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RADIOLOGICAL CONSIDERATIONS OF PHOSPHOGYPSUM
UTILIZATION IN AGRICULTURE

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Radiological Considerations of Phosphogypsum Utilization in Agriculture

C. L. Lindeken

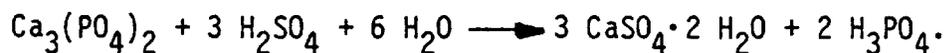
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Introduction

Gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) is an amendment that is widely used to improve the permeability of saline alkali soils. It also is used as a substitute for lime or limestone when a source of calcium is required and raising the pH of the soil is inadvisable. Agriculture is a minor outlet for gypsum. In 1979, 21,833,000 tons of gypsum were sold in the United States. Of this total, only 1,700,000 tons were used in agriculture. Byproduct gypsum accounted for 828,000 tons or nearly half of the agricultural usage.¹ The balance of agricultural gypsum is supplied by quarried gypsum. Figure 1 shows annual consumption of gypsum according to use, indicating that agricultural consumption has not changed materially over the last 25 years.

The principal source of byproduct gypsum is the phosphate fertilizer industry, and in the United States, Florida is the major source of phosphate rock.² To produce phosphoric acid, the phosphate rock—commonly fluorapatite $\text{Ca}_5\text{F}(\text{PO}_4)_3$ —is treated with sulfuric acid and the CaSO_4 (termed phosphogypsum) precipitates and is filtered from the acid. A simplified version of this reaction is shown by the following equation,



Florida phosphate rock may contain from 10 to 200 ppm of uranium. In the acid dissolution of the rock, the uranium tends to go into the acid solution, whereas the radium in the uranium decay chain coprecipitates with the gypsum. The radium content of phosphogypsum varies with the source of the phosphate rock. Phosphogypsum from Florida's Central land pebble district generally contains about 30 pCi/g of ^{226}Ra . The radium content of phosphogypsum from Florida's Northern district averages about 15 pCi/g.

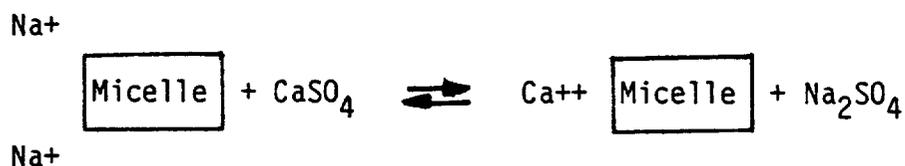
There are three areas of radiological concern associated with phosphogypsum utilization in agriculture and all of these are related to its radium content. First, there is concern over the buildup of radium in soil as a result of long term use, and the consequent radiation exposure to agricultural workers. Second, and also related to this buildup, is the uncertainty regarding radium transfer to man via uptake of radium by agricultural crops. The third concern presupposes that land use will ultimately change from agricultural to residential and that the radium in the soil might then constitute a hazard to occupants of residences built on the land.

Why gypsum is used in agriculture

Before discussing these radiological concerns, the reasons for using gypsum in agriculture should be reviewed. At present, phosphogypsum is most widely used in California. Much of the inland valley areas of California are arid and the soils are alkaline. Alkaline soils may either be saline - having a high content of soluble salts, or they may be alkali in which case their cation exchange sites are largely occupied by sodium ions. Alkaline soils

generally are characterized by poor drainage, which is often caused by a dispersal of colloidal clay particles resulting in surface crusts and blocked soil pores.

The treatment of either saline, alkali or saline-alkali combination soils to improve drainage is called reclamation. Saline soils can usually be reclaimed by leaching. But treatment of soils with an amendment prior to leaching is recommended for alkali or saline alkali soils. The amendment most often employed is gypsum. When the dispersed particles contact the gypsum, the Na⁺ ions on the cation exchange sites are replaced by Ca⁺⁺ and the colloid is flocculated.



Following gypsum application and tilling (to assure mixing) the soil may be leached to remove the salt (Na₂SO₄) released. As long as the particles remain flocculated, a granular soil state and good drainage will prevail. Initial application of gypsum should provide sufficient excess to drive the reaction to completion and convert Na₂CO₃ to CaCO₃ and Na₂SO₄. This will reduce the soil pH and the Na₂SO₄ can be removed by leaching. Regularly cultivated, the soil should not require annual applications of gypsum; when subsequent applications are used it is more for soil quality maintenance than for reclamation.

