Uranium, Radium, and Thorium Content in Phosphate Rocks and Their Possible Radiation Hazard

Ronald G. Menzel

A survey of phosphate rock samples from all major phosphate-producing areas of the world showed that phosphate rocks from Florida, the main source of fertilizer phosphates in the United States, ranked relatively high in content of uranium, radium, and thorium. In areas where crops are fertilized with high rates of phosphate from Florida, the addition of uranium and radium may equal the amounts occurring naturally in the plow layer of soils, but the addition of thorium would be less than the amount occurring naturally. The radiation hazard, which might result from uptake of radium into food plants, appears to be negligible.

Phosphate fertilizers may carry appreciable amounts of radioactive material from the uranium and thorium present as trace constituents in phosphate rock. This source of radiation has little significance for plant growth (Alexander, 1950; Hopkins and Sachs, 1915; Ross, 1914), although much work has been done on the "stimulating effect" of radioactive fertilizers (Sax, 1963). However, humans may receive small radiation exposures from excessive use of such fertilizers on special crops. An example is the uptake by tobacco leaves of radium-226 and lead-210 from heavily fertilized soils (Tso *et al.*, 1964).

To evaluate the extent of possible hazard, a survey of uranium, thorium, and radium contents was made on phosphate rock samples collected from all major phosphate-producing areas of the world over the past 40 years. Records of United States fertilizer practices were examined to locate areas of the greatest use of phosphate fertilizers. These data are discussed with reference to probable maximum accumulation of radioactive materials in plants.

Many phosphate rock deposits have been examined for uranium content (Altschuler *et al.*, 1959; Davidson and Atkin, 1952; Mazor, 1963), since they are potentially an important source of uranium for atomic energy. Contents higher than 1000 p.p.m. have been reported, but most phosphate rocks contain between 30 and 200 p.p.m. uranium. Radium is reported generally to be in radioactive equilibrium with the uranium (Davidson and Atkin, 1952; Mazor, 1963). The few reported thorium analyses indicated less than 10 p.p.m. in phosphate rock (Davidson and Atkin, 1952; Mazor, 1963).

Phosphate fertilizers contain various fractions of the uranium, radium, and thorium originally present in the rock, depending on the manufacturing process. For example, all of these elements are retained in the manufacture of ordinary superphosphate. This material, which dominated the phosphate fertilizer market for many years, is made by adding sulfuric acid to phosphate rock and curing the mixture. On the other hand, a considerable separation of phosphorus from radium is achieved in the wet process manufacture of phosphoric acid (Shiraishi, 1957), and furnace process phosphoric acid should be nearly free of uranium, radium, and thorium. Phosphoric acid is being used increasingly in the manufacture of concentrated superphosphate and ammonium phosphate, or in high-analysis liquid fertilizers. Therefore, relative to the phosphorus content, the content of uranium, radium, and thorium would be lower in these materials than in ordinary superphosphate.

U.S. Soils Laboratory, Soil and Water Conservation Research Division, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Md. 20705

MATERIALS AND METHODS

Analysis of the gamma spectra was used to determine the uranium, radium, and thorium contents of 316 phosphatic materials. These were mainly ground samples of phosphate rocks, consisting of microcrystalline fluorapatite minerals and impurities. Many of these were beneficiated rocks, ready for fertilizer manufacture. A few samples of guano, macrocrystalline apatite, and other mineral phosphates were analyzed. The origins of the samples are summarized in Table I.

A scintillation detector with a 3 × 3 inch sodium iodide crystal and a 400-channel analyzer were used for the analysis. Each sample was put into a 6-ounce salve tin ($1^1/_4$ × 3-inch I.D.) and placed on top of the crystal for accumulation of counts in the gamma spectrum during a 2-hour period. If available, 150 grams of each sample, as taken from storage, were placed in the tin. To analyze as many samples as possible, 85 samples weighing less than 150 grams were counted. Of these, 39 weighed less than 100 grams and 12 weighed less than 50 grams.

