

Using Hydrus-HP1 to Estimate ^{226}Ra Transport in Soils Following the Use of Phosphogypsum in Agriculture

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Abstract

Agricultural soils generally require the use of fertilizers and soil conditioners for optimal production. Phosphate fertilizers produced from igneous phosphate rock often contain small amounts of natural radionuclides (most notably ^{238}U and ^{232}Th), while the byproduct phosphogypsum (dihydrated calcium sulfate) is enriched in ^{226}Ra and ^{210}Pb . Our study focused on the long-term (200 year) subsurface fate of ^{226}Ra when phosphogypsum (PG) is applied annually for 27 years as an amendment to a typical Brazilian Cerrado soil profile, after which PG applications ceased but agriculture continued. Expected water flow and solute transport processes were estimated first using the standard HYDRUS-1D software package assuming linear equilibrium transport, followed by simulations using the HP1 module of HYDRUS-1D. Analyses with HP1 considered a range of geochemical and physical parameters affecting ^{226}Ra transport in the vadose zone, especially the effects of varying calcium concentrations resulting from the PG applications. Several aspects related to the modeling approach, such using daily versus monthly averaged weather data and assuming long-term steady-state flow conditions, are discussed also.

1. Introduction

Natural radioactivity is common in most or all soils and rocks. This natural radioactivity may change when fertilizers or amendments are used in agricultural operations to improve crop production. For example, phosphate fertilizers often contain small amounts of radionuclides from the uranium (^{238}U) and thorium (^{232}Th) decay chains. During the phosphate production process, the naturally occurring U and Th decay series in the host rock are disrupted and some of the radionuclides tend to accumulate in both the fertilizer itself (approximately 86% of ^{238}U and 70% of ^{230}Th) and the by-product phosphogypsum (about 80% of ^{226}Ra and its daughter products) (Mazzilli et al., 2000; Papastefanou et al., 2006, Saueia and Mazzilli, 2006). For every ton of phosphoric acid being produced (the basic constituent for the production of phosphate fertilizers), about 4.8 tons of phosphogypsum (PG) is being generated. Because of its ^{226}Ra content, PG in many countries is considered a waste and stockpiled in very large quantities.

In Brazil, a major agricultural production area is the Cerrado region. Cerrado soils typically are highly weathered, slightly acidic, leached, have a relatively low cation exchange capacity, and are poor in nutrients such as P, Ca and Mg. Natural gypsum has long been used as an amendment or soil conditioner for such situations. Since PG is rich in P, Ca and Mg, many studies have

advocated the use of PG as both a fertilizer and soil conditioner to reduce subsoil acidity and Al toxicity, as well as to promote sodic soil reclamation and reduce soil erosion (Oster, 1982; Oates and Caldwell, 1988; Embrapa, 2005; among others).

Detailed analyses are needed to understand the possible accumulation of radionuclides when fertilizers and/or phosphogypsum are being applied routinely over long periods of time to the same field (Jacques et al., 2008; Batalha et al. 2011b). For this purpose we used the HYDRUS-1D flow and transport simulator (Šimůnek et al., 2008) to predict the long-term fate and transport of ^{226}Ra present in PG into and through the vadose zone to groundwater, assuming linear equilibrium transport. Rather than considering one single application, which should have very little impact on the environment (e.g., Rothbaum et al., 1979; Zielinski et al., 1997), the application is assumed to be repeated once every year for 27 years to a typical soil profile in the Cerrado region of Brazil. The transport of ^{226}Ra in the vadose soil is subsequently followed for another 170 years.

A recent study by Jacques et al. (2008) shows that radionuclide transport in soils is affected by a range of physical and geochemical processes. Their study focused on the transport of uranium following the long-term use of phosphate fertilizers, as opposed to radium in this study. Since radium and calcium released from applied PG may compete for the same sorption sites, several simulations were performed using the HP1 (Jacques and Šimůnek, 2010) multicomponent transport module of HYDRUS-1D. The module was obtained by coupling HYDRUS-1D with the PHREEQC biochemical code (Parkhurst and Appelo, 1999). We were especially concerned about the possible effects of varying calcium concentrations on ^{226}Ra transport. Several aspects related to the modeling approach, such as the use of daily versus monthly weather data and the effect of assuming different transport regimes in the vadose zone (notably transient versus long-term steady-state flow) are discussed also. Additional details of the simulations are presented elsewhere (Batalha et al., 2011, 2012).

