboratory batch method (EPA, 1991; Roy *et al.*, 1991). [226]Ra was used as a tracer. In 50-mL polypropylene centrifuge tubes, soil (1g) and 30 mL groundwater (1:30 S/L ratio) with known activity of [226]Ra were shaken at room temperature. The experiment was carried out at different time intervals (0–170 hours) to find out the equilibration time. The laboratory batch method was carried out in a dual rotating shaker bath (model SK-300) with a shaking rate of 0.8–1.2 oscillations per second. The solution mixture was centrifuged and filtered through 0.45-μm syringe filter paper. [226]Ra was analyzed in the filtrate (after keeping it for one month in a shield container) using a high-resolution gamma spectrometry system consisting of a coaxial p-type high-purity germanium (HPGe) detector with 50% relative efficiency with respect to 7.62 cm × 7.62 cm NaI(Tl). The amount of adsorbed [226]Ra was estimated from the difference in the radium activity in the aqueous phase before and after the adsorption.

2.5 Sorption experiments for estimation of the distribution coefficient of radium in soil

The distribution coefficient is defined as the ratio of the activity of [226]Ra in the sorbent and in the solution at equilibrium.

The distribution coefficient (K_d) was calculated as per the following equation:

$$K_d = \left(\frac{A_0 - A - A_w}{A} \right) \times \frac{V_w}{W_{s1}}$$

where V_W is the volume of water in the suspension:

$$V_w = 30 + \left(\frac{W_{s2} - W_{s1}}{\rho} \right)$$

where W_{s1} and W_{s2} are the weights of the soil before and after equilibration with water, ρ is the density of the water, and A_w, A_0 and A are the activity sorbed on the wall of the polypropylene tube, initial activity and activity at equilibrium, respectively.
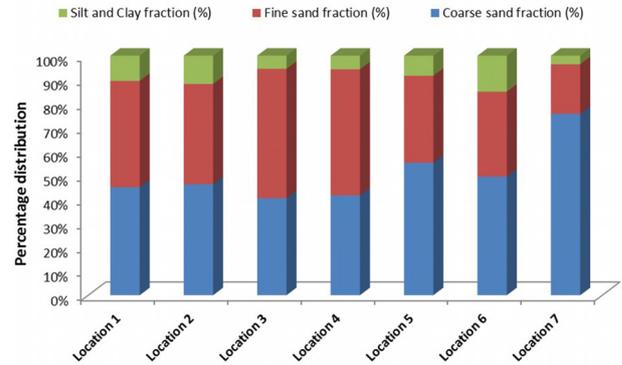
Figure 2. Particle size distribution of soil samples collected from different locations across the Turamdih uranium mining area.

3 Results and discussion

3.1 Physico-chemical characterization of soil samples

The particle size distribution of soil samples was carried out to know the soil type. In all the locations, except locations 3 and 4, coarse sand basically predominates in varying percentages (Figure 2), whereas the major constituent is fine sand for locations 3 and 4. The percentage of silt and clay is very low in comparison with the other two components. Figure 2 clearly depicts that the soil samples are mostly sandy type. Different chemical parameters such as the pH, concentration of calcium carbonate, cation exchange capacity (CEC) and organic matter for soil samples are shown in Table 2.
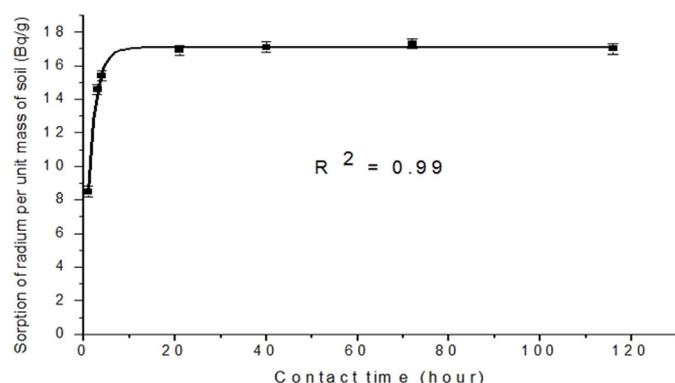
3.2 Estimation of the distribution coefficient of radium around the Turamdih uranium mining area

For determination of the distribution coefficient, knowledge of sorption equilibrium is very important. For this, the sorption of radium in soil at different time intervals was carried out using the laboratory batch method given in Figure 3, which clearly indicates that sorption equilibrium for radium was achieved at around 27 hours.