Peanut farming in the southeastern states may use gypsum as a source of calcium, often substituting it for lime or limestone when the alkalinity of the latter materials must be avoided. A supply of calcium is a major requirement for proper nutrition of this crop. Optimum peanut growth is also favored by slightly acid soil conditions (pH 5.5 - 6.5), hence the use of gypsum.

Radiological Concerns

The radiological concerns of using phosphogypsum in agriculture can be placed in perspective by considering a hypothetical case of extended heavy applications of phosphogypsum. In California, initial gypsum applications as high as 10 tons/acre may be made for reclamation followed by alternate year applications of 5 tons/acre for maintenance of soil quality. This initial application is about ten times the application rate typically employed in peanut farming in the southeast. Furthermore, peanuts are usually not grown on the soil every year, but are rotated with crops such as corn. As a result, gypsum is applied to these soils about every three years at application rates of 1 ton or less per acre.

1. Radium buildup

If the radium content of the phosphogypsum were 15 pCi/g and the till depth 6 inches, the initial 10 ton/acre and alternating 5 ton/acre schedule could be maintained for more than 100 years before the radium buildup would reach a proposed federal concentration limit of 5 pCi/g. This estimate is really conservative since no allowance is made for radium washout (leaching)

or uptake by crops grown on the soil. Such an assumption, although conservative, may be unrealistic; without losses through runoff or uptake by plants, the soil would probably become poisoned by the buildup of salt long before the radium concentration reached 5 pCi/g. The 15 pCi/g for the radium content for phosphogypsum may be considered too low; however, most of the phosphogypsum used in California comes from Northern Florida phosphate, and, as previously noted, this source has a lower radium content than that generally quoted for Florida phosphogypsum.³ It should be noted that the proposed federal concentration limit for radium in soil of 5 pCi/g applies to lands contaminated by uranium mill tailings on which residences have been or will be constructed.⁴

Terrestrial radiation

Essentially all the gamma radiation exposure from the ^{238}U decay chain is due to ^{214}Pb and ^{214}Bi , daughter products of ^{222}Rn , as shown in Table 1.⁵ The effect of depth on the fraction of total exposure rate from a uniformly mixed naturally occurring source has been derived by Beck⁶ and is shown in Figure 2. From these data it has been estimated that a uniform concentration of 5 pCi/g of ^{226}Ra distributed through the top 6 inches of soil would result in an exposure rate of about 7 $\mu\text{R/hr}$.

This exposure rate must be added to that of normal background. If the average terrestrial background observed in the United States of approximately 6 $\mu\text{R/hr}$ ⁷ were added to the estimated exposure from the 5 pCi/g of ^{226}Ra , the resulting 13 $\mu\text{R/hr}$ would be within the range of terrestrial exposure rates

found in many populated areas. If an agricultural worker spent 40 hrs a week on this soil, he would receive an estimated annual radiation dose above background of about 15 milli-rem. This dose is about 3% of the recommended limit for an individual in an unrestricted area.⁸

Airborne radon daughters

When a ^{226}Ra atom decays into a ^{222}Rn (radon) atom the gaseous daughter atom may escape into the soil air instead of remaining in the soil matrix. Once into the soil air, the radon can diffuse up through the soil into the atmosphere. Whether the radon enters the atmosphere or remains in the soil, it undergoes the radioactive decay shown in Figure 3. Up to about 50% of the radon produced by the decay of radium may diffuse into the atmosphere depending upon atmospheric pressure and the porosity of the soil. In the atmosphere, the concentration of radon and its daughter products are determined more by the mixing rate in the atmosphere than by the concentration of radium in the soil.⁹

Fall months are normally characterized by a high degree of atmospheric stability. During this period the days are often warm and there is little surface wind. After sunset, the ground cools faster than the air above it and a temperature inversion develops. As a result, radon and its daughter products accumulate near the surface during the night. During the day, vertical dispersion of this activity may be curtailed due to lack of surface wind. During the spring and early summer, windy weather is quite frequent, and surface released radon and its daughters are carried aloft by wind-induced

vertical mixing. As a result of these seasonal differences in meteorology, the atmospheric radon concentration is highest during the fall months and lowest in the spring and summer. Figure 4 shows typical seasonal concentration differences observed at Livermore and the difference between morning and afternoon concentrations induced by night time temperature inversions.

