Detoxification of White Phosphorus in Soil

White phosphorus added to soils was quickly rendered nontoxic to plants and supported growth as well as additions of $Ca(H_2PO_4)_2$. When placed at 5 and 10 cm depths, none of the phosphorus escaped to the atmosphere. Phosphorus in small amounts and its oxidation products diffused 0.5 to 1 cm in fine and coarse-textured soils, respectively.

Dumping elemental phosphorus and lower phosphorus oxides into fresh and marine waters has caused pollution and fish kills in Muscle Shoals, Ala., and Long Harbour, Newfoundland. The soil might be a more suitable site for disposal of these and other oxidizable phosphorus compounds because of the lower mobility of phosphorus compounds (Widdowson, 1966), higher oxidation rates, and the greater chemical and biochemical reactivity in soils than in waters.

White phosphorus applied apparently to the surfaces of plants and soil as a solute in CS_2 was highly phytotoxic (MacIntire *et al.*, 1950). The toxicity was attributed to the phosphorus; CS_2 alone had little effect. A volatile phosphorus compound, said to be phosphine, emanated from the treated plants and soils for several days after application. Red and black phosphorus and compounds of intermediate phosphorus oxidation states oxidize slowly and may be slightly phytotoxic (Mattingly and Talibudeen, 1967; Sharratt, 1969). This report is concerned with the toxicity of white phosphorus in soils.

EXPERIMENTAL

Equivalent amounts, 0.36 g white phosphorus or 1.46 g $Ca(H_2PO_4)_2$, were applied at 5 and 10 cm depths in 7 kg of calcareous Anthony gravelly sandy loam or Pima clay loam soils in pots. $Ca(H_2PO_4)_2$ was applied in the commercially pelleted form. White phosphorus was applied as pellets made by adding molten white phosphorus to a test tube containing enough water to cover the phosphorus and allowing the phosphorus to cool and solidify. During transfer to the soil, the water layer remaining on the pellet surface prevented oxidation. No problems in handling white phosphorus occurred so long as it was kept under water or was covered by sufficient soil. Grain sorghum (*Sorghum vulgare*) was planted immediately and thinned to four plants per pot after germination.

RESULTS AND DISCUSSION

Preliminary experiments had shown that 8 g of white phosphorus per pot applied at a 12.5 cm depth in calcareous soils had no effect on germination of sorghum planted 0 to 10 days after treatment. The plant growth was greater in the P-treated pots than in untreated pots.

White phosphorus and the common fertilizer compound $Ca(H_2PO_4)_2$ were then compared as to their effects on sorghum germination rate, dry matter yield, and plant height. The data in Table I show that germination and growth were similar in both treatments. The differences are statistically insignificant. The germination rates are low because old seed was used. These weakly-viable seeds should have been highly sensitive to any toxicity effects. No visual toxicity symptoms could be found.

Table I. Growth and Development of Sorghum as Affected by Applications of 1.46 g $Ca(H_2PO_4)_2$ and the Equivalent 0.36 g White Phosphorus to Two Soils

Fertilizer	Depth of Placement, cm	Percent Germination	Max Plant Height, cm	Dry Matter, g/pot
	Anthony Sandy Loam			
$Ca(H_2PO_4)^2$	5	50	69	8.96
$Ca(H_2PO_4)^2$	5	70	56	8.29
$Ca(H_2PO_4)_2$	10	80	67	7.79
$Ca(H_2PO_4)_2$	10	80	62	6.36
Average		70	64	7.85
White phosphorus	5	70	64	6.37
White phosphorus	5	40	62	9.96
White phosphorus	10	50	78	9.01
White phosphorus	10	70	64	8.72
Average		56	67	8.52
	Pima Clay Loam			
$Ca(H_2PO_4)_2$	5	50	74	8.79
$Ca(H_2PO_4)_2$	5	30	74	9.70
$Ca(H_2PO_4)_2$	10	80	58	5.79
$Ca(H_2PO_4)_2$	10	80	80	10.35
Average		60	72	8.66
White phosphorus	5	50	71	9.21
White phosphorus	5	50	72	9.47
White phosphorus	10	90	76	9.82
White phosphorus	10	50	72	10.47
Average		60	72	9.76

The lack of toxicity was probably due to a rapid oxidation of white phosphorus and any intermediate phosphorus compounds to phosphate. Observations of the heat evolved indicated that the reaction was complete within 2 hr in dry soil. The oxidation rate is nonbiological and is controlled by oxygen and water diffusion, the formation of an oxidized coating, and the conversion of white phosphorus to the more stable red phosphorus.

After 1 month the soils treated with white phosphorus were sectioned. The volume of soil affected could be readily distinguished by a gray coloration due to a white coating, presumably phosphate, on the soil particles and by the low root density within the gray zone. The plant roots extended only to the outer edge of this volume. Soil conditions within this zone prevented root entry and thus minimized any effects of possible phytotoxic compounds within it. This volume was about 5 cm^3 in the clay loam and 14 cm^3 in the sandy loam. This corresponds to radial phosphorus diffusion of about 0.5 cm in the clay loam and 1 cm in the sandy loam soil. This radial diffusion is a function of soil permeability and some inverse function of the initial amount of white phosphorus. Larger amounts of white phosphorus would cause higher temperatures and greater conversion to the immobile and more stable red phosphorus form.

No odor of phosphorus compounds could be detected at the soil surface in any treatments in which the phosphorus was covered by several centimeters of soil. When white phosphorus was mixed throughout the soil so that some reached the surface, however, traces of P_2O_5 could be detected above the soil for more than a week. No PH_3 emanation was detected at any time, nor would it be expected because of the oxidizing conditions present in nonflooded soils, because of PH_3's instability (Riemann and Beukenkamp, 1961), and its retention and rapid oxidation in soil (Hunter and Thornton, 1956). MacIntire *et al.* (1950) apparently confused phosphine for the phosphorus pentoxide.

The lack of toxicity and the immobility of white phosphorus and its oxidation products in soils indicate that soil is a far safer disposal site for elemental phosphorus than is water.

LITERATURE CITED

Hunter, F., Thornton, I., *Nature* (London) **178,** 866 (1956).
MacIntire, W. H., Winterberg, S. H., Hardin, L. J., Sterges, A. J., Clements, L. B., *Agron. J.* **42,** 543 (1950).
Mattingly, G. E. G., Talibudeen, O., "Topics in Phosphorus Chemistry," M. Grayson and E. J. Griffith, Eds., Vol. 4, p. 176, Interscience, N.Y. (1967).
Riemann, W., Beukenkamp, J., "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Eds., Part III, Vol. 5, pp. 323–330, Interscience, N.Y. (1961).
Sharratt, W. J., *Soil and Water*, Univ. Calif. Agr. Ext. Service, p. 7, summer issue (1969).
Widdowson, J. P., *New Zealand J. Sci.* **9,** 882 (1966).

Hinrich L. Bohn*
Gordon V. Johnson
Joan H. Cliff

Department of Agricultural Chemistry
and Soils
University of Arizona
Tucson, Ariz. 85721

Received for review May 12, 1970. Accepted July 20, 1970. ** To whom correspondence should be addressed.*