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The Radium-226 Content of Agricultural Gypsums*

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Abstract

Gypsum ($CaSO_4.2H_2O$), used as a soil amendment for saline-alkali soils is obtained either by quarrying or as a by-product in the phosphate fertilizer industry. The latter, termed "phospho gypsum" contains variable amounts of ^{226}Ra, depending on the uranium content of the phosphate rock. Radium-226 contents of both quarried and phospho gypsum were determined by gamma counting in a low-background Ge(Li) spectrometer equipped with Compton suppression. Quarried samples from Nova Scotia, Iowa, Texas, and California were compared with phospho gypsum derived from Florida land pebble phosphates. Quarried gypsums showed an average radium content of 0.21 pCi/g. The average radium in phospho gypsum was 14.6 pCi/g. Uranium-238 measurements showed that near secular equilibrium existed between the uranium and radium in the quarried samples. Disequilibrium in the phospho gypsums, occurred because of preferential separation of radium during chemical processing. At the levels observed, no health hazard is implied from uptake of radium by plants grown in phospho gypsum treated soil.

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Introduction

Gypsum ($CaSO_4.2H_2O$) is widely used as an amendment to improve water movement in saline-alkali soils, and may also be substituted for limestone or lime to supply calcium to soils that are alkaline. Most agricultural gypsum is obtained by quarrying the mineral, but substantial quantities are also produced as a by-product in various chemical processes. In 1975, 1,482,000 tons of agricultural gypsum were sold in the United States; by-product gypsum accounted for 369,000 tons, or about 25% of the total sold for agricultural use (Minerals Yearbook, 1975a).

At present, the principal source of by-product gypsum is the phosphate fertilizer industry, and in the United States, Florida is the major source of phosphate rock (Minerals Yearbook, 1975b). To produce phosphoric acid, the phosphate rock – commonly fluorapatite [$Ca_5F(PO_4)_3$] – is treated with sulfuric acid and the $CaSO_4$ (termed phospho gypsum) is filtered from the acid. Florida phosphate rock may contain from less than 10 to more than 200 ppm of uranium (Guimond et al., 1975a). In a previous study, it was found that soils heavily treated with phosphate fertilizers contained elevated levels of ^{238}U over those expected from ^{226}Ra measurements (Lindeken et al., 1975). In the soil, the relative immobility of uranium with respect to plant uptake is well recognized (Spalding et al., 1972). However, since the properties of radium in the uranium decay chain are similar to those of calcium, the radium content of phospho gypsum is of greater health physics interest. This paper compares the ^{226}Ra and the ^{238}U content of quarried and phospho gypsums.

Sample Sources

Samples of quarried gypsum were obtained from Nova Scotia, Iowa, Texas, and California. Phospho gypsum samples were derived from Florida land pebble phosphates. Commercially active land pebble areas are found principally in north Florida in Columbia and Hamilton Counties, and in west central Florida (the Bone Valley formation) in Polk, Hillsborough, Mantee, Hardee, and Desoto Counties (Roessler et al., 1976). Figure 1 is a map showing the location of these phosphate districts in Florida.

Measurements

An aliquot of approximately 250 g from each sample source was sealed in a 200-ml^3 thin-walled, aluminum can. These samples were gamma-counted using an 80-ml^3, low-background Ge(Li) spectrometer equipped with a Compton suppression system (Camp et al., 1974). Counting periods were nominally 6×10^4 s.

The ^{226}Ra activity can be determined from the counts in the gamma-ray spectrum at the energies shown in Table 1. Normally, the samples are stored after sealing in the container to allow secular equilibrium to be established between the radium and radon since the ^{226}Ra measurements are usually based on the activities of the radon daughters, ^{214}Pb and ^{214}Bi. The 186.14-keV gamma ray directly associated with the ^{226}Ra alpha decay to ^{222}Rn is seldom employed because of its lower abundance and because of interference from the

185.72-keV gamma ray associated with the decay of ^{235}U. However, in the present samples, the concentration of ^{235}U is so low that this interference is negligible, and comparison of the 186.14-keV ^{226}Ra decay gamma with those of ^{214}Pb and ^{214}Bi serves as a check for ^{226}Ra – ^{222}Rn equilibrium.