Such variations have radiological monitoring implications, since it is obvious that extended sampling must be performed to accurately establish the average or typical radon daughter concentration. Once this is established for open land the measurements must be repeated when a building is constructed, since the extent of building ventilation greatly influences the radon daughter concentration. The present national emphasis on energy consumption-weather stripping, caulking, etc - has reduced ventilation rates with the result that radon daughter concentrations within these energy efficient buildings have been increased.

Health effects of radon and its daughter products

The primary hazard associated with working or living in an environment containing excessive amounts of ^{222}Rn and its daughters involves inhalation and subsequent deposition in lung tissue of the short-lived daughters. This concept has been established by epidemiological surveys of uranium miners who, under conditions of extreme exposure, exhibit an increased incidence of lung cancer.

Several organizations have established standards for maximum permissible concentrations in air of radon and its daughter products. The Environmental Protection Agency utilizes the concept of a working level. One working level (WL) being defined as that concentration of short-lived daughter products in a liter of air that will yield 1.3×10^5 million electron volts (MeV) of alpha energy in decaying through RaC'. This definition specifies the concentration of the radioactivity of concern - the daughter alpha emitters, and does not specify the necessity for equilibrium between the parent radon and its daughters. If equilibrium does exist, one WL is equivalent to 100 pCi/l of ^{222}Rn .

An atmospheric radon daughter concentration of 0.1 pCi/l expressed as a working level would be 0.001 WL, assuming equilibrium conditions. However, such conditions are rarely achieved. At Livermore, we found an average annual percentage of secular equilibrium to be 75% in surface air based on measurements made in the Livermore Valley.¹⁰ Accordingly, an 0.1 pCi/l concentration of radon daughters at 75% of equilibrium would have an equivalent WL value of 0.00075 or 7.5×10^{-4} WL.

Table 2 shows that 5 pCi/g of radium in the soil would be expected to result in an airborne radon daughter concentration equivalent to an average working level of 0.012.¹¹ The range of concentrations shown are attributed to variations in meteorology, and the degree of ventilation in basement and living areas of the building. Although this range exceeds the concentration proposed for residential exposure,¹² such a guidance should not be applied to agricultural workers because of the seasonal nature of their work.

2. Uptake of radium by crops

Radium uptake expressed as the ratio of radium in dry weight foodstuff to the radium in the soil is in the range of 0.01. Assuming a consumption of 80 g/day (dry weight) of foodstuff¹³ grown on soil containing 5 pCi/g of radium, would result in a radium intake of 4 pCi/day. The mean daily intake of ^{226}Ra in the standard U.S. diet is about 1.4 pCi, but varies at least from 0.7 to 2.1 pCi.¹⁴

Assuming an adult's total vegetable diet consisted of items grown on soil containing 5 pCi/g of radium and that this consumption was continuous over a period of 50 years, the integrated radiation dose to the surface of the bone (the critical organ) would be 1.4 rem.¹⁵ For reference, persons in unrestricted areas are permitted to receive an annual radiation dose to the bone of about 2 rem.¹⁶

In the case of radium associated with gypsum, the radium uptake ratio of 0.01 may be too high. When applied to the soil in a matrix containing calcium in such excess, the use of gypsum could be expected to block plant uptake of radium, as it has been demonstrated that increasing the calcium in plant nutrients reduces the uptake of other alkaline earth cations present.¹⁷ This common ion effect is illustrated by the data in Table 3, which compares the radium uptake in both root and leaf vegetables grown in test gardens containing two different levels of calcium.

3. Land Use Conversion

Land use conversion from agricultural to residential would be of concern if our hypothetical application schedule would in fact result in a 5 pCi/g radium concentration in the soil. Table 2 shows this radium concentration could generate radon daughter concentrations that exceed the federal proposed guidance for residential occupancy. Although the present analysis was based on hypothesis, evidence of radium buildup in agricultural areas treated with phosphogypsum should be monitored, since any such buildup may gain added importance as residential construction becomes more energy efficient.

