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Fate of Zinc Phosphide and Phosphine in the Soil-Water Environment

H. Wayne Hilton* and William H. Robison

Zinc phosphide, mixed with three soils at five moisture levels, decomposed with the liberation of variable amounts of phosphine gas. Oxidation at the soil surface yielded zinc and phosphate ions as the ultimate products. In a closed system the soils slowly reabsorbed and oxidized the PH_3 . Phosphine placed at high concentration in contact with the same soils oxidized slowly and incompletely to phosphate ion. The rate of zinc phosphide decomposition increased with increasing moisture;

phosphine absorption decreased with added water. Soil types differed markedly in the ability to oxidize Zn_3P_2 or PH_3 . The differences could not easily be related to known soil properties. Zinc phosphide did not decompose in water from streams, domestic source, or the ocean. Acids and bases hydrolyzed Zn_3P_2 to PH_3 , but the reaction was not entirely pH dependent. A phosphate buffer of pH 7.00 extensively hydrolyzed Zn_3P_2 at room temperature.

Most of the zinc phosphide (Zn_3P_2) applied over sugarcane fields as a constituent of a rodenticide bait could be expected to reach the soil (Elmore and Roth, 1943; Hayne, 1951; Nass *et al.*, 1970). There appears to be no information on the fate of Zn_3P_2 in soil or in natural waters, nor on the fate of any phosphine gas (PH_3) liberated as a result of hydrolysis.

The gas chromatographic procedure for the measurement of PH_3 (Robison and Hilton, 1971) made it possible to determine PH_3 released from the incubation of Zn_3P_2 with soils and water, and to determine the fate of PH_3 placed in a closed system with the same substrates. Another study (Hilton and Mee, 1972) indicated that PH_3 , as $^{32}\text{PH}_3$, reacted in part with strong acid, plant tissue, and soil to form nonvolatile water-soluble oxidation products. We designed the present experiments to measure the PH_3 resulting from Zn_3P_2 hydrolysis and the phosphate ion (as H_3PO_4) resulting from the oxidation of Zn_3P_2 or PH_3 .

MATERIALS AND METHODS

Soils and Water Sources. Three oxide clay soils of volcanic origin represented 60 to 70% of the sugarcane topsoils in Hawaii: a Hydrol Humic Latosol (HHL) from the high rainfall climate on the island of Hawaii, pH 5.7, with a high organic matter content of 12 to 15%; a Humic Ferruginous

Latosol (HFL) from a moderate rainfall windward Kauai location, pH 5.4, with an intermediate organic matter content of 5 to 8%; and a Low Humic Latosol (LHL) from a low rainfall area of Oahu and typical of soils on Maui and leeward Kauai, pH 6.9, with low organic matter content of 3 to 5%.

Water sources included the Wailua River (Kauai, pH 7.05), Grove Farm Co. irrigation water (Kauai, pH 7.20), Keapana Stream (Kauai, pH 7.65); Wailuku River (Hawaii, pH 7.52); Honolulu domestic water (Oahu, pH 7.90), laboratory-distilled water (pH 6.00), ocean water (Oahu, pH 8.20). Buffer solutions of pH 4.00 and 7.00 were also included.

Gas Chromatography. A Microtek MT 220 (Tracor Instruments, Austin, Texas), fitted with a flame photometric detector and a Melpar filter, isolated the 526-nm band specific for volatile phosphorus compounds. Phosphine gas generated from Zn_3P_2 and diluted to 1.00 ppm with N_2 served as a reference standard (Robison and Hilton, 1971; Berck *et al.*, 1970), with a sensitivity limit of 20 pg.

Operating conditions were: detector temperature, 150°, inlet temperature, 220°; column, 4 ft \times 1/4 in. borosilicate glass packed with 5% QF-1 on Gas Chrom Q, 80 to 100 mesh, and heated isothermally at 48°; nitrogen carrier gas, 60 ml/min; detector gases, H_2 at 150 ml/min; air at 35 ml/min; and O_2 at 15 ml/min. Phosphine eluted 20 sec after injection; peak heights were linear with amounts of PH_3 . There were no interferences and no detectable volatile compounds other than PH_3 .