Uranium-238 was determined by measuring the 63.3-keV transition from the decay of ^{234}Th (Coles et al., 1976). Such a measurement, although depending on equilibrium between the 24 d decay of ^{234}Th and its parent ^{238}U, avoids the potential equilibrium problems associated with ^{238}U uher measurements depend on daughters subsequent to the long-lived trio ^{234}U, ^{230}Th, and ^{226}Ra. Because many of the samples contained ^{238}U at levels below 1 ppm, several of these samples were also analyzed for ^{238}U by isotopic dilution mass spectrometry using ^{233}U as a tracer (Landrum et al., 1969).

Results and Discussion

Table 2 shows the ^{226}Ra and ^{238}U activities in the samples analyzed. Samples 1 through 4 represent quarried gypsum, and it is clear that the natural mineral is generally characterized by low ^{226}Ra levels. By comparison, the average uranium content of the continental crust is about 3 ppm (Phair et al., 1964). Assuming that the uranium decay series is in secular equilibrium, the associated ^{226}Ra activity would be about 1 pCi/g. Livermore Valley soils contain about 0.6 pCi/g of ^{226}Ra (Silver et al., 1974). As indicated by the activity ratios in the quarried gypsum, near secular equilibrium exists between the parent ^{238}U and the ^{226}Ra. In the phospho

gypsums, illustrated by samples 5 and 6, this equilibrium is disrupted. During the chemical processing of the raw material, the uranium tends to go into the acid phase – probably as a uranyl sulfate, while the radium coprecipitates with the gypsum as $RaSO_4$. As the sulfate, the radium is essentially insoluble in water – 2×10^{-6} g/100 ml at 25°C, or two orders of magnitude less soluble than the very insoluble $BaSO_4$ (Handbook of Chemistry and Physics, 1969).

The ^{226}Ra content of the phospho gypsum samples compares well with the approximately 14 pCi/g observed by Bolch et al. (1976) in typical phospho gypsums, but is lower than the 33 pCi/g reported by Guimond et al., (1975b). Again, assuming that the uranium decay series is in equilibrium and the removal of radium is quantitative, then 33 pCi/g of radium activity in the gypsum would correspond to about 100 ppm of uranium in the land pebble. It turns out that the partition of radium and uranium is quite variable. Guimond et al. (1975c) found that approximately 80% of the product ^{226}Ra was in the phospho gypsum. However, the fact is that the radium content of phospho gypsum cannot be reliably predicted from the uranium content of the phosphate rock.

Any consideration of radiological hazard associated with the use of phospho gypsum must be based on how it is applied to the soil, as well as its radium content. In California, where most of the gypsum is used, applications are seldom at rates greater than 2.2 kg/m^2, and are usually 0.2-0.6 kg/m^2. Since the principal reason for adding gypsum is to improve drainage by replacing the adsorbed sodium on clay particles by the divalent calcium, it is impor-

tant to thoroughly mix the gypsum into the soil. This mixing is usually accomplished by disking to a depth of about 15 cm. When greater till depths are required, plowing is employed. As long as the clay particles remain flocculated, a granular soil state and good drainage will prevail. Regularly cultivated, this soil should not require annual applications of gypsum; and when applied, such gypsum applications are more for soil quality maintenance than for soil reclamation.

Based on the above application practices and the average 15 pCi/g ^{226}Ra content from Table 2, the radium contribution from extended usage of phospho gypsum can be estimated.

Assume

- gypsum application = 0.66 kg/m^2
- till depth = 15 cm
- soil density = 1.5 g/cm^3
- number of applications = 10.

Using these assumptions, 0.45 pCi/g of ^{226}Ra will be added to the soil as a result of the ten gypsum applications.

