path through an area not containing $Ca(OH)_2$ (Fig. 2D).

Further hydration results in the extension of $Ca(OH)_2$ areas as well as a strengthening and densification of the calcium silicate hydrate zones. This densification reduces the difference in strength between the two hydrated phases and makes the properties of the paste more uniform on a microstructural scale. Fracture within the system propagates along a more direct path as differences in the microstructural components decrease.

An increase in the w/s ratio increases the porosity of the Ca_3SiO_5 particle areas but does not change the porosity of the $Ca(OH)_2$ crystals. However, the distance between $Ca(OH)_2$ crystals increases and the degree to which the crystals grow together decreases as the w/s ratio increases. As a result of these factors, the fracture continues to go through the calcium silicate hydrate zones and around $Ca(OH)_2$ at later ages (increased degrees of hydration). For example, in a sample with a w/s ratio of 0.7 hydrated for 20 days, the $Ca(OH)_2$ covers about 35 percent of the paste area and the fracture still goes around the $Ca(OH)_2$ crystals (Fig. 2F).

The relevance of the fracture observed in the paste sections to that of bulk samples may be questioned. However, the fracture surface of the thin sections of the paste at early stages of hydration would contain a preponderance of calcium silicate hydrate, in agreement with observations by scanning electron microscopy made by Young and Lawrence (*4*) of the fracture surface of bulk Ca_3SiO_5 paste samples.

A completely hydrated Ca_3SiO_5 paste contains about 42 percent $Ca(OH)_2$ as compared to 25 percent in ordinary portland cement paste. In addition, the $Ca(OH)_2$ crystals in portland cement paste are smaller and have more of a platy habit because of the presence of sulfate and other ions in solution. Although the quantity and morphology of $Ca(OH)_2$ differ in the two systems, the influence of $Ca(OH)_2$ on fracture propagation would be expected to be the same since it represents low-porosity areas in both systems.

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2. The apparently large areal coverage of $Ca(OH)_2$ includes engulfed Ca_3SiO_5 particles, calcium silicate hydrate, and gel pores. If we use a density of 2.2 g/cm^3 for both $Ca(OH)_2$ and calcium silicate hydrate, the total volume of hydrated solid would be approximately 56 cm^3 starting with 100 g of Ca_3SiO_5. This corresponds to about 79 percent of the total volume of the original mix with a w/s ratio of 0.4 (40 ml of H_2O and 31 cm^3 of Ca_3SiO_5). Since the $Ca(OH)_2$ grows in the space between particles, it can at late stages of hydration appear to cover much of the sample area. In addition, the excess paste squeezed from the slide during preparation appeared to have a higher w/s ratio than that left on the slide. The lower porosity paste system on the slide would result in less space to be filled by the $Ca(OH)_2$ and thus a higher areal coverage by the $Ca(OH)_2$.
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Uranium in Runoff from the Gulf of Mexico Distributive Province: Anomalous Concentrations

Abstract. *Uranium concentrations in North American rivers are higher than those reported 20 years ago. The increase is attributed to applications to agricultural land of larger amounts of phosphate fertilizer containing appreciable concentrations of uranium. Experiments showing a constant phosphorous-uranium ratio for various types of fertilizers and for the easily solubilized fraction of 0–46–0 fertilizers support this view.*

High uranium concentrations are reported for present-day North American rivers relative to those found 10 to 20 years ago for the same rivers or for rivers in other parts of the world draining less intensively cultivated areas. This anomaly has been attributed to high concentrations of uranium thought to be present in phosphate fertilizers (*1, 2*). Lack of knowledge of uranium depletion or enrichment in the various stages of fertilizer production and of the behavior of uranium during weathering of a fertilized soil has made these observations rather speculative. This report describes experiments designed to answer these questions and attempts to evaluate the pollution potential of uranium, a heavy metal whose toxic levels in organisms are similar to those of mercury and lead.

Table 1. Spring 1971 distribution of uranium versus phosphate in the Brazos River and its tributaries.

Collection date (1971)	Phosphate (μg/liter)	Uranium (μg/liter)	P/U ratio
	Brazos River		
3–12*	36.10	1.16	31.0
3–25†	130.0	1.48	88.0
4–16‡	46.0	1.51	30.4
4–17§	62.0	1.32	47.0
4–21*	10.8	1.88	10.8
5–4‖	41.9	1.90	22.0
5–6*	64.3	2.07	31.6
5–11‡	53.5	0.94	57.0
5–25§	28.0	2.70	10.4
	Little Brazos River		
3–12*	60.5	0.69	87.5
3–25†	48.8	1.27	38.2
	Navasota River		
5–11‡	234.5	2.01	116.0

* After storm. † No rain. ‡ Rain, about 1 inch. § Showers. ‖ Dry for 2 weeks.