The analysis was carried out by solving simultaneous equations for the count rates from uranium, radium, and thorium in each of three characteristic regions of the gamma spectrum. These regions were dominated by the

Table I. Median Contents of Radium, Uranium, and Thorium in Phosphate Rocks from Different Sources

Origins of Rocks	Number of Samples	Median Content of Element: Ra, ng./kg.	U, mg./kg.	Th, mg./kg.
Florida land pebble, 1926–1935	11	73	208	14
Florida land pebble, 1939	4	74	222	11
Florida land pebble, 1946–1955	14	53	148	13
Florida land pebble, 1959–1964	12	43	127	17
Florida soft phosphate, 1927–1945	7	31	102	19
Florida waste pond and misc. phosphate, 1928–1943	9	21	76	17
Tennessee brown rock, 1927–1935	17	4	11	6
Tennessee brown rock, 1939	8	4	13	5
Tennessee brown rock, 1944–1955	3	4	10	6
Tennessee blue rock, 1926–1930	3	7	16	3
Tennessee white rock, 1930–1936	4	5	10	2
Tennessee phosphatic limestone, 1926–1929	3	3	8	2
South Carolina, 1927–1937	11	133	399	19
North Carolina, 1957–1964	3	18	79	9
Arkansas, 1938	13	11	30	13
Oklahoma, 1932–1941	5	10	25	8
Montana, 1930–1953	10	41	114	7
Idaho, 1928–1955	5	49	151	8
Wyoming, 1929–1961	4	62	183	12
Utah, 1936–1961	9	50	128	7
Misc. U. S. and Canada, 1927–1962	10	4	12	10
Mexico and Guatemala, 1953–1962	5	12	27	4
West Indies, 1944–1951	12	3	8	14
Curacao, 1929–1948	9	5	14	1
Venezuela, 1953–1960	4	27	72	12
Peru, washed phosphate, 1961–1964	7	22	106	8
Peru, beneficiated phosphate, 1961	7	38	167	11
Brazil, Olinda, 1951–1960	4	96	274	40
Brazilian apatite, 1949–1951	6	1	9	35
Chile and Ecuador islands, 1945–1955	9	1	3	6
Morocco, 1937–1943	5	46	141	8
Algeria, 1927–1936	12	31	104	14
Tunis, 1927–1955	6	14	48	23
Egypt, 1936–1937	6	37	122	6
Senegal and other African phosphates, 1949–1963	6	37	107	17
Spain and other Western European phosphates, 1927–1936	5	0	5	4
Russian and Polish phosphorite, 1930–1936	5	15	50	7
Russian apatite, 1932–1943	5	2	6	23
Jordan and Turkey, 1956–1963	6	25	48	0
India, China, and Southeast Asia, 1947–1962	5	4	12	6
Christmas Island, 1925–1960	5	9	27	2
Nauru Island, 1925–1937	4	23	65	2
Ocean Island, 1925–1937	5	32	98	4
Makatea Island, 1930–1937	3	32	101	5
Australia and misc. island phosphates, 1929–1937	6	11	30	5
Seychelles guano, 1931–1935	4	4	20	2
Total / Median content	316	18	59	8

following gamma rays: I, 185 k.e.v. from U-235 and 187 k.e.v. from Ra-226; II, 239 k.e.v. from Pb-212 (daughter of Th-232) and 242 k.e.v. from Pb-214 (daughter of Ra-226); and III, 295 k.e.v. from Pb-214. Reference spectra were obtained with the same counting conditions by mixing known amounts of each element with aliquots of a finely ground phosphate rock sample from Tennessee which was known to have relatively low radioactivity.

The variability in these analyses was measured by counting six samples at regular intervals over the whole period that samples were counted (Table II). The standard deviation for each radionuclide increases with increasing radium and uranium content in the samples. Also, the standard deviations for radium and uranium apparently increase in the presence of larger than usual amounts of thorium. The standard deviation for thorium probably increases with increasing thorium content, but there is no evidence for such an increase within these samples. The sensitivity of the analysis is approximately twice the standard deviation at low levels of each element, or 0.2 ng. of radium, 4 mg. of uranium, and 1 mg. of thorium per kg. of sample. In the usual type of samples that were run, the standard deviations probably are less than 1 ng. of radium, 10 mg. of uranium, and 2 mg. of thorium per kg. of sample.

Confirmation of the accuracy of the standardization is found in the uranium-to-radium ratios calculated from the analyses. If the uranium and radium are in radioactive equilibrium, as would be expected from the age of most phosphate deposits, this ratio would be 2.94×10^6. The calculated ratios for the samples in Table II, excluding the sample of bone ash, range from 2.53 to 3.38×10^6.