2. Simulation Methodology

The scenario of concern is the repeated application of phosphogypsum to the same Cerrado soil profile, and resultant ^{226}Ra accumulation and transport in the vadose zone, and possibly into underlying groundwater. We considered a 2-m deep physically and chemically uniform soil profile, without any preferential water flow. Since contaminant transport is very much affected by the rates of water flow into and through the soil profile as a function of local weather conditions, transient precipitation and evaporation conditions were evaluated. Phosphogypsum was assumed to be applied once each year for 27 years to the soil surface in the form of a short pulse with known composition. Free drainage conditions were imposed at the bottom of the profile. In this study we did not consider any uptake of water and solutes by plant roots.

Water flow in the soil profile is described using the standard Richards equation (Šimůnek et al., 2008):

$$\frac{\partial \theta(h)}{\partial z} = \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} + 1 \right) \right] \quad (1)$$

where h is the soil water pressure head [L], θ is volumetric water content [L^3L^{-3}], t is time [T], z is the spatial coordinate (positive upward in this study) [L], and K is the hydraulic conductivity [LT^{-1}].

The volumetric water content (θ) and the hydraulic conductivity (K) in Equation (1) are strongly nonlinear functions of the pressure head, h . These functions are described here using the constitutive relationship of van Genuchten (1980) as follows:

$$S_e(h) = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \begin{cases} (1 + |\alpha h|^n)^{-m} & h < 0 \\ 1 & h \geq 0 \end{cases} \quad (2a)$$

$$K(h) = K_s S_e^l \left[1 - (1 - S_e^{1/m})^m \right]^2 \quad (2b)$$

where S_e is effective saturation [L^3L^{-3}], θ_r and θ_s are the residual and saturated volumetric soil water contents, respectively [-], K_s is the saturated hydraulic conductivity [LT^{-1}], and α [L^{-1}], $n > 1$ [-], $m = 1 - 1/n$ [-] and l [-] are mostly empirical shape factors. Following van Genuchten (1980), the pore-connectivity parameter l was fixed at a value of 0.5.

Radionuclide transport was simulated initially with HYDRUS-1D using the standard linear equilibrium advection-dispersion equation:

$$\frac{\partial(\theta RC)}{\partial t} = \frac{\partial}{\partial z} \left(\theta D \frac{\partial C}{\partial z} - qC \right) - \mu \theta RC \quad (3)$$

where C is the solution concentration [ML^{-3}], R the retardation factor [-], D is the dispersion coefficient [L^2T^{-1}], q is the Darcy-Buckingham volumetric flux [LT^{-1}], and μ is the decay coefficient [T^{-1}] for the particular radionuclide being considered (in our case ^{226}Ra). Since the half-life of ^{226}Ra (1600 years) is much greater than the time period of our study (200 years), radioactive decay will not be considered here (i.e., $\mu=0$). The parameters R and D in Eq. (3) are given by:

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (4)$$

$$D = D_d \tau + \lambda \frac{|q|}{\theta} \quad (5)$$

in which ρ_b is the bulk density of the soil [ML^{-3}], K_d is the distribution coefficient for linear sorption [L^3M^{-1}], λ is the longitudinal dispersivity [L], D_d is the diffusion coefficient in free water [L^2T^{-1}], and τ is the porous medium tortuosity factor [-] given by $\theta^{7/3} \theta_s^{-2}$ (Millington and Quirk, 1961).

Geochemical transport involving phosphogypsum was represented by a system of N_m reaction equations for the primary (or master) species, in canonical form given by

$$\sum_{j=1}^{N_m} \nu_{ji} A_j = A_i \quad (6)$$

and correspondent mass action equations assuming equilibrium:

$$K_i = \gamma_i C_i \prod_{j=1}^{N_m} (\gamma_j C_j)^{-\nu_{ji}} \quad (7)$$

where N_m the number of master aqueous species, A_j and A_i are the chemical equations for the master and secondary species, respectively, ν_{ji} are stoichiometric coefficients of the reaction, K_i is the equilibrium constant of a reaction, γ_i is the activity coefficient of the aqueous complex, and γ_j is the activity coefficient for the j^{th} master species in solution.