The distribution coefficients (K_d) of radium for top and one-meter-depth soil samples at different places around the Turamdih uranium mining site were determined and are shown in Figure 4. K_d values of radium in both top and 1-meter-depth soil samples were determined to see whether any difference is observed in K_d values in the surface soil and at a moderate depth such as in one-meter-deep soil. K_d values of radium were observed to be higher for one-meter-depth soil samples compared with top soil samples in all the sampling locations. In the top and one-meter-depth soil samples radium K_d values vary from 580 ± 6 mL g^{-1} to $1,835 \pm 16$ mL g^{-1} and 796 ± 9 mL g^{-1} to $2,285 \pm 52$ mL g^{-1}, respectively. The K_d values obtained
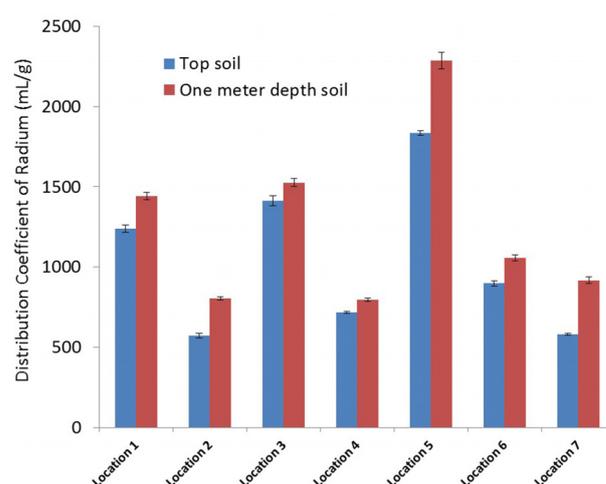
Table 2. Different parameters of the soil samples (surface and one meter depth) collected from seven different locations across the Turamdih uranium mining area.

Sampling location	Location 1	Location 2	Location 3	Location 4	Location 5	Location 6	Location 7
pH (surface soil)	6.75	6.00	6.48	6.75	7.30	6.93	5.95
pH (one-meter-depth soil)	7.10	6.30	6.93	6.60	7.37	6.88	6.15
$CaCO_3$ (mg/g) (surface soil)	4.79	2.30	2.30	5.91	4.38	3.07	6.03
$CaCO_3$ (mg/g) (deep soil)	5.79	4.37	3.50	5.02	6.57	4.91	6.91
CEC (meq/100g) (surface soil)	9.52	4.38	9.41	3.58	10.26	5.62	4.50
CEC (meq/100g) (one-meter-depth soil)	8.86	5.89	10.03	9.15	11.19	6.72	8.30
Organic matter (%) (surface soil)	6.29	3.86	4.72	4.64	6.42	4.93	3.77
Organic matter (%) (one-meter-depth soil)	6.16	4.15	5.40	5.34	7.47	5.53	4.70

Figure 3. Variation of sorption for radium on soil at different contact times.

Figure 4. Distribution coefficient of radium in top and one-meter-depth soil samples around the Turamdih uranium mining area.
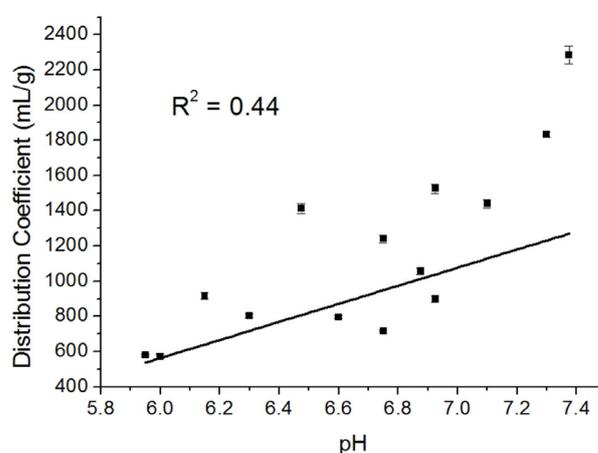
Figure 5. Variation of the distribution coefficient of radium with pH in soil samples around the Turamdih uranium mining area.

from the present study $(796 \pm 9$–$2,285 \pm 52$ mL g^{-1}) are compared with the reported values (Serne, 1974; Looney *et al.*, 1987; Sheppard *et al.*, 2006; Vandenhove and Van Hees, 2007) for soils. Serne (1974) measured K_d values for radium on four sandy, arid soil samples from Utah using a simulated river water solution. The K_d values ranged from 214 to 467 mL g^{-1} for the four soil samples. For radium, Looney *et al.* (1987) recommended K_d of 100 mL g^{-1}, and a range from 10 to 1,000,000 mL g^{-1}. Sheppard *et al.* (2006) recommended a K_d(Ra) value of 47 mL g^{-1} irrespective of soil type. Vandenhove and Van Hees (2007) reported K_d values of radium ranging from 38 mL g^{-1} to 446 mL g^{-1} in nine soil samples. Ra(K_d) was found to vary from 570 to 2,600 mL g^{-1} in different water samples reported by Mishra *et al.* (2012).