Table II. Reproducibility of Determination of Radium, Uranium, and Thorium Contents in Phosphate Rock by Gamma Spectrometry

Sample	Number of Determinations	Content and Standard Deviation		
		Ra, ng./kg.	U, mg./kg.	Th, mg./kg.
Bone ash, Camden, N. J., 1931	6	0.38 ± 0.11	−1.01 ± 2.16	0.47 ± 0.66
Russian apatite, 1933	6	1.79 ± 0.91	6.05 ± 3.62	22.29 ± 0.97
Tennessee brown rock, 1939	6	4.10 ± 0.22	13.90 ± 3.27	5.29 ± 0.74
Tennessee white rock, 1935	19	11.93 ± 0.45	30.13 ± 4.56	3.73 ± 0.92
Montana phosphate, 1930	6	40.66 ± 0.84	117.30 ± 7.91	8.90 ± 1.84
South Carolina phosphate, 1930	18	149.18 ± 3.12	433.87 ± 14.35	21.94 ± 4.38

RESULTS

The results of the analyses are summarized in Table I, which shows the median contents of radium, uranium, and thorium in the samples grouped according to geographic origin. Generally, the uranium-to-radium ratio indicates radioactive equilibrium of these elements, so that only uranium and thorium contents will be commented on.

The highest uranium content was 460 p.p.m. in a sample from Bulow mine, John's Island, S. C. The six highest uranium contents, all over 399 p.p.m., were in samples from South Carolina. Six other samples had more than 300 p.p.m. uranium, including two from South Carolina, two from Florida, and two from Brazil. All these samples had a correspondingly high radium content, except one sample of apatite from Ipira, Brazil. In this sample, the analysis for uranium may be erroneously high due to an unusually high thorium content, 1460 p.p.m.

Guano and macrocrystalline apatite predominated among those samples showing unusually low uranium contents. Although most of the samples had correspondingly low radium contents, the correlation was not as good as at high uranium and radium contents. This might be expected because of relatively greater analytical error at low uranium and radium contents. The median uranium content for 20 samples of macrocrystalline apatite was 6.0 p.p.m., and for 13 samples of guano it was 7.0 p.p.m. Comparison with their median radium contents showed a uranium to radium ratio of 4.3×10^6 for the apatites and 6.4×10^6 for the guanos. Since the uranium to radium ratio in apatites would be expected to be 2.94×10^6 (the radioactive equilibrium value), there appears to be a systematic tendency to underestimate low contents of radium or to overestimate low contents of uranium. In the guano samples, radioactive equilibrium would not be expected, and the high uranium to radium ratio probably indicates a relative enrichment of uranium in these materials.

Four of the five samples containing more than 100 p.p.m. of thorium were apatite samples. The highest content was 2096 p.p.m. found in apatite magnetically separated from magnetite from Nemegos, Ontario. High thorium contents were found in apatites from Ipira, Brazil (1460 p.p.m.), Norway (312 p.p.m.), and Quebec (200 p.p.m.). However, the median thorium content for 20 apatites was only 23 p.p.m. A thorium content of 664 p.p.m. was found in one phosphate rock sample from Olinda, Brazil, but three other samples from Olinda contained only 31, 39, and 42 p.p.m. of thorium.

A variety of phosphates contained less than 1 p.p.m. of thorium. Six of the samples were high-grade phosphate rocks from Makatea Island, Christmas Island, Jordan (2 samples), Curacao, and dicalcium phosphate from Jamaica. Five low-grade phosphatic materials were included, from Jordan (2 samples), Spain, Venezuela, and Tennessee. Two iron and aluminum phosphate minerals completed the group of samples with less than 1 p.p.m. of thorium. All of the samples from Jordan were low in thorium, but there were only four small samples for analysis.

In the Florida land pebble phosphates, there was a trend toward lower uranium contents in later years (Table I). The thorium contents, on the other hand, did not show this trend. The Florida land pebble is the major source of phosphate for fertilizers in the United States (Hill, 1964) and was the most extensively sampled source in this investigation. In no other case were enough samples taken from the same locality to discern trends in uranium and thorium content with time.

DISCUSSION

Large amounts of phosphate fertilizers, exceeding 200 pounds of P_2O_5 per acre, are commonly applied for potatoes, sugar beets, tobacco, or vegetable crops in different areas of the United States (Ibach *et al.*, 1964). Hawkins *et al.* (1947) estimated that many potato fields in Maine had received more than 2000 pounds of P_2O_5 per acre in the 20 years preceding 1944. The total application on many of these fields has probably amounted to more than 6000 pounds of P_2O_5 per acre to the present time. Normal superphosphate has been used almost exclusively to supply P_2O_5 in Maine. Thus, the equivalent of about 18,000 pounds of phosphate rock, with its associated uranium, radium, and thorium contents, has been added to each acre in many potato fields. Undoubtedly, most of this rock originated from Florida.

