Environmental Safety Assessment of Natural Radioactive Contaminants in Fertilizers and Phosphogypsum

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ABSTRACT. This study presents results of modeling study the subsurface transport of natural radionuclides often present in Brazilian fertilizers and phosphogypsum. Phosphate fertilizers produced from igneous phosphate rock often contain small amounts of radionuclides (notably the U and Th natural series), as does the byproducts phosphogypsum (dehydrated calcium sulfate). We present results of measured ^{238}U and ^{234}U contents of Brazilian fertilizers, and of the ^{226}Ra and ^{210}Pb contents of phosphogypsum (PG). HYDRUS-1D was used to compare possible soil and groundwater pollution scenarios following their long term (200 year) use in agricultural operations.

INTRODUCTION. Phosphate fertilizers are obtained by treating igneous phosphate rock with concentrated sulfuric acid to produce phosphoric acid, and phosphogypsum (PG) as a by-product. Phosphoric acid is the starting material for simple super-phosphate (SSP), triple super-phosphate (TSP), mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP). After desiccation, phosphogypsum (PG) is generally stockpiled as a waste (Fig. 1) because of elevated levels of impurities, including radionuclides. Each ton of phosphoric acid produces about 4.8 tons PG. The natural U and Th decay series in phosphate rock are at equilibrium. During processing this equilibrium is disrupted and radionuclides migrate to the fertilizers and phosphogypsum. It is important to understand the possible accumulation of the radionuclides in the subsurface when applied to agricultural lands.

Figure 1. Aerial View of Phosphogypsum Piles from Minas Gerais, Brazil.

PG can possibly be used as a soil conditioner (e.g., as a replacement of gypsum), such as in the Cerrado Region of Brazil where soils are slightly acidic (pH between 4.3 and 6.2) with high levels of exchangeable aluminum and low levels of phosphorus, Ca and Mg. The Cerrado Bioma ecosystem is similar to savannas. The climate of the region is tropical with a very dry season, and a wet period from October to April. The average annual temperature is between 20 and 30^0 C, and annual rainfall 800 - 1,700 mm. Most Cerrado soils are weathered oxisols (Latosols) and comprise 46% of the Brazilian territory.

According to the Brazilian Agricultural Research Corporation (EMBRAPA), the use of PG is justified: (a) when there is a need to supply calcium and sulfur to plants; and (b) to decrease toxic concentrations of exchangeable aluminum and increase of calcium to improve root growth.

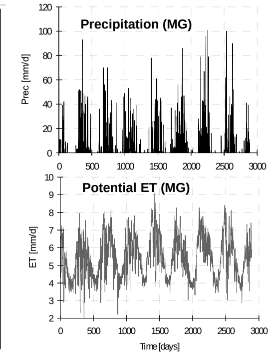


Table 1. Measured average activities of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{228}Ra, and ^{210}Pb in simple super-phosphate (SSP), triple super-phosphate (TSP) and Phosphogypsum (PG)

Radionuclide	SSP Bq kg^{-1}	TSP Bq kg^{-1}	Phosphogypsum Bq kg^{-1}	Employed Methodology
^{238}U	390 - 400	394 - 403	68 - 88	Spectrophotometry
^{234}U	430 - 440	430 – 440		"
^{230}Th	370 – 380	420 – 430	82 – 93	
^{226}Ra	100 - 120	110 - 120	226 - 255	Gamma Spectrometry
^{228}Ra	300 - 350	120 - 130	203 - 235	"
^{210}Pb			204 - 256	"

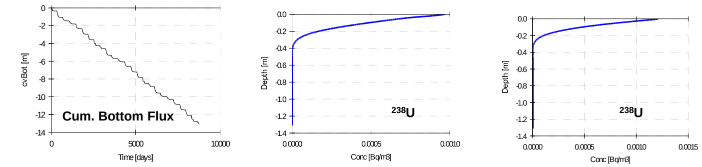
HYDRUS-1D Simulation Scenarios:

- Apply 180 kg of P_2O_5 and 1000 kg of phosphogypsum per ha annually.
- Apply as a short pulse each year on November for 24 years.
- Assume TSP application of 430 kg/ha.
- Soil is typical for Cerrado.
- Analyze fertilizer and phosphogypsum transport separately.
- Use measured radionuclide contents in phosphate and PG as shown in Table 1.
- Potential ET_p estimated from daily temperatures (Hargreaves equation).
- 24 year transient simulations using daily weather data from Minas Gerais, Brazil.
- Measured precipitation and estimated Et_p values are shown above (repeated 3 times).
- Atmospheric boundary conditions; no root water uptake in current simulations
- Hydraulic properties estimated from soil texture using Rosetta
- Linear distribution (K_d) and decay coefficients are generic literature values
- Compare results with steady-state flow simulation using average recharge rate
- 200 year simulations (steady-state flow) of transport after 24 years of application

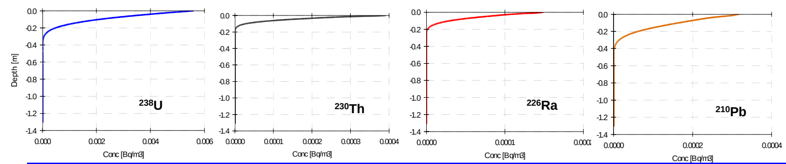
Table 2. Selected physical and chemical properties of the red Latosol

Soil Horizon	Depth (cm)	% Sand	% Silt	% Clay	Kd Uranium (m^3 kg^{-1})	Kd Thorium (m^3 kg^{-1})	Kd Radium (m^3 kg^{-1})	Kd Lead (m^3 kg^{-1})
A1	0 - 20	61.5	11.6	26.9	0.280	2.03	1.00	0.256
AB	20 - 50	52.6	10.3	37.1	0.326	2.28	1.86	0.282
BA	50 - 75	44.4	9.0	46.6	0.418	2.51	2.56	0.306
Bw1	75 - 130	37.5	10.6	51.9	0.457	2.67	2.67	0.322

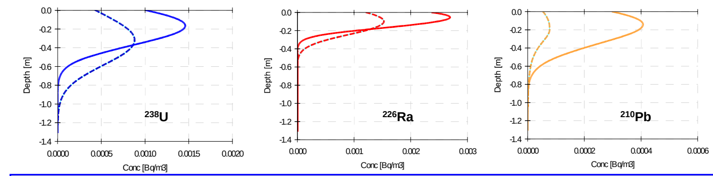
Results



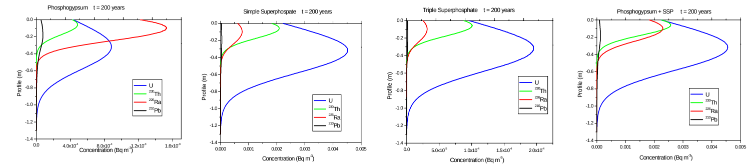
Calculated ^{238}U distributions after 24 years of TSP application assuming transient (middle) and steady-state flow simulations. The long-term average recharge rate as estimated from the transient cumulative bottom flux (left) was 0.0051 m/year. Similar results for the other radionuclides.



Calculated radionuclide distributions versus depth after 24 years of phosphogypsum application (steady flow).



Calculated distributions versus depth 100 (solid lines) and 200 (dashed lines) years after starting 24 years of phosphogypsum application; Th concentrations were extremely small and are not shown here.



Calculated radionuclide concentrations versus depth 200 years after starting 24 years of application of phosphogypsum (left), simple superphosphate, triple superphosphate and phosphogypsum plus simple superphosphate combined (right).

Conclusions

- Phosphogypsum caused similar levels of contamination as, or less than, simple superphosphate.
- Radionuclide concentrations originating from PG, SSP and TSP were relatively modest; more studies are needed with different sources of fertilizers and phosphogypsum.
- The effects of nonequilibrium transport processes may need to be considered in future studies.

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