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FUNGICIDE DECOMPOSITION

The Degradation of Organomercury Fungicides in Soil

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Metallic mercury vapor and trace amounts of phenylmercury acetate (PMA) were present in the air surrounding PMA-treated soil. About equal amounts of the vapors of metallic mercury and a volatile ethylmercury compound were present when ethylmercury acetate was used. With the use of methylmercury compounds, methylmercury vapor was present with trace amounts of mercury vapor. The chloride was about twice as volatile as the dicyandiamide. A large portion of the organic mercurial applied to the soil was found to be in the organomercury form after the lapse of 30 to 50 days. Moisture in soil decreased the amount of escaping organic mercury vapor.

Decomposition of mercurial fungicides in contact with soil has long been known (*1, 2, 9*). The escape of metallic and organic mercury vapors and the amount of organic mercurial remaining in soil, however, have not been investigated except through indirect biological techniques, because of inadequacy of chemical methods. Booer (*1*), basing his conclusions on biological phytotoxicity experiments, postulated a mechanism for organic mercury decomposition in soil. He suggested that organic mercury compounds reacted with the clay micelle in soil to form an intermediate which subsequently gave a dialkylmercury or diphenylmercury and a mercury-clay compound. Based on this hypothesis, the dialkylmercury compounds would escape into the atmosphere while diphenylmercury would accumulate in the soil. Metallic mercury would result from the further degradation of the mercury-clay compound. However, repeated attempts in this laboratory to detect the disubstituted organic mercury compounds formed in soil through degradation failed, indicating that decomposition was not by Booer's mechanism.

More recently, work has been done on the absorption and inactivation of organomercurials by microorganisms that tolerate and even thrive on mercurials (*3, 8*). It has been postulated that inactivation occurred by the uptake of fungicide by microorganisms, followed by metabolic breakdown and by possible utilization of portions of the byproducts. However, whether or not biological inactiviation and mercury evolution occur together has not been determined.

This paper presents chemical data on the nature of residual mercurials in soil and in the atmosphere surrounding the treated soil to further elucidate the phenomena of degradation in soil.

Experimental

Soil Treatment, Sampling, and Vapor Collection. Puyallup sandy loam, the principal bulb-growing soil and the most extensive agricultural soil in Pierce County, Wash., was used in these experiments. It is an alluvial soil occurring on the floor of the Puyallup and Stuck River Valleys. This soil, taken from the field as required, was air dried several days and passed through a 30-mesh seive to remove rocks and roots. A 650-gram portion of the soil was spread out on a plastic sheet and sprayed with a measured amount of an aqueous mercurial sufficient to give a concentration in soil of about 100 μg. mercury per gram of dry soil. The soil was transferred to a large beaker, and water was added in small increments, while mixing, to bring the moisture contents to the approximate desired level. The soil was mixed until analytically uniform. Where autoclaved soil was used, it was heated 3 hours at 15 pounds steam pressure prior to the addition of mercurials in the manner above. A 50-gram portion of the soil was set aside in a sealed container for analysis within 24 hours.

Soil treated with phenylmercury acetate (PMA) or ethylmercury acetate (EMA) was placed in unglazed clay pots and immediately placed under a bell jar-type adapter connected to an aeration train composed of a carbonate-phosphate and an acid permanganate absorber, previously described (*4*) for fractionation of the vapor into the metallic mercury and monosubstituted organomercury compound. A wet test

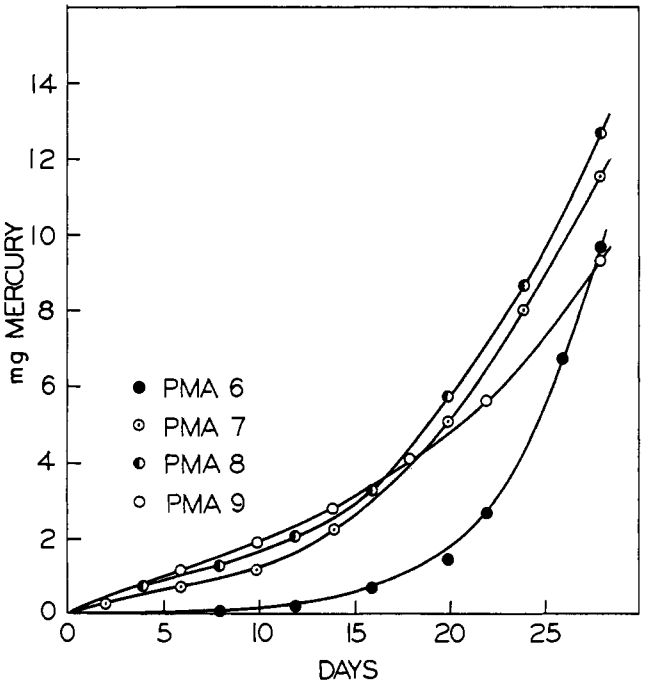

Figure 1. Cumulative mercury vapor from PMA-treated soil in relation to elapsed days