In the present study it is observed that with increasing soil pH, K_d(Ra) increases linearly, Ra(K_d) $= -2,519\,(\pm 994) + 514\,(\pm 153) \times$ pH ($R^2 = 0.44$), shown in Figure 5. Meier *et al.* (1994) reported the adsorption of radium increased with increasing pH. For the pH conditions of most natural waters, dissolved radium will be present primarily as the uncomplexed Ra^{2+} cation. Because adsorption of cations is coupled with a release of H^+ ions, cation adsorption is greatest at high pH and decreases with decreasing pH. The K_d values measured by Meier *et al.* (1994) for the adsorption of radium on a sandy sediment in groundwater were 6.7, 12, 6, 26.3 and 26.3 mL g^{-1} at pH values of 6, 7, 8 and 9, respectively.

Organic matter (OM) and the cation exchange capacity affect the distribution coefficient of radium. With increasing OM K_d(Ra) increases linearly, K_d(Ra) $= -719\,(\pm 291) + 331\,(\pm 63) \times$ OM ($R^2 = 0.68$); shown in Figure 6. Similarly, K_d(Ra) increases linearly with increasing CEC in soil samples,
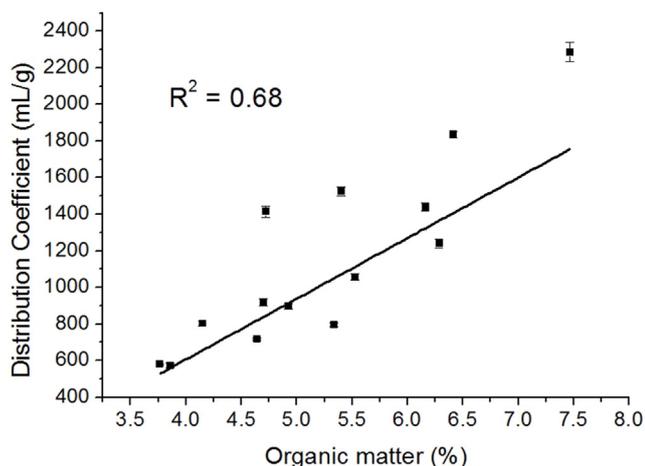
Figure 6. Variation of the distribution coefficient of radium with organic matter (OM) content in soil samples around the Turamdih uranium mining area.
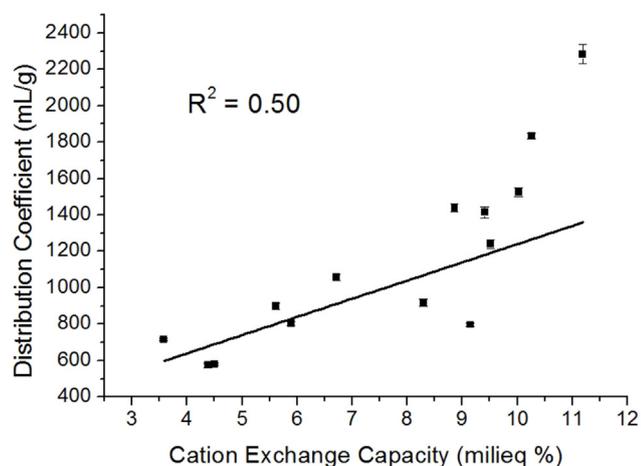
Figure 7. Variation of the distribution coefficient of radium with the cation exchange capacity (CEC) in soil samples around the Turamdih uranium mining area.

$K_d(Ra) = 239\ (\pm160) + 100\ (\pm27) \times CEC\ (R^2 = 0.50)$; shown in Figure 7. The adsorption of radium has been shown to be strongly dependent on ionic strength and concentrations of other competing ions. Organic matter and clay were determined to be the dominant phases contributing to the adsorption of ^{226}Ra on soils. Nathwani and Phillips (1979a) suggested that the adsorption affinity of organic matter and clays was primarily due to their cation exchange capacity (CEC). Their results also indicated that organic matter adsorbed approximately 10 times more ^{226}Ra than clays. The results of Nathwani and Phillips (1979b) show that the addition of competing alkaline earth cations to the system can greatly affect radium sorption on the clay minerals. Vandenhove *et al.* (2007), exploring the effect of soil properties on the radium availability in a small-scale study covering 9 soils, concluded that $K_d(Ra)$ could be predicted by the CEC [$K_d(Ra) = 0.71 \times CEC - 0.64$, $R^2 = 0.3$] and soil organic matter content [$K_d(Ra) = 27 \times OM - 27$, $R^2 = 0.4$]. A linear relationship between the distribution

coefficients of Ra on soil and the Cation Exchange Capacity (CEC) was obtained to suggest the cation exchange sorption reaction of Ra^{2+} on the soil surface (Sakamoto *et al.*, 2000).