When applied to the soil in a matrix containing calcium in such excess, the use of gypsum can be expected to block the plant uptake of radium, since it has been demonstrated that increasing the calcium of plant nutrients reduces the uptake of other alkaline earth cations present (Hungate et al., 1958). This common ion phenomenon 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.

The radium uptake by the vegetation is taken as the ratio of the radium in the vegetation to the radium in the soil. The data for garden No. 1 in Table 1 gives the higher, more conservative uptake. This ratio, 5.6×10^{-2}, is then used with the ^{226}Ra content of the soil after ten gypsum applications to estimate the radium in vegetation grown on that soil which can be attributed to the phospho gypsum. The estimated dry-weight radium content of this vegetation is, therefore, $5.6 \times 10^{-2} \times 0.45$, or 2.5×10^{-2} pCi/g.

The radiation dose an individual would receive if his total vegetable diet consisted of items grown in soil containing 0.45 pCi/g of ^{226}Ra was calculated using methods outlined in ICRP-2 (ICRP, 1959a). The maximum organ burdens for the bone were obtained using the following assumptions:

- Radium in the vegetation is soluble in biological fluids.
- Radium concentration in the vegetation is 2.5×10^{-2} pCi/g.
- A hypothetical person consumes 400 g/day (wet weight) (Agriculture Statistics, 1969) or 80 g/day (dry weight) of vegetables over a 50-year period.
- Absorption fractions, transfer coefficients, and other ^{226}Ra factors are as given in ICRP-2 (ICRP, 1959b) and ICRP-10a (ICRP, 1969).

Under these assumptions, the total 50-year integrated dose to the bone, which is the critical organ, is 1.6×10^{-1} rem, or 1.1×10^{-3} expressed as a fraction of the guide value (ERDAM Chap. 0524, 1972).

This radiation dose assessment is probably too conservative, but at present it is impossible to evaluate the probable reduction in radium plant uptake due either to the low solubility of $RaSO_4$ or the effect of the presence of calcium. However, the conservative approach taken does tend to assure that the radiation dose should be less than calculated. It follows then that, at present, there is little basis for concern regarding a radiological hazard from uptake of ^{226}Ra by plants grown on phospho gypsum treated soils.

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Table 1. Prominent gamma rays from ^{226}Ra and its daughters.

Energy (keV)	Intensities (gammas/dis)	Source nuclide
186.14	0.040	^{226}Ra
295.20	0.202	^{214}Pb
351.92	0.401	^{214}Pb
609.27	0.484	^{214}Bi
1120.28	0.160	^{214}Bi
1764.49	0.166	^{214}Bi

Table 2. ^{226}Ra and ^{238}U content of agricultural gypsums.

	Activity pCi/g		
Sample	^{226}Ra [b]	^{238}U [a]	^{238}U [b]
1	0.500 ± 5%[c]	0.509 ± 1.2%	0.414 ± 31%
2	0.143 ± 4%	0.163 ± 1.3%	0.200 ± 30%
3	0.064 ± 16%	0.067 ± 1.4%	d
4	0.090 ± 14%	0.076 ± 1.4%	d
5	18.4 ± 2%	--	3.66 ± 32%
6	10.8 ± 1.4%	--	0.618 ± 74%

a mass spectrometry measurements

b gamma spectrometry measurements

c all error values are at the 2 σ level

d below minimum detection limit

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

	Soil		^{226}Ra in plants, pCi/g (dry wt)	
Garden	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	$1.09 \times 10^{-2} \pm 100\%$	$1.32 \times 10^{-2} \pm 70\%$