Summary

The radiological concerns associated with phosphogypsum utilization in agriculture have been placed in perspective by considering the consequences of a hypothetical case involving heavy long term applications of phosphogypsum. In California, such a schedule might consist of an initial gypsum application of 10 tons/acre followed by alternate year applications of 5 tons/acre. If the radium content of the gypsum were 15 pCi/g and the till depth 6 inches, this schedule could be maintained for more than 100 years before the radium buildup in the soil would reach a proposed federal concentration limit of 5 pCi/g. An agricultural worker spending 40 hrs a week in a field containing 5 pCi/g of radium would be exposed to terrestrial radiation of about 7 μ R/hr above background. This exposure would result in an annual radiation dose of about 15 mrem, which is 3% of the recommended limit for an individual working in an uncontrolled area. Five pCi/g of radium in the soil could generate

airborne radon daughter concentrations exceeding the concentration limit proposed for residential exposure. However, as residential exposure limits are predicated on 75% of continuous occupancy, these limits should not be applied to agricultural workers because of the seasonal nature of their work. Radium uptake by food crops grown in the hypothetical soil would result in a 50 year integrated dose to the bone surface of 1.4 rem. This dose is conservatively based on the assumption that an adult's total vegetable diet comes from this source and that consumption was continuous during the 50 year period. For comparison individuals in unrestricted areas are permitted annual radiation doses to the bone of about 2 rem. Land use conversion from agricultural to residential has a potential for concern, since soil containing 5 pCi/g of radium can generate airborne concentrations of radon daughters in buildings which exceed the federal guidance for residential occupancy.

Acknowledgment

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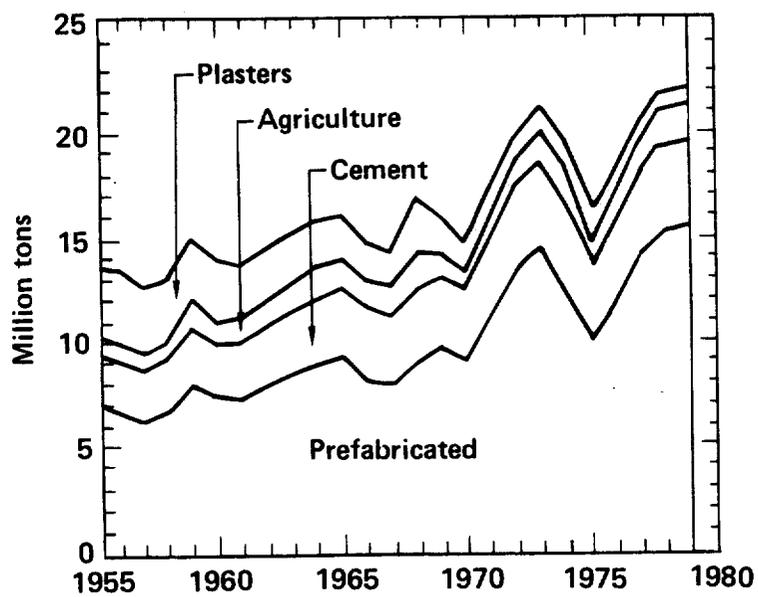


Figure 1. Sales of gypsum products by use (from Mineral Yearbook reference 1)

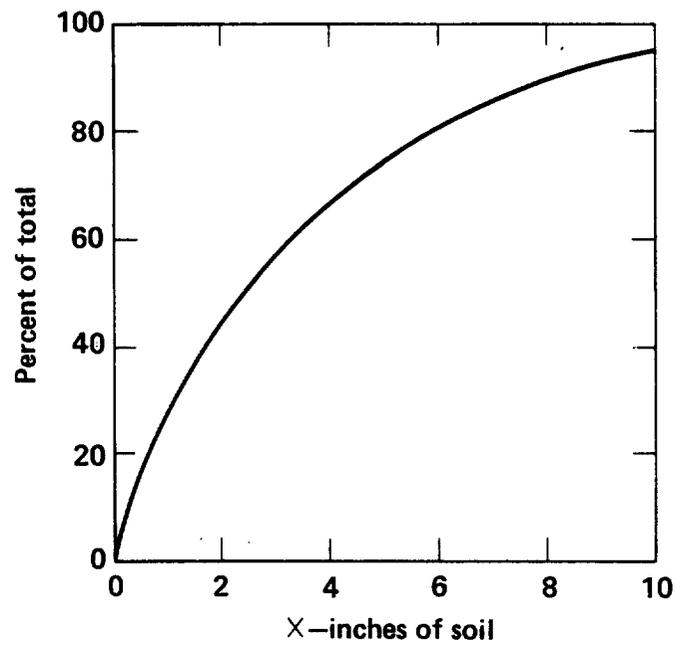


Figure 2. Percent of integral exposure rate due to natural emitter sources at various depths (from Beck, reference 5)