Zn_3P_2 Incubation with Soils. Zinc phosphide in amounts equivalent to 1000 ppm of P (4.17 mg of Zn_3P_2 per g of soil)

*Experiment Station, Hawaiian Sugar Planters' Association, Honolulu, Hawaii 96822.

was mixed with each of the three air-dried soils. The mixtures were weighed in amounts of 2.5 g of soil into 20 × 125 mm borosilicate glass culture tubes, of 27 to 27.5 ml volume. In addition to the air-dried mixtures, we added water to prepare a set of each soil type at 25, 50, 75, and 100% saturation. At 100% the soils contained about 38% water. The tubes were sealed with rubber serum bottle closures and incubated at room temperatures of 27 to 28°. Gas samples of 1 to 25 μ l were periodically withdrawn from the headspace for PH_3 chromatography. Control tubes without soil contained Zn_3P_2 as a dry sample without water and with the various amounts of water.

After completion of PH_3 evolution and reabsorption (34 days maximum), measured by the appearance and disappearance of PH_3 in the headspace gas volume, we injected 10 ml of 0.1 *M* acetic acid into each tube. (NOTE: H_2SO_4 catalyzed the oxidation of Zn_3P_2 or PH_3 to phosphate ion, especially in the presence of soil. Weak acids gave acceptable recoveries of PH_3 from undecomposed Zn_3P_2 .) After heating the tubes 3 hr in boiling water and then cooling, we sampled the air space for PH_3 . The tubes were then opened and flushed with N_2 to remove PH_3 , filled with 1 *N* H_2SO_4 to extract phosphate, and allowed to stand overnight. Phosphate determinations were made in the acid liquid.

Phosphate Analysis. Soils or water samples were mixed with 1 *N* H_2SO_4 and either heated for 2 hr in boiling water or allowed to stand overnight. (Care must be taken in heating sealed tubes containing acid. If tubes are to be left sealed, it is advisable to withdraw part of the headspace gas before adding the acid.)

After centrifuging, 100 μ l of clear liquid was placed in a test tube. The water was evaporated over a low flame and the sample was ashed in a furnace at 420 to 440°. After cooling, 3.00 ml of 5 *N* H_2SO_4 and 10.0 ml of distilled water were added. The sample was shaken in a sonic cleaner bath for 5 min, and then 0.75 ml of 0.15% aqueous hydrazine sulfate and 1.5 ml of 2.5% aqueous ammonium paramolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, were added. The tube was heated in boiling water for 10 min. The quantity of phosphorus (as P) in the cooled solution was determined in 1-cm cells at 820 nm against a reagent blank, in comparison with a linear standard curve for KH_2PO_4 from 2 to 20 μ g of P. Soil analyses were corrected for natural P background and for the extraction efficiency of H_2SO_4 for KH_2PO_4 , added at 1000 ppm of P equivalent to the individual soil.

PH_3 in Contact with Soils and Water. Sealed culture tubes were prepared with 1.0 g of each soil (air-dry basis) at each of five moisture levels: air-dry and at 25, 50, 75, and 100% saturation.

Pure PH_3 gas, 1.097 mg (0.72 ml), to make 1000 ppm of P on the weight of soil, was injected by syringe into each sealed tube. Samples of the headspace gas, usually 1 μ l until the amounts of PH_3 decreased, were withdrawn periodically for gas chromatographic analysis of remaining PH_3 . When the PH_3 had disappeared from all the soil-containing tubes—a maximum of 40 days—the tubes were opened and 10 ml of 1 *N* H_2SO_4 was added to extract phosphate overnight. The phosphate analyses were corrected for soil background and for extraction efficiency.

Controls for these experiments contained PH_3 with and without water, but without soil. Analysis of PH_3 in these control tubes with time indicated the rate of seepage through the septum or reaction with it. Tubes without soil, containing PH_3 in N_2 rather than air, showed the same rate of loss. Phosphine did not entirely disappear in 40 days from the air space

Table I. Recovery of Phosphate from Soils Containing Various Sources of Phosphorus at 1000 ppm of P

Phosphorus source	Acid-extractable phosphate in soils		
	HHL	HFL	LHL
Control	163 ppm	163 ppm	184 ppm
Zn_3P_2	75.5%	49.0%	69.3%
KH_2PO_4	71.4%	46.9%	81.6%
H_3PO_4	71.4%	46.9%	81.6%

Limit of detection with the molybdate reagent was about 40 ppm. Figures are not corrected for extraction efficiency.

of tubes containing water, although it was lost from the dry tube and from all the tubes containing soil.