4 Conclusions

The distribution coefficient of radium varies from $796 \pm 9\ mL\,g^{-1}$ to $2,285 \pm 52\ mL\,g^{-1}$. K_d values of radium were observed to be higher for one-meter-depth soil samples compared with top soil samples in all the sampling locations. In the present study it is clearly observed that the distribution coefficient of radium is very much dependent on different soil parameters such as the pH, organic matter and cation exchange capacity (CEC). With increasing soil pH, the organic matter (OM) and CEC K_d of radium increases linearly. Estimated site-specific distribution coefficient values of radium will be useful for prediction of contaminant transport from a uranium mining site.

References

Ball D.E. (1964) Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils, *J. Soil Science* **15**, 84-92.

Ben-Dor E., Banin A. (1989) Determination of organic matter content in arid zone soils using a simple "loss-on-ignition" method, *Communications in Soil Science and Plant Analysis* **20**, 1675-1695.

Bianchi S.R., Miyazawa M., de Oliveira E.L., Pavan M.A. (2008) Relationship between the mass of organic matter and carbon in soil, *An international journal Brazilian Archives of Biology and technology* **51**, 263-269.

EPA (U.S. Environmental Protection Agency) (1991). Site Characterization for Subsurface Remediation. EPA/625/4-91/026, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

Jackson M.L. (1958) In: *Soil chemical analysis*, p. 225. Prentice-Hall, Englewood Cliffs NJ.

Looney B.B., Grant M.W., King C.M. (1987) Estimating of Geochemical Parameters for Assessing Subsurface Transport at the Savannah River Plant. DPST-85-904, Environmental Information Document, E.I. Dupont de Nemours and Company, Savannah River Laboratory, Aiken, South Carolina.

Maity S., Pandit G.G. (2014) Estimation of K_d of lead and ^{210}Po in 11 soils from India, *J. Environ. Radioact.* **138**, 434-437.

Meier H., Zimmerhacki E., Zeitler G., Menge P. (1994) Parameter studies of radionuclide sorption in site – specific sediment/groundwater system, *Radiochimica Acta* **66/67**, 277-284.

Mishra S., Maity S., Pandit G.G. (2012) Estimation of distribution coefficient of natural radionuclides in soil around uranium mines and its effect with ionic strength of water, *Radiat. Prot. Dosim.* **152** (1-3), 229-33.

Nathwani J.S., Phillips C.R. (1979a) Adsorption of ^{226}Ra by soils, *Chemosphere* **5**, 285-291.

Nathwani J.S., Phillips C.R. (1979b) Adsorption of ^{226}Ra by soils in the presence of Ca^{2+} ions, *Chemosphere* **5**, 293-299.

Roy W.R., Drapac I.G., Chou S.F.J., Griffin R.A. (1991) EPA/530-SW-87-006-F, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Sakamoto Y., Takebe S., Ogawa H., Muraoka S., Ishii T., Inagawa S., Gunji Y. (2000) Sorption Behavior of Radium and Actinium on Soils, *MRS Proceedings* **663**, 1207.

Serne R.J. (1974) Waste Isolation Safety Assessment Program Task 4. In: *Contractor Information Meeting Proceedings. PNL-SA-6957*, Pacific Northwest Laboratory, Richland, Washington.

Sheppard S.C., Sheppard M.I., Tait J.C., Sanipelli B.L. (2006) Revision and meta-analysis of selected biosphere parameter values for chlorine, iodine, neptunium, radium, radon and uranium, *J. Environ. Radioact.* **89**, 115-137.

Storer D.A. (1984) A simple high sample volume ashing procedure for determining soil organic matter, *Commun. Soil Sci. Plant Anal.* **15**, 759-772.

Vandenhove H., Van Hees M. (2007) Predicting radium availability and uptake from soil properties, *Chemosphere* **69**, 664-674.

Vandenhove H., Gil-Garcia C., Rigol A., Vidal M. (2009) New best estimates for radionuclide solid-liquid distribution coefficients in soils. Part 2. Naturally occurring radionuclides, *J. Environ. Radioact.* **100**, 697-703.