Soil in PMA pot 6 was autoclaved before addition of PMA; others (PMA pots 7, 8, 9), containing unautoclaved treated soil, varied in initial moisture

Table I. Pot Mercury Analyses by Soil Depth

Pot No.		Depth, Inches	Total Hg, P.P.M. 0 Days	Total Hg, P.P.M. n[a] Days	Extractable Organic Mercury as P.P.M. Hg 0 Days	Extractable Organic Mercury as P.P.M. Hg n[a] Days
PMA	6	0–1	113	78	113	59
	6	1–2	113	111	113	83
	6	2–B[b]	113	95	113	75
	7	0–1	125	116	121	102
	7	1–2	125	112	121	82
	7	2–B	125	101	121	73
	8	0–1	126	105	122	74
	8	1–2	126	113	122	77
	8	2–B	126	106	122	76
	9	0–1	112	94	114	60
	9	1–2	112	112	114	75
	9	2–B	112	105	114	79
EMA	10	0–1	77	46	63	28
	10	1–2	77	63	63	45
	10	2–B	77	66	63	42
	11	0–1	84	50	69	29
	11	1–2	84	61	69	38
	11	2–B	84	60	69	36
	12	0–1	84	46	69	29
	12	1–2	84	67	69	47
	12	2–B	84	65	69	45
	13	0–1	102	78	83	56
	13	1–2	102	91	83	66
	13	2–B	102	71	83	49
MMD	19	0–1	84	74	73	59
	19	1–B	84	83	73	67
	20	0–1	86	72	74	58
	20	1–B	86	82	74	68
	21	0–1	80	63	67	51
	21	1–B	80	80	67	66
MMC	22	0–1	76	59	63	47
	22	1–B	76	70	63	59

[a] PMA, 28 days; EMA, 53 days; MMD and MMC, 35 days.
[b] Two-inch depth to bottom.

meter was attached to one of each four pots to determine the air flow rate. In the other three pots run simultaneously, air was allowed to bubble under the bell jar.

In the methylmercury dicyandiamide and chloride (MMD and MMC) study, pots were set up in the same manner as above except that the adapter used was a large inverted funnel (*4*) and the pots were of glass. Air flow was regulated by vacuum adjustment and a capillary tubing to the approximate air flow rate of the PMA and EMA pots. A water bubbler was necessary to prevent clogging of the carbonate-phosphate absorber with the use of the inverted funnel adapter. The acid permanganate absorption solution was replaced with 50 ml. of a 4:1 mixture of 2*N* potassium dichromate and 18*N* sulfuric acid. This was more suitable for extended use than permanganate.

The absorbers were changed periodically depending on the amount of mercurial captured. The bubbler when used contained sufficient water to evaporate to dryness about 2 to 6 hours before the absorbers were changed. If water remained, this was added to the carbonate-phosphate solution.

When aeration was concluded, the pots were removed and the contents were separated into component layers by depth. The components were placed in tared and sealed containers, weighed, mixed thoroughly, and analyzed. Moisture, total mercury, extractable ionic mercury, and extractable organomercury analyses, in final analyses, were made on each component of a given pot. Values of mercurial concentration obtained for each of the components were multiplied by the layer weight and divided by the fractional part solids (% dry matter ÷ 100) to obtain the subtotal weight mercurial per pot. Subtotals for the component layers were added to obtain the total weight mercurial per pot. Average per cent of final moisture in a given pot was obtained by multiplying the layer percentage by the layer weight, adding the products of component layers, and dividing by the total final soil weight of a given pot.

Analytical Methods. Phenyl and alkylmercury compounds were extracted from about 1 gram of soil by shaking for 2 hours with 25 ml. of 0.1*M* phosphate pH 8 buffer containing 6 mg. of thiomalic acid, added ju t prior to use, and analyzed after dilution of a 5-ml. aliquot of the centrifuged extract with 5 ml. water, and acidification with 5 ml. of 9*N* hydrochloric acid containing 150 mg. of hydroxylammonium chloride. The final determination was made by the dithizone microprocedure of Miller and Polley (*6*).

Diphenyl and dialkylmercury compounds were extracted from 1 gram of soil by shaking for 2 hours with 10 ml. of chloroform and analyzed by cleaving the disubstituted mercurial to give an aryl or alkylmercury salt, using 9*N* or 12*N* hydrochloric acid, followed by the dithizone microprocedure cited (*6*).