Transport of each species is represented in the above manner by a set of N_m multicomponent reactive transport equations of the form (Jacques et al., 2008):

$$\frac{\partial(\theta C_j)}{\partial t} = \frac{\partial}{\partial z} \left(\theta D \frac{\partial C_j}{\partial z} - q C_j \right) + R_{0,j} \quad (8)$$

where $R_{0,j}$ is the reaction term representing the sources/sinks for each aqueous component, C_j is the total concentration of master species j

$$C_j = c_j + \sum_{i=1}^{N_s} \nu_{ji} c_i \quad (9)$$

in which N_s the number of secondary aqueous species, and c_i is the concentration of secondary species i .

For ^{226}Ra sorption we assumed a relatively simple equilibrium approach that lumps all of the sorption processes onto the solid phase into a single linear isotherm in which the distribution coefficient is a nonlinear function of the calcium concentration, as described in Batalha (2011b).

$$K_d = K_{d0} C_{Ca}^p \quad (10)$$

in which K_d is the reference distribution coefficient for ^{226}Ra when the calcium activity is 1, C_{Ca} is the calcium activity in soil solution, and p is an empirical parameter whose value was fixed at -0.4 as deduced from data in USEPA (2004).

3. Cerrado Soils and PG Application Data

Flow boundary conditions at the soil surface were defined by meteorological data (rainfall and temperature) obtained from a weather station in the western part of Minas Gerais state in Brazil (17° 25' 11" S, 46° 88' 64" W) for the period 1982-2005. These values were repeated many times for the long-term (200 year) simulations. Daily potential evapotranspiration rates were calculated with the Hargreaves equation (e.g. Jensen et al., 1997) from available weather data and the geographic location of the site. Data of the rainwater composition were taken from Maier et al. (1992) and adapted for use in HP1 module: pH 6.3; $5.59 \cdot 10^{-5}$ mol/L of Ca and $6.05 \cdot 10^{-5}$ mol/L of Mg. The soil chosen for the study is a typical Brazilian Cerrado oxisol, whose physical and chemical data were obtained from Oliveira (2008). Chemical parameters are listed in Table 1.

The granulometric composition of the soil was 16% sand, 63% fine sand, 5% silt and 16% clay. Values of the soil hydraulic parameters needed for the water flow simulations were estimated from the soil textural data using the Rosetta neural network based pedotransfer functions of Schaap et al. (1998) as implemented in HYDRUS-1D. The soil bulk density was taken to be 1.50 g/cm^3 . For solute transport we used a diffusion coefficient in free water (D_d) of $1.0 \text{ cm}^2/\text{d}$, while a dispersivity (λ) of 20 cm was used for the simulations involving transient flow and 30 cm for the steady-state flow regime.

Table 1. Soil chemical parameters of the Cerrado oxisol.

	P	Ca ²⁺	K ⁺	Mg ²⁺	Al ³⁺
pH	mmol/L				
5.3	0.081	0.500	0.410	0.100	0.333

Simulations of the cumulative flux leaving the bottom of the 2m soil profile over a period of 27 years assuming transient water flow were used to define the recharge rate (0.152 cm/d) used for the long-term simulations assuming steady-state flow. Equation (1) for this purpose must be augmented with a set of initial and boundary conditions. For Equation (1) we assumed an initial pressure head of -100 cm , the presence of atmospheric boundary conditions at the soil surface (i.e., given precipitation and calculated potential evapotranspiration data), and a free drainage condition ($dh/dx=0$) at the bottom of the profile.

For the phosphogypsum and ²²⁶Ra transport calculations we considered PG application rates that are common in Brazil (1.000 kg/ha year). The annual application was pulsed in 1 cm of rainwater in the wet season (November). Measurements of the amount of ²²⁶Ra in the PG were carried out at the Poços de Caldas Laboratory of the Brazilian Nuclear Energy Commission (CNEN). Results indicated an activity of $252 \pm 26 \text{ Bq}$ per kg of PG. Mass balance calculations produced values of 73.45 mmol/L of CaSO₄ and $3.04 \times 10^{-13} \text{ mol/L}$ of ²²⁶Ra when applied in 1 cm of rainwater for the transient simulations, and values of 483.2 mmol/L of CaSO₄ and $20 \times 10^{-10} \text{ mmol/L}$ of ²²⁶Ra when simulating the constant flow regime using an averaged flux of 0.152 cm/day . A distribution coefficient (K_d) of $2000 \text{ cm}^3/\text{g}$ was used for radium based on data provided by ISAM (1999) as described in Batalha (2011a).