Stability of Zn_3P_2 in Water. Water samples, 13.5 ml, were incubated at room temperature in sealed culture tubes with 5.82 mg of Zn_3P_2 (100 ppm of PH_3 equivalent). Two sealed tubes contained dry Zn_3P_2 : the commercial technical product and a commercial material washed overnight with water to remove easily decomposed impurities. The latter product, when dried, had no detectable odor. The PH_3 evolved in each case was measured in the headspace gas volume until it reached a maximum concentration and declined, usually within 7 days.

RESULTS AND DISCUSSION

Zn_3P_2 in Soils. In a preliminary experiment Zn_3P_2 , mixed with a single moist soil in amounts equivalent to 1, 10 and 100 ppm of PH_3 , liberated detectable PH_3 only at the highest concentration. In a closed container, PH_3 appeared in the headspace gas within 24 hr, increased to 0.87 ppm (on the weight of soil) at 48–72 hr, and then diminished and disappeared within a week. Injection of acid and hydrolysis for a further incubation period of 2 weeks failed to generate more PH_3 . The analytical procedure would have measured PH_3 had it been present in amounts greater than 0.008 ppm. On the basis of this preliminary data, and because the soils contained background phosphate in amounts of 100 to 200 ppm, we concluded that Zn_3P_2 should be incubated with soils at 1000 ppm of P equivalent in order to monitor PH_3 and to measure phosphate resulting from the oxidation of Zn_3P_2 or PH_3 . In the absence of soil, in the water experiments, Zn_3P_2 at 100 ppm of P sufficed. These quantities are hundreds to thousands of times greater than would result from rodenticide applications in the field.

The absence of PH_3 after acid treatment in the preliminary trial seemed to indicate that the Zn_3P_2 had decomposed. The initial low PH_3 recovery suggested either concurrent reabsorption and reaction to nonvolatile compounds, rapid leakage through the septum (or reaction with it), or direct reaction of Zn_3P_2 to nonvolatile forms of P, with PH_3 appearing only as a side reaction product.

Hot, dilute H_2SO_4 treatment in sealed containers of the three sugarcane soils mixed with Zn_3P_2 , KH_2PO_4 , or H_3PO_4 resulted in the conversion of Zn_3P_2 to phosphate ion (Table I). With the exception of the LHL soil, which oxidized Zn_3P_2 incompletely, the recovered phosphate approximated that from the phosphate sources. The same hydrolytic conditions without soil converted Zn_3P_2 quantitatively to PH_3 , although prolonged treatment oxidized part of the PH_3 to H_3PO_4 . At least in the presence of H_2SO_4 the soils acted as oxidizing substrates for PH_3 .

Room temperature incubation of Zn_3P_2 in soils of varying moisture content produced PH_3 gas in quantities ranging from none in any of the air-dried soils to a maximum of 32% of

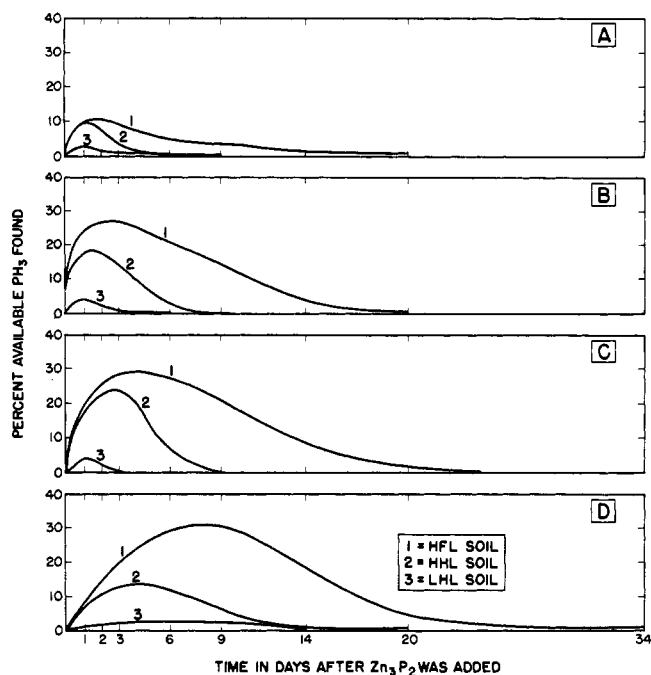


Figure 1. Phosphine from zinc phosphide in soils of varying moisture content. Curves A, B, C, and D represent soils with 25, 50, 75, and 100% moisture saturation