Vapors of mercury, phenyl, and alkylmercury compounds were collected and measured as previously described (*4*) except that the dichromate absorption solution was analyzed by the mercury reduction technique (*5*) after treatment with an excess of hydroxylammonium chloride solution.

Ionic mercury was extracted from about 1 gram of soil by shaking for 2 hours with each of two 25-ml. portions of 2*M* sodium chloride. The combined centrifuged and filtered (using 1*M* sodium chloride for washing) extract was analyzed by the procedure of Polley and Miller (*7*).

Total mercury was determined in the PMA and EMA pots according to Polley and Miller (*7*), and according to Kimura and Miller (*5*) in the MMC and MMD pots.

Results and Discussion

Phenylmercury acetate (PMA) was used in three pots of soil—PMA-7,-8, and -9—with initial moistures of 6.5, 13.6, and 22.5%, respectively. A fourth pot containing autoclaved soil

Table II. Analyses of Phenylmercury Acetate (PMA)-Treated Soil

Pot No.	H_2O in Soil, %	Total Hg in Soil	Extractable PMA in Soil	Extractable Hg^{+2} in Soil	Uncharacterized Hg in Soil (by Difference)	Carbonate Absorber PMA in Air	$KMnO_4$ Absorber Hg^0 in Air
INITIAL ANALYSES			EXPRESSED AS MG. HG PER POT (DRY BASIS)				
PMA-6	14.1	66.4	67.6 (102%)[a]	0.7 (1.1%)			
PMA-7	6.5	75.8	73.3 (96.7%)	0.6 (0.8%)			
PMA-8	13.6	76.2	73.8 (96.8%)	0.8 (1.1%)			
PMA-9	22.5	65.0	66.2 (102%)	0.0 (...)			
FINAL ANALYSES,[b] AFTER 28 DAYS							
PMA-6	7.4	55.1 (83.0%)	42.3 (63.7%)	1.1 (1.7%)	13.2 (19.9%)	0.2 (0.3%)	9.6 (14.5%)
PMA-7	4.5	67.5 (89.1%)	52.8 (69.7%)	2.0 (2.6%)	9.2 (12.1%)	0.3 (0.4%)	11.5 (15.2%)
PMA-8	7.1	65.2 (85.6%)	46.1 (60.5%)	2.2 (2.9%)	15.1 (19.8%)	0.2 (0.3%)	12.6 (16.5%)
PMA-9	12.0	60.2 (92.6%)	39.5 (60.8%)	1.6 (2.5%)	14.5 (22.3%)	0.1 (0.2%)	9.3 (14.3%)

[a] All percentages are based on the total mercury of the initial analyses. [b] Values calculated as described under *Experimental*.

Table III. Analyses of Ethylmercury Acetate (EMA)-Treated Soil

Pot No.	H_2O in Soil, %	Total Hg in Soil	Extractable EMA in Soil	Extractable Hg^{+2} in Soil	Uncharacterized Hg in Soil (by Difference)	Carbonate Absorber EMA in Air	$KMnO_4$ Absorber Hg^0 in Air
INITIAL ANALYSES			EXPRESSED AS MG. HG PER POT (DRY BASIS)				
EMA-10	12.0	44.1	35.6 (80.7%)[a]	0.9 (2.1%)	7.6 (17.2%)		
EMA-11	5.7	48.6	40.1 (82.5%)	0.8 (1.6%)	7.7 (15.9%)		
EMA-12	12.9	48.6	39.9 (82.1%)	0.8 (1.7%)	7.9 (16.3%)		
EMA-13	24.9	49.6	40.4 (81.5%)	0.9 (1.8%)	8.3 (16.7%)		
FINAL ANALYSES,[b] AFTER 53 DAYS							
EMA-10	2.40	33.6 (76.2%)	22.0 (49.8%)	0.5 (1.2%)	11.4 (25.8%)	4.8 (10.9%)	5.4 (12.2%)
EMA-11	2.81	33.2 (68.4%)	19.9 (41.0%)	0.6 (1.3%)	11.9 (24.5%)	8.1 (16.7%)	8.1 (16.7%)
EMA-12	2.97	34.0 (69.9%)	23.2 (47.7%)	0.3 (0.5%)	12.0 (24.7%)	4.8 (9.8%)	8.3 (17.1%)
EMA-13	6.09	39.2 (79.0%)	27.6 (55.6%)	0.4 (0.8%)	11.3 (22.8%)	1.4 (2.9%)	8.9 (18.0%)

[a] All percentages are based on total mercury of the initial analyses. [b] Values calculated as described under *Experimental*.