4. Results and Discussion

Figure 1 shows calculated net infiltration fluxes (actual evaporation minus precipitation) into the soil profile for nine years using transient conditions of precipitation and potential evaporation. Results indicates two main seasons (wet and dry) during the year. The simulations using daily weather data from Minas Gerais state (Brazil) revealed no run-off.

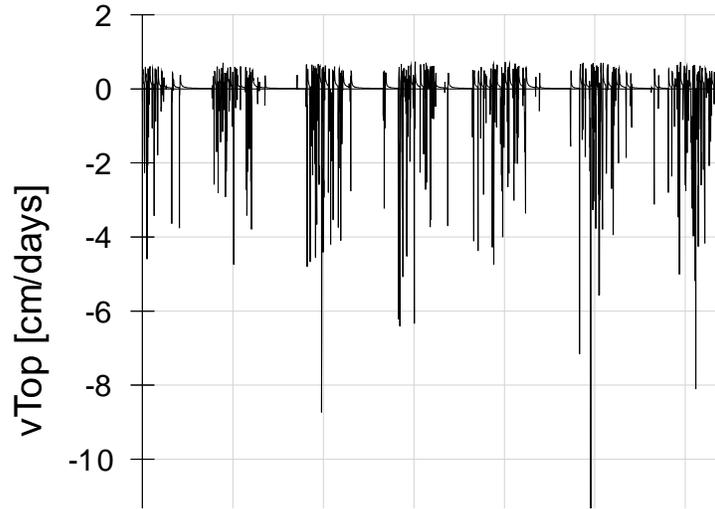


Figure 1. Net fluxes across the soil surface during the first 9 years of the simulations (negative fluxes are downward into the soil profile).

Cumulative drainage fluxes from the soil profile are showed in Figure 2. Results are for both transient flow using daily weather data (left) and monthly averaged precipitation and evaporation data (right). The importance of using daily weather data can be evaluated by the slopes of the two plots. The results indicate an average recharge rate of 0.152 cm/day when using daily weather data, and a nearly 50% lower value of 0.079 cm/d when monthly averaged values for precipitation and potential evaporation are used. This means that time-averaging weather data (especially precipitation) can lead to significantly lower estimates of the recharge rate.

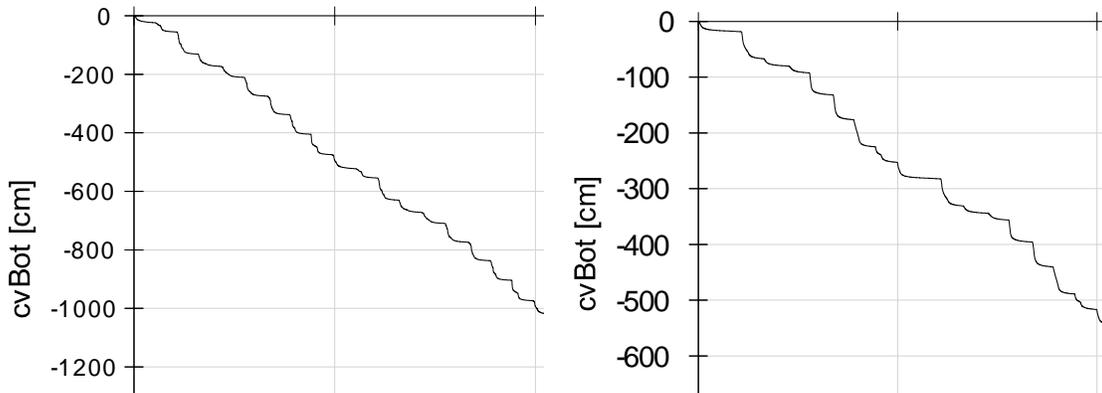


Figure 2. Calculated cumulative recharge rates from the soil profile during 27 years using daily (left) and monthly averaged (right) weather data.