Table II. Residual Zn_3P_2 after 34 Days of Incubation with Soils having Various Amounts of Moisture

Amounts of water	Zinc phosphide remaining in soils, ^a %		
	HHL	HFL	LHL
Air dry	35.3	39.8	36.2
25% saturated	3.4	10.0	13.6
50% saturated	None	None	None
75% saturated	None	None	None
100% saturated	None	None	None

^a Corrected for efficiency of hydrolysis of Zn_3P_2 by acetic acid in each soil.

that theoretically available in the HFL soil at complete saturation (Figure 1). The amounts and persistence of PH_3 increased with increasing moisture and with decreasing pH. Concentration maxima for PH_3 in the headspace gas—the resultant of release, reabsorption, and septum losses—were reached at times varying from 1 to 8 days. Thereafter PH_3 diminished to undetectable amounts within 34 days.

At the end of the incubation period, acetic acid released PH_3 only from the air-dried and 25% moisture-saturated soils (Table II). The amounts of undecomposed Zn_3P_2 remaining in the three soils were remarkably similar, with no apparent influence of soil pH or correspondence with the release and persistence of PH_3 shown in Figure 1. Sixty-three percent of the Zn_3P_2 decomposed in the air-dried soils, but slowly enough that no PH_3 appeared in the air space above the soils. Since the dryer soils had more available void space not occupied by water, it seemed probable that oxidation occurred more readily with increased soil surface. Zinc phosphide decomposition presumably requires water; however, either Zn_3P_2 or PH_3 may have been oxidized.

Phosphorus from decomposed Zn_3P_2 could be accounted for as phosphate ion (Table III). At least for the relatively small fractions of PH_3 in the headspace gas, the septum losses were minor. Phosphine released during the incubation period was reabsorbed and oxidized.

Table III. Phosphate Resulting from the Incubation of Zn_3P_2 with Soils

Amounts of water	Phosphate ion recovered from soils, ^a %		
	HHL	HFL	LHL
Air dry	62.8	58.3	44.0
25% saturated	83.5	114.6	89.3
50% saturated	83.1	101.9	90.4
75% saturated	94.3	113.4	82.6
100% saturated	105.6	109.6	82.6

^a Corrected for extraction efficiency of removing KH_2PO_4 from each soil under similar conditions.

Table IV. Phosphine Released from Zinc Phosphide in Soil Treated with H_2SO_4 , and Conversion to Phosphate Ion

Days after sample prepared	Phosphine, %			
	No soil present	Hydrol Humic Latosol	Humic Ferruginous Latosol	Low Humic Latosol
0 (2 hr)	71.10	3.28	10.67	2.99
1	119.42	0.23	43.76	2.81
2	84.78	0.24	20.00	1.22
3	..	0.17	13.77	0.49
6	104.83	None	7.24	0.41
9	101.19	None	3.57	None
14	76.21	None	0.07	None
20	59.25	None	None	None
34	24.61	None	None	None
Recovery of phosphorus as phosphate (% P added as Zn_3P_2) ^a				
34	53.6	96.4	73.2	91.1

^a Incubated with acid for 34 days during measurement of PH_3 ; then the acid solution was analyzed for H_3PO_4 . No corrections were made for extraction efficiency.