Quite possibly, the applications of superphosphate for potatoes in Maine have unintentionally resulted in as large applications of uranium, radium, and thorium as have been made on cropland. The uranium, radium, and thorium contents through the years are probably approximated rather closely by the median values found in Florida land pebble from 1926 to 1965. Calculations from the contents in Table I show that 1 ton of Florida

land pebble contains about 45 μc. each of uranium and radium, and 1.7 μc. of thorium. Thus, 400 μc. each of uranium and radium and 15 μc. of thorium would have been added per acre in some Maine potato fields. The estimated addition of radium agrees with the possible additions to highly fertilized tobacco soils, as estimated from radium analyses reported by Tso *et al.* (1964). The additions of uranium and radium are nearly equal to the amounts naturally occurring in the plow layer of soils (Talibudeen, 1964), but the addition of thorium is considerably less than the naturally occurring amount.

The major loss of the added radionuclides from the surface soils probably occurs by water erosion. Uranium, radium, and thorium are rather strongly adsorbed on soil (Schulz, 1965), as is phosphate, so that erosion losses of the added radionuclides may be similar to the loss of added fertilizer phosphate. This has been estimated to range from 25 to 60% in long-term experiments on sandy soils in the southeastern United States (Pierre and Norman, 1953).

Radium is the radionuclide likely to result in the greatest uptake of radioactivity by plants from applications of fertilizer phosphate (Menzel, 1965). However, no measurements have been made of the availability to plants of radium contained in phosphate fertilizers. Its availability may be higher or lower than that of native soil radium. In the extreme, but unlikely, case that radium in superphosphate is as available as water-soluble radium, data on radium uptake from soils (Menzel, 1965) indicate that, after application of 400 μc. of radium per acre (approximately 400 pc. per kg. of plow layer soil), concentrations in dried leaf tissue might reach 40 pc. per kg. For comparison, the Federal Radiation Council has recommended a radiation protection guide limiting the daily intake of radium-226 to less than 20 pc. (Federal Radiation Council, 1961).

Phosphate fertilizer applications probably have not resulted, or will not result, in an appreciable radiation hazard. The evaluation just given applies to the most intensive known applications of phosphate fertilizers. Considering that the availability of radium in phosphate fertilizer may be limited, and that erosion losses may be appreciable, even these intensive fertilizer applications must result in negligible radiation hazard. With the increasing trend toward using concentrated phosphate fertilizers, which have a lower radium content, additions of radium to soils will probably be no greater in the future than they have been in the past.

LITERATURE CITED

Alexander, L. T., *Agron. J.* **42,** 252 (1950).
Altschuler, Z. S., Clarke, R. S., Jr., Young, E. J., *U. S. Geol. Survey Profess. Papers* **314D,** 45–90 (1959).
Davidson, C. F., Atkin, D., *Geol. Survey (Gt. Brit.) and Museum, Atomic Energy Div. Rept.* No. **124,** 16 pp. (1952).
Federal Radiation Council, Rept. No. **2,** 11–13, Washington, D. C., 1961.
Hawkins, A., Chucka, J. A., Mackenzie, A. J., *Maine Agr. Expt. Sta. Bull.* No. **454,** 243–44 (1947).
Hill, W. L., "Superphosphate: Its History, Chemistry, and Manufacture," Chap. 4, 97–8, U. S. Dept. Agr., ARS, Washington, D. C., 1964.
Hopkins, C. G., Sachs, W. H., *Science* **41,** 732 (1915).
Ibach, D. B., Adams, J. R., Fox, E. I., *U. S. Dept. Agr. Statist. Bull.* **348,** 39–140 (1964).
Mazor, E., *Israel J. Earth Sci.* **12,** 41 (1963).
Menzel, R. G., *Health Physics* **11,** 1325 (1965).
Pierre, W. H., Norman, A. G., Eds., "Soil and Fertilizer Phosphorus," p. 413, Academic Press, New York, 1953.
Ross, W. H., *U. S. Dept. Agr. Bull.* **149,** 14 pp. (1914).
Sax, K., *Radiation Botan.* **3,** 179 (1963).
Schulz, R. K., *Health Physics* **11,** 1317 (1965).
Shiraishi, Y. (to Osaha Metal Industries, Co.), Japanese Patent **8853** (Oct. 18, 1957).
Talibudeen, O., *Soils Fertilizers* **27,** 347 (1964).
Tso, T. C., Hallden, N. A., Alexander, L. T., *Science* **146,** 1043 (1964).

Received for review October 9, 1967. Accepted January 8, 1968. This research was supported in part by the U. S. Atomic Energy Commission.