Figure 3 compares calculated ^{226}Ra concentration distributions in the soil profile assuming transient (left) and steady-state (right) flow conditions. Results for transient flow were obtained using observed daily weather data, while those for steady-state flow assumed a constant long-time average recharge rate of 0.152 cm/d as deduced from the transient simulations (Fig. 2, left). Since the transient regime produced a slightly more dispersed contaminant front, a higher longitudinal dispersivity ($D_L = 30$ cm) for the steady flux scenario was used. The results in Figure 3 indicate that long-term predictions can be based equally well assuming steady-state water flow, rather than transient flow, provided the correct long-term deep drainage (recharge) rate is used for the steady-state simulations.

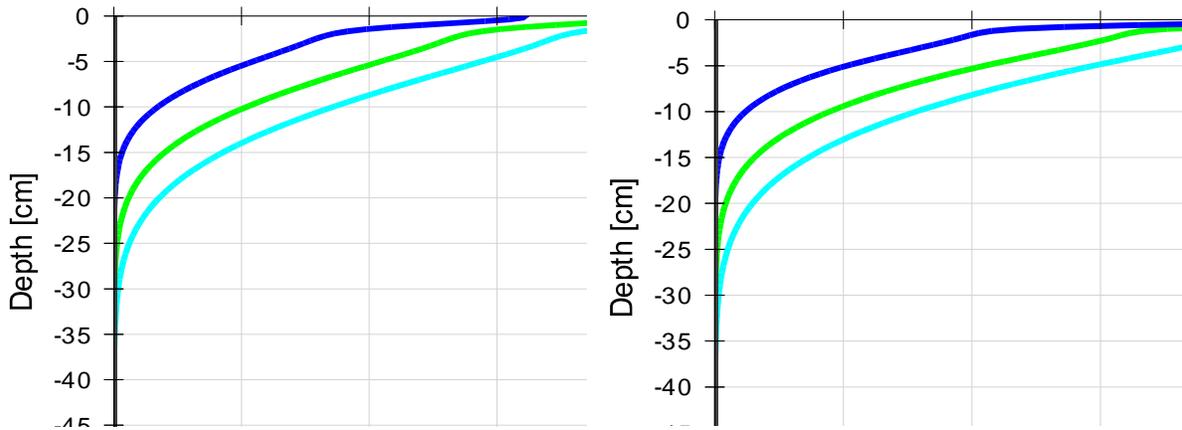


Figure 3. Calculated ^{226}Ra concentrations after $T_0=0$, $T_1=9$, $T_2=18$, and $T_3=27$ years assuming transient weather data (left) and a constant long-term average recharge rate (right).

Figure 3 shows that after 27 years of PG application, essentially no ^{226}Ra had reached a depth of about 30 or 40 cm. Subsequent transport after PG applications ceased, but while maintaining the same water flow conditions, remained equally slow. This is shown in Figure 4 which presents calculated ^{226}Ra distributions in the soil profile after 27, 100 and 200 years. The plots show very little movement into the lower part of the profile, with essentially no ^{226}Ra reaching a depth of 1 m after 200 years. Cumulative amounts leached beyond 40 cm depth after 100 and 200 years were estimated to be 3.58×10^{-13} and 1.85×10^{-12} mmol/cm². Also notice that the maximum concentrations in the upper part of the profile decreased substantially with time.

Figure 5 shows the influence of the calcium concentration on ^{226}Ra transport after 9, 18 and 27 years of phosphogypsum application. The plots compare simulations for a constant distribution coefficient, K_d (left) and for a distribution coefficient that varies as a function of Ca^{2+} activity (right). Results indicate that Ca^{2+} resulting from the PG application has a major effect on both the transport rate of ^{226}Ra and the solution concentration. However, this trend is only present initially. Once the PG is no longer applied (after 27 years), calculated ^{226}Ra curves slowly converged to the point that after 100 or 200 years they became very similar (results not further shown here).