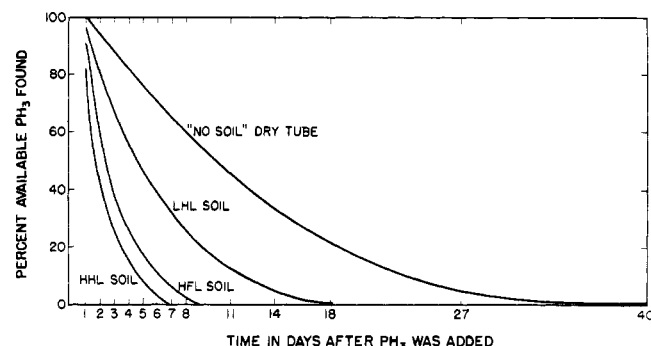


Figure 2. Disappearance of PH_3 placed in the headspace air volume above air-dried soils

Soils mixed with Zn_3P_2 and treated at room temperature with H_2SO_4 released small to moderate amounts of PH_3 , with conversion to phosphate ion over a period of time (Table IV). Phosphine without soil remained stable for at least a week; thereafter a slow oxidation to H_3PO_4 accompanied septum losses of 22%.

PH_3 in Contact with Soils and Water. Phosphine at 1000 ppm of P in contact with the soils at the same five moisture levels diminished and disappeared from the headspace gas in a period of 40 days. The air-dried (Figure 2) and completely saturated soil conditions (Figure 3) are shown. The rate of PH_3 absorption decreased with increasing moisture, as expected of a more rapid diffusion into the void spaces of the dryer soils. Tubes containing only PH_3 (as a mixture in air), or PH_3 with small amounts of water, showed a slower rate of PH_3 loss than when soils were present. Water reduced the rate of disappearance.

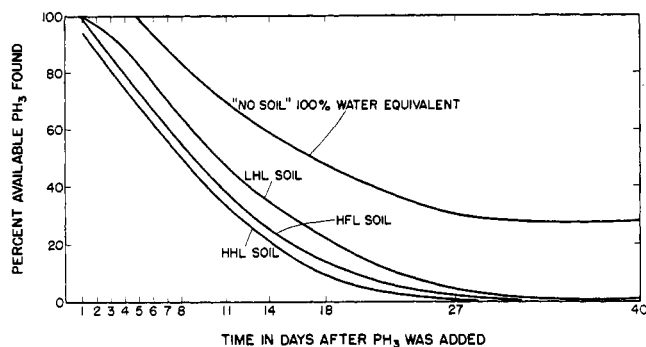


Figure 3. Disappearance of PH_3 placed in the headspace air volume above soils 100% saturated with water

Table V. Recovery of Phosphorus, as Phosphate Ion, from the Incubation of PH_3 with Soils, and with Equivalent Amounts of Water without Soil

Amounts of water	Phosphorus recovered from soils and water, %			
	HHL	HFL	LHL	Water only
Air dry	60.0	30.5	19.5	0.42
25% saturated	69.2	16.3	18.1	0.25
50% saturated	47.7	12.3	9.7	0.12
75% saturated	36.6	12.3	15.3	1.56
100% saturated	None	6.1	9.7	0.40

Recoveries of phosphate from the oxidation of PH_3 were low for two soils and moderately high for the third (Table V). Drier conditions resulted in more phosphate ion, as expected, but the differences were not dramatic. Phosphine without soil, with or without water, failed to produce more than traces of H_3PO_4 in 40 days. Since these tubes contained air, with PH_3 added at about 2.5% by volume, the phosphate produced from Zn_3P_2 or PH_3 in the presence of soils could not have been due simply to the oxidation of PH_3 with the enclosed air. Phosphine is a highly reactive substance, yet at the conditions of these experiments and in the absence of an oxidizing catalyst, it appeared to be stable in air for an indefinite period.

The differences of PH_3 absorption by the three soils (HHL > HFL > LHL) could not be correlated with pH, with "oxi-

Table VI. Hydrolysis of Zinc Phosphide at Room Temperature in Water^a

Days after preparation	Phosphine found, % of total available				
	Dry	25%	50%	75%	100%
0	0.00	0.00	0.00	0.00	0.00
1	0.00	0.09	0.12	0.12	0.12
2	0.03	0.10	0.14	0.14	0.14
6	0.00	0.05	0.05	0.04	0.03
9	0.00	0.03	0.05	0.03	0.05
14	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00	0.00