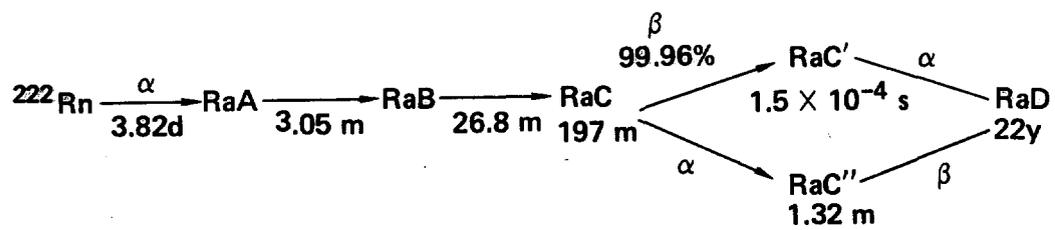


Figure 3. Radioactive decay scheme for ^{222}Rn

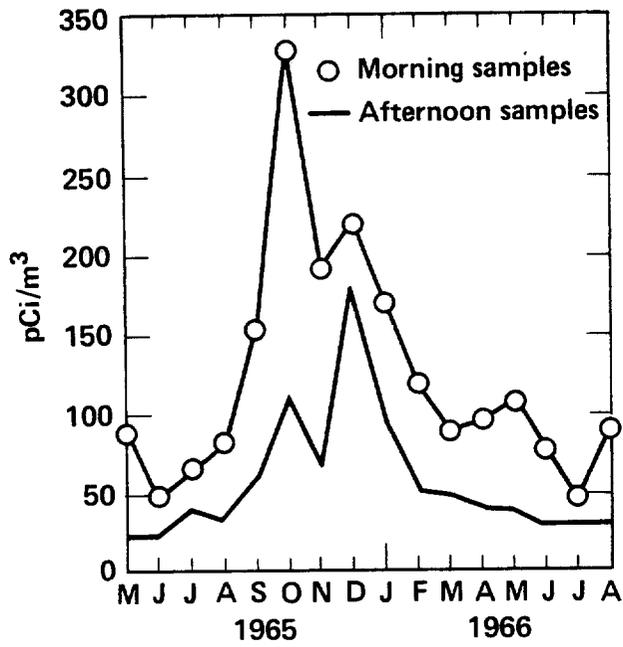


Figure 4. Morning and afternoon variations in airborne radon daughter concentration

Isotope	$\frac{\mu R/h}{pCi/g}$
^{238}U + daughters	1.82
^{226}Ra + daughters	1.80
^{214}Pb (RaB)	0.20
^{214}Bi (RaC)	1.60

Table 1. Radiation Exposure rate at 1 m above ground for ^{238}U + daughters and ^{226}Ra + daughters

Soil concentration pCi/g ²²⁶ Ra	Working level	
	Ranges (a)	Average (b)
1.0	0.0002-0.008	0.002
3.0	0.0007-0.024	0.006
5.0	0.0024-0.04	0.012
10.0	0.0048-0.08	0.020

(a) 1 pCi/l ²²²Rn = 0.005 WL assuming 50% of equilibrium

(b) Average based on midpoint of the range of input parameters

Table 2. Estimated airborne radon daughter working levels versus radium soil concentrations

Garden	Soil		²²⁶ Ra in plants, pCi/g (dry wt)	
	Calcium, ppm	²²⁶ Ra, pCi/g	Broccoli	Turnip
1	3,100	0.477	$2.83 \times 10^{-2} \pm 34\%$	$2.55 \times 10^{-2} \pm 39\%$
2	5,200	0.482	$1.09 \times 10^{-2} \pm 100\%$	$1.32 \times 10^{-2} \pm 70\%$

Table 3. Effect of calcium on ²²⁶Ra uptake by plants