Uranium concentrations were determined by a delayed neutron technique (*3*). The method is nondestructive, rapid (about 5 minutes), and precise (sigma is about 5 percent for a single determination on a 2-g solid sample with about 1 ppm). Briefly, samples are weighed into a polyethylene vial which is inserted into a "rabbit." The "rabbit" is blown into a flux of neutrons (about 10^{12} neutrons cm^{-2} sec^{-1} in this case) via a pneumatic system for 1 minute, removed, allowed to cool for 30 seconds, and then counted for 1 minute with BF_3 neutron counters in a 4π arrangement. Sample activities are compared with standards treated in the same manner.

River and other aqueous samples were filtered through 0.8-μm Millipore filters and evaporated to dryness. The dried solids were treated as described above. Concentrations were determined on the basis of the sample volume and total weight of dissolved solids.

Uranium concentrations for 22 samples taken from 15 different rivers that flow into the Gulf of Mexico are shown in Fig. 1. Most samples have considerably higher concentrations than were found years ago in several North American rivers (*4*). High uranium in the Rio Grande, Nueces, Frio-Atascosa, Guadalupe, and San Antonio rivers are due presumably to their flow through uranium-bearing strata. Uranium is actually being mined in certain locations in south Texas; ores contain 0.1 to 0.5 percent uranium. In general, for rivers that flow through this region, there is a uranium addition of approximately 1 μg/liter. In the highly agricultural regions, drained by the Colorado, Brazos, and Trinity rivers, values reflect similar concentrations found previously for the Rio Grande, Arkansas-Cimarron, and Yegua rivers (*2*). It is our contention that these high values are due to the uranium in phosphate fertilizers. Some evidence supporting this view is that the rivers flowing through the nonagricultural pine-forested regions of extreme eastern Texas show much less dissolved uranium. Low uranium concentrations were also noted in samples from several rivers draining the nonagricultural Mexican tropical rain forest.

Two experiments were performed to illustrate the chemical behavior of uranium during fertilizer production. First, 27 commercial fertilizer samples were chosen at random from hundreds of preanalyzed samples acquired from Texas A & M's Agricultural Service Division. The samples contained from 0 to 46 percent P_2O_5. Most contained varying percentages of nitrogen and potassium. The results (Fig. 2) showed an apparent linearity of uranium with respect to the percentage of P_2O_5. It is also apparent from the data that extremely high concentrations of uranium are found in the heavily used triple superphosphates (0–46–0). Second, in order to determine whether or not uranium is being concentrated in phosphate fertilizers of different types, a suite of samples was run from Texas Gulf Sulphur's phosphate mining and processing plant in Aurora, North Carolina. Nine samples from different processing steps were analyzed for uranium. In addition, a fossil shark tooth and a phosphorite pebble were extracted from the ore and run separately. The results of these nine analyses (Fig. 2) show a step-by-step magnification of uranium concentration with an increased percentage of P_2O_5. The results from the fossil tooth and phosphorite pebble indicate a higher uranium concentration than was determined in the phosphorite sand. High uranium concentrations in Florida phosphorite pebbles have been attributed to secondary enrichment processes (*5*).

In a 5-year span from 1962 to 1967, fertilizer consumption increased from 25 billion to 36 billion short tons per year (*6*). In 1967 this amounted to over 2.9 billion short tons of P_2O_5 applied to U.S. regions draining into the Gulf of Mexico. If we assume an average value of uranium in phosphate fertilizer to be 150 μg/g, this amounts to 285 short tons of U_3O_8 applied to the soils of the U.S. portion of the Gulf of Mexico distributive province. Since uranium is soluble in the +6 oxidation state, increased use of phosphate fertilizer in agriculture should produce increased concentrations in runoff.

Phosphate-uranium ratios measured in the spring of 1971 for the Brazos River and its tributaries are quite variable (Table 1). The reason is basically that phosphate in a water system is an extremely nonconservative species. It is, of course, taken up by land plants. Algae quickly assimilate phosphate as it enters a stream or river and incorporate the dissolved phosphate in their tissue. Additional phosphate may enter streams from domestic sewage, cattle pens, and industrial wastes.