^a Control samples for comparison with Zn_3P_2 in soils. Amounts of water are based on that needed for the given percent saturation of soil

ductive capacity" in the presence of H_2SO_4 (Table IV), or with the amounts of PH_3 released from Zn_3P_2 incubated with the same soils (Figure 1). Oxidation to phosphate ion was incomplete and comparatively slow, in contrast to the rapid and more complete oxidation of Zn_3P_2 . The differences of PH_3 absorption between soils were minimized by increasing the moisture content, as expected from the decrease in the void-space surface. Yet the differences of PH_3 appearance and disappearance from Zn_3P_2 in soil (Figure 1) were accentuated by moisture. Increased water content of soils caused more rapid decomposition of Zn_3P_2 , but it is difficult to explain the presence of large amounts of phosphate ion if PH_3 were the only direct decomposition product. Two hypotheses are possible. Zinc phosphide might have oxidized directly to $\text{Zn}_3(\text{PO}_4)_2$ in soils, with PH_3 appearing as a secondary hydrolysis product, or the intimate mixture of Zn_3P_2 with soil released PH_3 directly in contact with the oxidizing surfaces. The greater concentrations of PH_3 introduced directly into the gas space would lead to greater septum losses, and diffusion from the gas into the soil voids would result in a slower oxidation.

With the restrictions imposed by the artificial experimental conditions, in particular the use of closed systems, it would be difficult to assume an exact correspondence of the results of this investigation with those in the field. Microbiological activity can not be ruled out as a possible influence in Zn_3P_2

Table VII. Hydrolysis of Zn_3P_2 in Various Waters at 27°

Sample description	pH ^a	Hydrolysis time, hr										pH at termination of test
		0.25	1.5	3.0	5.5	22	29	96	168	192	264	
Buffer solution	4.00	0.000	4.752	11.228	12.456	29.649	63.158	75.438	100.00	84.127	74.58	4.50
Distilled water, lab	6.00	0.000	0.011	0.057	0.132	0.228	0.254	0.137	0.077	0.064	0.029	7.73
Buffer solution } old	7.00	0.130	0.651	...	15.000	9.231	6.90
Buffer solution } fresh	7.00	0.069	0.645	1.808	3.010	15.850	21.600	17.400	15.500	12.100	9.120	6.80
Wailua river water above falls	7.05	0.000	0.104	...	0.052	0.037	7.28
Grove Farm irrigation water, above quarry	7.20	0.000	0.113	...	0.061	0.032	7.23
Wailuku river water	7.52	0.000	0.003	0.011	0.022	0.059	0.076	0.046	0.047	0.051	0.029	7.55
Keapana river water, upper Kealia	7.65	0.004	0.096	...	0.046	0.030	7.58
Tap water, lab	7.90	>0.002	0.005	0.022	0.044	0.154	0.209	0.161	0.097	0.138	0.078	7.65
Ocean water	8.20	0.000	0.006	0.017	0.031	0.096	0.105	0.089	0.039	0.019	0.005	8.45
Control, Wailuku river, no Zn_3P_2	7.52	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	6.80
Zn_3P_2 only, no water	...	0.000	0.000	0.000	0.003	0.005	0.007	0.020	0.032	0.033	0.013	...
Dry tube, water washed and dried Zn_3P_2 only	0.000	0.000	...	0.000	0.000

Expressed in % available PH_3 . Samples fortified with 100 ppm of PH_3 as Zn_3P_2 .

^a pH of water at starting day.

degradation or PH₃ oxidation. The most variable difference would appear to lie in the aerobic-anaerobic state of the closed system. Initially aerobic, the closed conditions would tend to become anaerobic from microorganism respiration, unless it were poisoned by PH₃. We assume that field conditions generally would be more aerobic. For all practical purposes we conclude that the amounts of Zn₃P₂ reaching field soils would convert rapidly to phosphate and zinc ions, without releasing detectable PH₃ into the atmosphere.

Zn₃P₂ in Water—the Influence of pH and Mineral Content. Zinc phosphide placed in neutral water at room temperature failed to produce more than trace quantities of PH₃ (Table VI and VII). Small amounts of PH₃ probably came from minor, easily hydrolyzed phosphide impurities—such as Ca₃P₂ or Mg₃P₂—in the commercial Zn₃P₂. Washed and dried Zn₃P₂ did not generate PH₃ when stored. Commercial Zn₃P₂ stored without water generated small easily detectable quantities of PH₃.