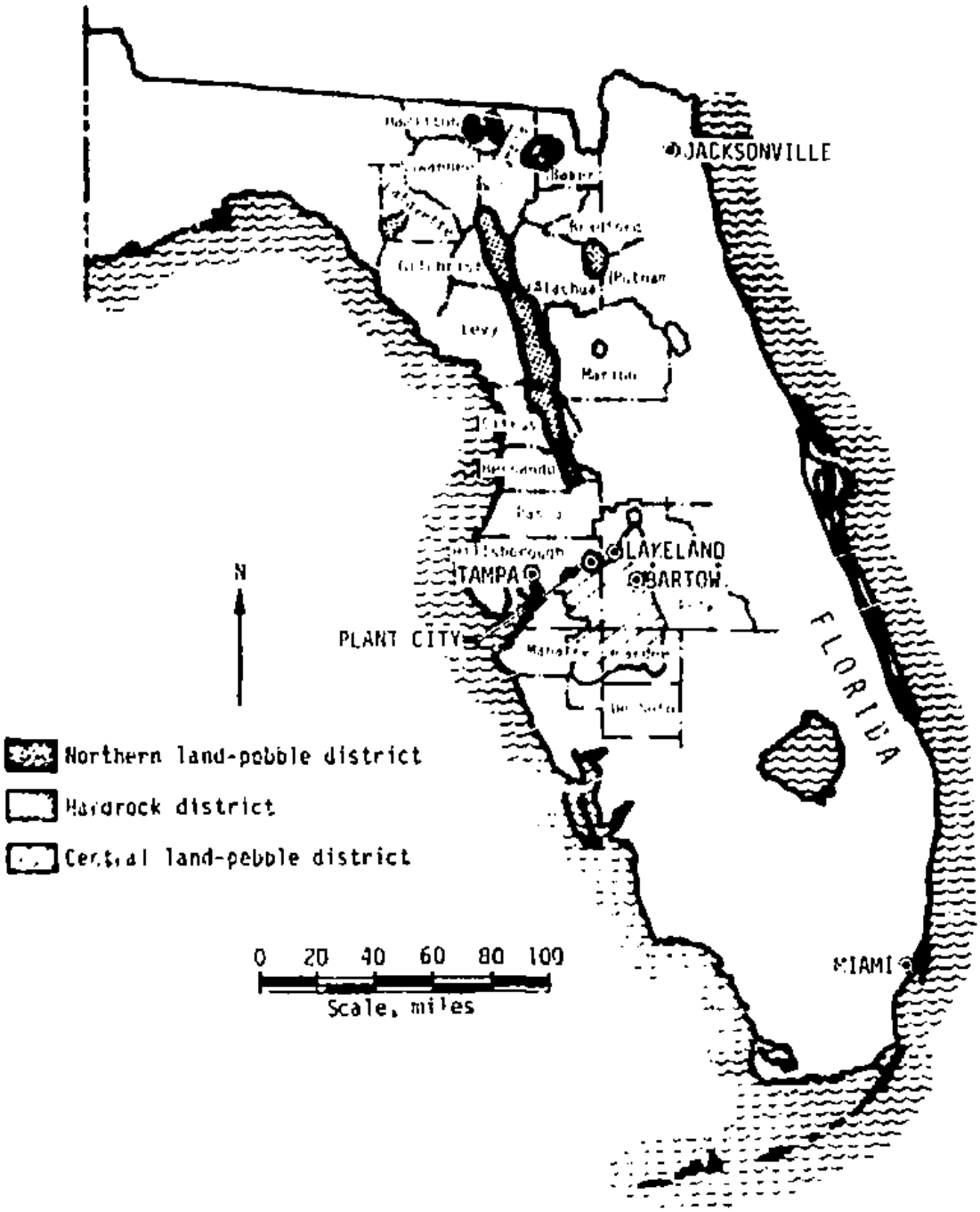
JACKSONVILLE
LAKELAND
BARTOW
TAMPA
PLANT CITY
MIAMI
FLORIDA
N
Northern land-pebble district
Hardrock district
Central land-pebble district
0 20 40 60 80 100
Scale, miles

Fig 1.

Figure Caption

Fig. 1. Phosphate deposits in Florida. (From Bureau of Mines Circular 8653, Economic Significance of the Florida Phosphate Industry.)

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