On the other hand, where other sources of uranium and phosphate are negligible, the constant PO_4/U ratio in fertilizer may be used to predict what phosphate utilization by land plants and algae has occurred. For ex-

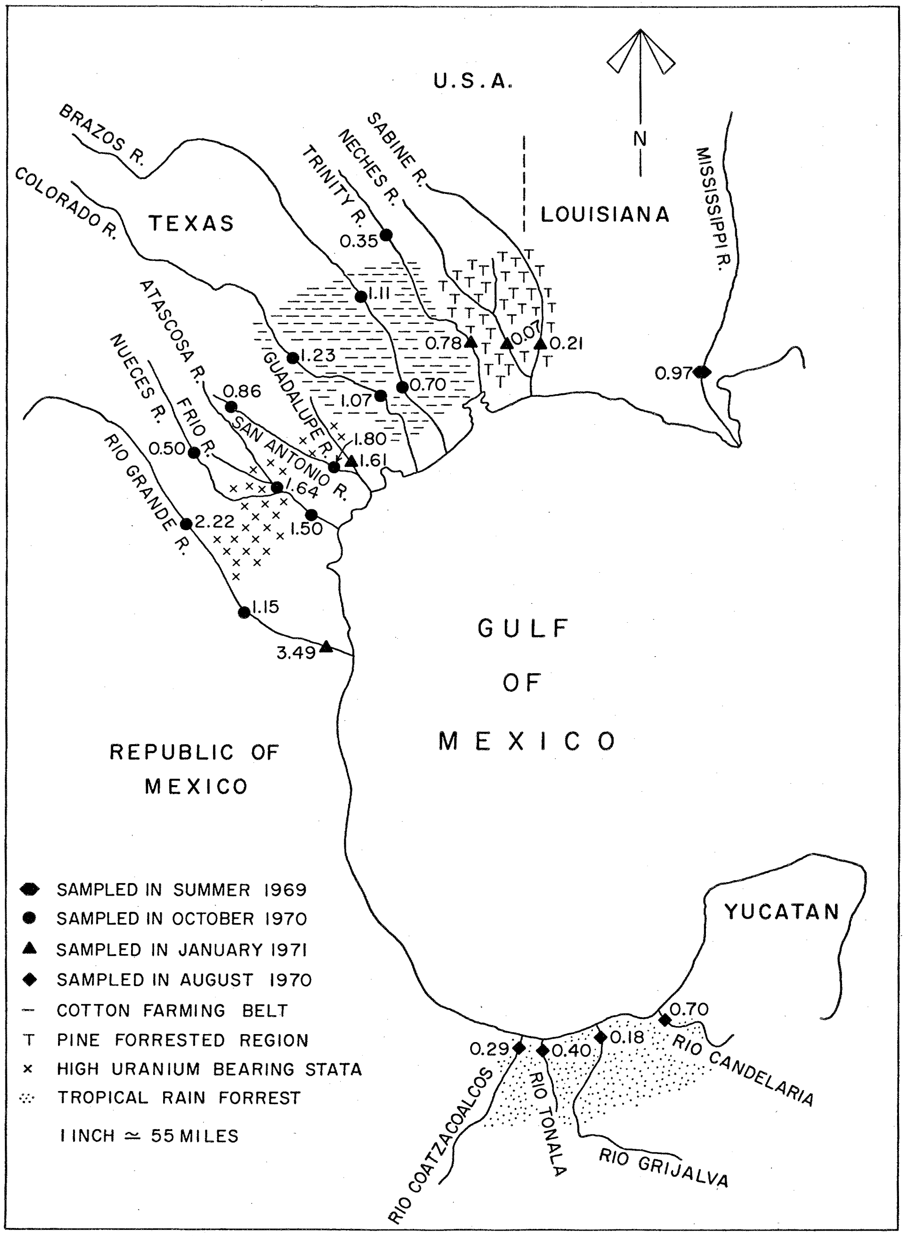

Fig. 1. Dissolved uranium concentrations (μg/liter) in selected rivers of southwestern United States and Mexico.

ample, the ratio of phosphate phosphorus to uranium (μgP/μgU) in fertilizers may be calculated to be approximately 1300, whereas the ratio in the Brazos River is in the range of 10 to 100. This difference between the ratio in fertilizers and rivers (Table 1) suggests that more than 90 percent of the applied phosphate has been taken up by plants, neglecting all other losses of phosphate and sources of uranium.

Although the data in Table 1 show little correlation between phosphate and uranium in this fluvial system, the average uranium concentration of the nine samples from the Brazos during the spring was 1.66 μg/liter, an amount approximately twice that in the fall of 1970. This correlates well with the increased use of fertilizer during the growing season.