Hydrolysis of Zn₃P₂ to PH₃ occurred in acid or basic solutions at a rate dependent on pH and temperature (Robison, 1970). That the hydrolysis was not a simple pH-dependent phenomenon became evident from the anomalous hydrolysis of Zn₃P₂ at room temperature in a conventional buffer solution of pH 7.00. The buffer contained sodium and potassium phosphates; the experiments were repeated with fresh preparations. We did not pursue this investigation, but we do suggest that pH and ionic activity contribute to the hydrolysis

of Zn₃P₂ to PH₃. This argument would help to explain the decomposition of Zn₃P₂ to PH₃ in soil, although the mechanism for oxidation to phosphate ion predominated in soil, whereas it was nearly absent in water. We did not determine whether the pH 7.00 buffer increased the rate of oxidation of PH₃.

Phosphine in air formed only traces of H₃PO₄ when stored over distilled water (Table V).

We concluded that Zn₃P₂ dropped or carried into streams or ocean water would not readily decompose. Bottom or suspended sediments would likely decompose Zn₃P₂, with the formation of PH₃ or H₃PO₄ in anaerobic or aerobic conditions, respectively.

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Fate of ¹⁴C-Labeled Diazinon in Rice, Paddy Soil, and Pea Plants

Tapio L. Laanio, Gerard Dupuis, and Herbert O. Esser*

[2-¹⁴C]Diazinon [*O,O*-diethyl *O*-(2-isopropyl-4-methylpyrimidin-6-yl) phosphorothioate] was rapidly absorbed by and translocated in rice plants. Loss of insecticide, of about 50% within 9 days, was due to volatilization from the paddy water and transpiration from the leaves. Less than 10% of the radioactivity remaining in the plants after 9 days was the parent compound. The metabolite fraction consisted of 2-isopropyl-4-methyl-6-hydroxypyrimidine (G 27550), 2-(1'-hydroxy-1'-methyl)ethyl-4-methyl-6-hydroxypyrimidine (GS 31144), the latter partly as a glucoside, and a small

fraction of polar metabolites. The same metabolites and traces of diazoxon were found after stem injection of the insecticide. Hydroxydiazinon [*O,O*-diethyl *O*-[2-(1'-hydroxy-1'-methyl)ethyl-4-methylpyrimidin-6-yl] phosphorothioate] if present represented only a minor metabolite. G 27550 and GS 31144 were also the main metabolites of paddy soil. Cleavage of the pyrimidine ring with the evolution of ¹⁴CO₂ proceeded at a low rate in rice plants and paddy soil. The degradative pathways found in rice also occurred in pea plants.

The behavior of the broad spectrum insecticide diazinon [*O,O*-diethyl *O*-(2-isopropyl-4-methylpyrimidin-6-yl) phosphorothioate] in plants has been followed thoroughly with the aid of chemical, radiochemical, and enzymatic methods (Aquino, 1970; Hirano and Yushima, 1969; Kansouh and Hopkins, 1968; Miles *et al.*, 1964; Onsager and Rusk, 1967; Randolph *et al.*, 1969).

After regular application of diazinon to a great variety of crops, diazoxon [*O,O*-diethyl *O*-(2-isopropyl-4-methylpyrimidin-6-yl) phosphate] was found, if present at all, in very small concentrations (Augustinsson and Jonsson, 1957;

Coffin and McKinley, 1964; Eberle and Novak, 1969; Harding *et al.*, 1969; Ralls *et al.*, 1966). Another oxidation product, hydroxydiazinon (CGA 14128) [*O,O*-diethyl *O*-[2-(1'-hydroxy-1'-methyl)ethyl-4-methylpyrimidin-6-yl] phosphorothioate], has been reported to occur in small amounts in kale (Pardue, 1968; Pardue *et al.*, 1970) and in rice plants (Miyazaki *et al.*, 1969).

The initial product of hydrolysis of both diazinon and diazoxon, in addition to the phosphorus moiety, namely 2-isopropyl-4-methyl-6-hydroxypyrimidine (G 27550), has been identified in several plant species (Kansouh and Hopkins, 1968; Ralls *et al.*, 1966, 1967). No metabolites, but a loss of insecticide by transpiration, have been found in alfalfa grown in diazinon-treated soil (Nelson and Hamilton, 1970).

*Agrochemicals Division, Ciba-Geigy Limited, Basle, Switzerland.