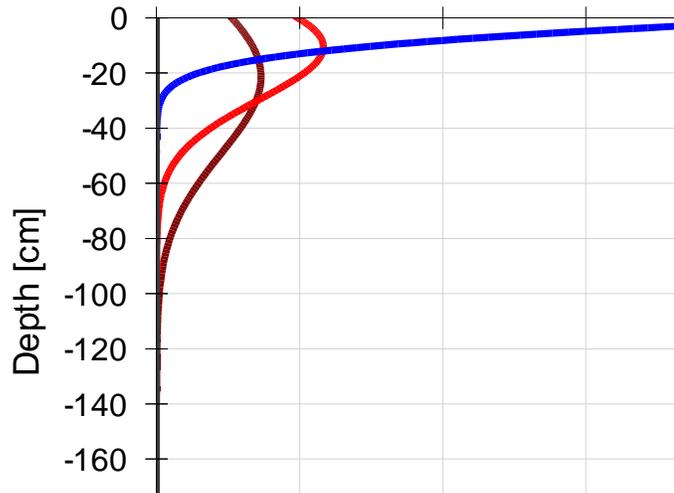


Figure 4. Calculated ^{226}Ra concentrations after $T_0=0$, $T_1=27$, $T_2=100$, and $T_3=200$ years (left).

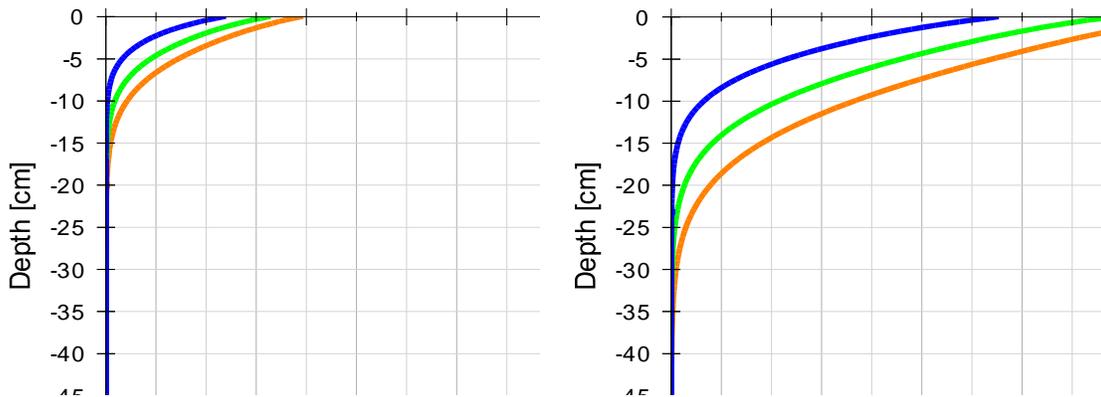


Figure 5. Calculated ^{226}Ra concentrations after $T_1=9$, $T_2=18$, and $T_3=27$ years, without (left) and with (right) accounting for the effect of the Ca^+ activity on the K_d of ^{226}Ra .

5. Conclusions

In this paper we analyzed the fate and transport of ^{226}Ra present in phosphogypsum when applied for many years as an amendment to a typical Brazilian Cerrado soil used for crop production. The main factors that influenced water flow and radionuclide transport were the deep drainage flux determined by rainfall and evaporation and the use of daily precipitation and potential evaporation data. Results indicate that for the assumed long-term transport scenario (200 years and having relatively low ^{226}Ra activities), steady-state flow conditions could be assumed without

significantly affecting the predictions. Most of the ^{226}Ra remained in the upper 40 cm of the soil profile.

The effect of PG derived calcium was important by decreasing the effective distribution coefficient of ^{226}Ra , and as such increasing the transport rate. All of the simulations in this study assumed equilibrium water flow and solute transport conditions. We did not consider preferential flow or nonequilibrium transport, or any other non-ideal transport process (such as colloid-facilitated transport). These processes could all lead to much higher rates of transport in the soil profile (e.g., Šimůnek and van Genuchten, 2008).

In conclusion, we believe that modeling efforts such as those in this study using HYDRUS-1D and HP1 are essential for detailed environmental assessment of the long-term use of phosphogypsum or other naturally occurring radioactive materials (NORMs). They are especially needed for scenarios that cannot be easily monitored and/or occur over relatively long periods of time.

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