Two experiments were undertaken to determine the effect of weathering on phosphate fertilizer. First, uranium and phosphate were leached from pellet fertilizer by successive applications of water. In this experiment a glass column 5 cm in diameter was filled with 959 g of 0–46–0 commercial fertilizer containing 178 ± 4 parts of uranium per million. Successive 500-ml samples of water were passed through the column until the flow stopped because of plugging. The eluent from seven fractions representing about 37 percent of the original material was freeze-dried and analyzed. Percentage of P_2O_5 ranged from 50 to 55; parts of uranium per million ranged from 136 to 172. This experiment shows the ease with which uranium may be leached from phosphate fertilizers. The reasons for the slight enrichment of phosphate and depletion of uranium in the leached fraction relative to the original material are unknown but seemingly unimportant insofar as the major implications of this study are concerned. A second experiment consisted of fertilizing a small plot of land with 10–20–10 commercial fertilizer. After an application of water equivalent to 0.5 inch of rain, the uranium in the runoff was found to be 28 times greater than it was in a similar blank application.

These experiments show that phosphate-derived uranium addition to runoff during weathering is a significant occurrence. If we assume 100 percent solution of uranium, which is unlikely, the contribution of uranium to the Gulf of Mexico distributive province amounts to 2.5×10^8 g of uranium per year. Dividing the annual contribution by 8.4×10^{14} liters, the annual flow from U.S. rivers into the Gulf of Mexico (*7*), yields a value of 0.3 μg of uranium per liter. Of course, during the spring season when fertilization and runoff peak, the increment is probably greatest. Considering the rough estimates that have to be made, 0.3 μg of uranium per liter is in reasonably good agreement for the difference in concentration of uranium between rivers draining the agricultural areas and nonagricultural areas shown in Fig. 1.

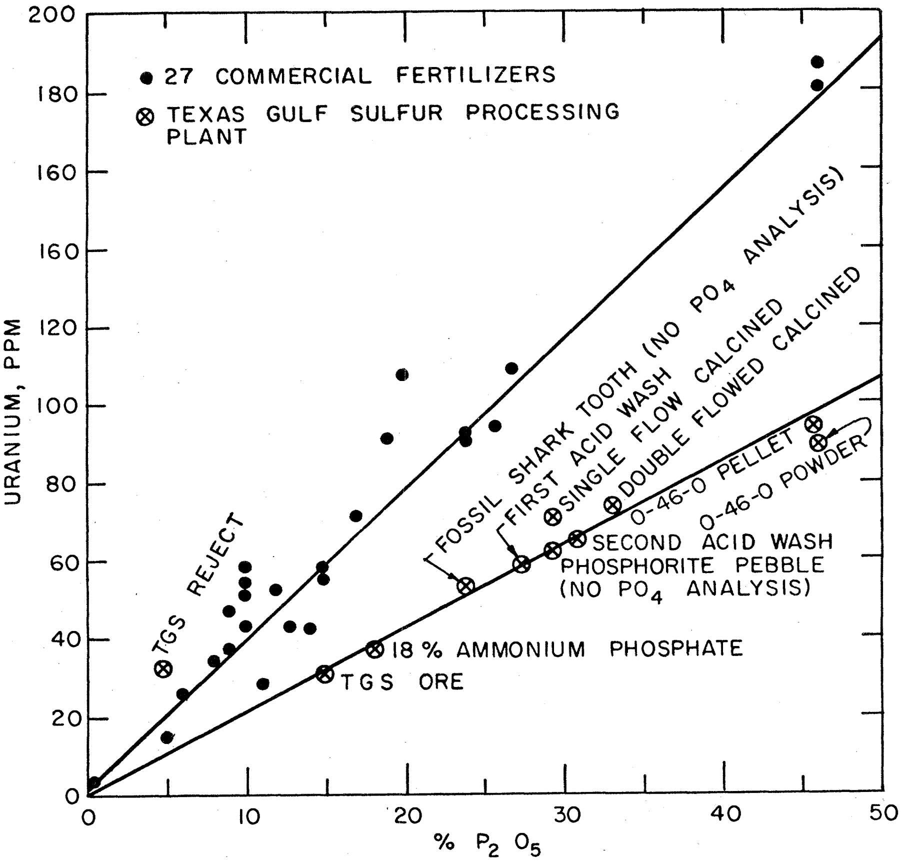

Fig. 2. Uranium and P_2O_5 in 27 commercial fertilizers (solid circles) and at various stages in a phosphate fertilizer processing plant (open circles).

From an analysis of corn, soybean, and alfalfa grown under varying applications of P_2O_5, it appears that very little, if any, uptake of uranium occurs —less than 0.05 ppm in ash. This experiment eliminates the possibility of uranium loss during plant development; however, radioactive decay of uranium-238 gives, among other products, radium-226, lead-210, and polonium-210. Since the properties of radium-226 are very similar to those of calcium, radium-226 is also absorbed by plant roots and transported to leaves (*8*). Polonium-210 and lead-210 also may be absorbed by plants; hence there is a potential hazard from radionuclide contamination of plants grown on phosphate-fertilized soils.

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