PMA-6 was prepared with an initial moisture of 14.1%. The accumulative values for mercury vapor evolution from these pots are shown in Figure 1. For the first 2 weeks of aeration, mercury vapor captured was increasingly greater with increasing initial moisture. The pot containing autoclaved soil (PMA-6) gave very little mercury during this period in comparison to a similar nonautoclaved pot (PMA-8), suggesting a microbiological mode of degradation. The increase in mercury vapor with increasing moisture where moisture should hinder volatilization of metallic mercury, suggests a mechanism of degradation requiring water. This is also consistent with microbiological degradation. While autoclaving decreased the rate of mercury evolution, as indicated by the slope of the cumulative curves, during the first several weeks, autoclaving increased the mercury evolution rate over that of comparable nonautoclaved pot after 3 weeks. If biological degradation were assumed as the only cause of mercury evolution, this could be interpreted as the building up of a PMA-degrading microbial population beyond that in the comparable nonautoclaved pot.

Traces of PMA were found in the carbonate absorbers. Cumulative PMA at the end of a 28-day period was 0.3, 0.2, and 0.1 mg. as Hg for PMA-7,

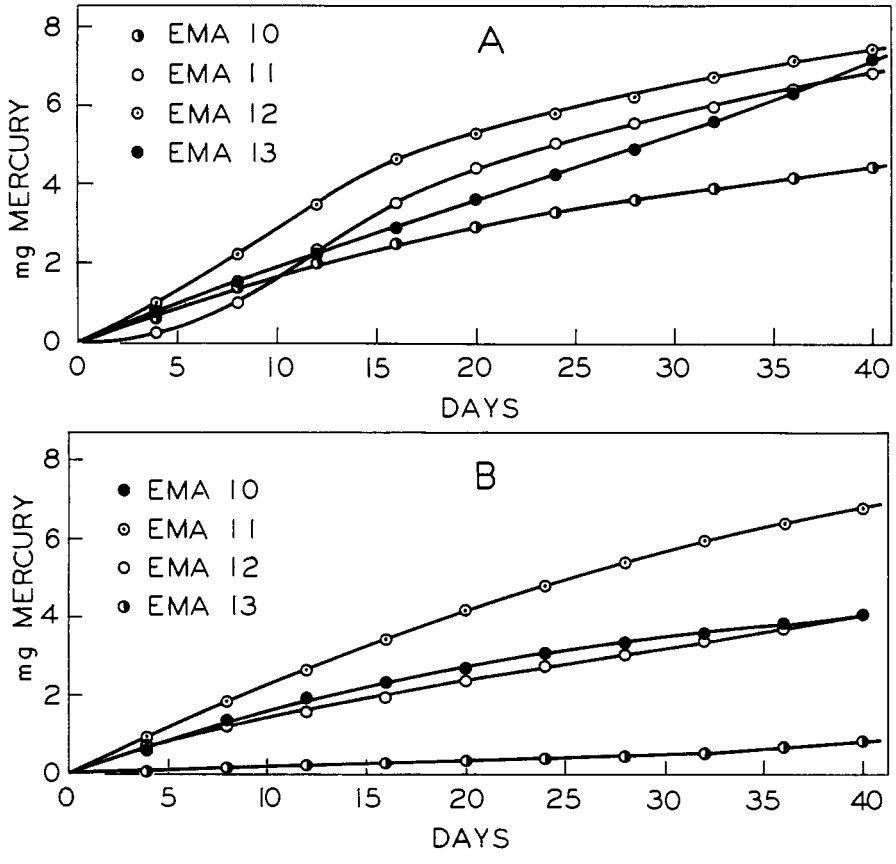

Figure 2. *(A)* Cumulative mercury vapor from EMA-treated soil in relation to elapsed days *(B)* Cumulative ethylmercury vapor from EMA-treated soil

EMA pot 10 contained soil which was autoclaved before addition of EMA; others (EMA pots 11, 12, 13), contained unautoclaved EMA-treated soil of varying initial moisture

Table IV. Analyses of Methylmercury Chloride (MMC) and Methylmercury Dicyandiamide (MMD) Treated Soil

Pot No.	H_2O in Soil, %	Total Hg in Soil	Extractable MMC or MMD in Soil	Uncharacterized Hg in Soil (by Difference)	Carbonate Absorber MMC or MMD in Air	$K_2Cr_2O_7$ Absorber Hg° in Air
INITIAL ANALYSES			EXPRESSED AS MG. HG PER POT (DRY BASIS)			
MMD-19	25.8	45.6	39.3 (86.2%)[a]	6.3 (13.8%)		
MMD-20	20.9	47.7	41.2 (86.4%)	6.5 (13.6%)		
MMD-21	16.0	43.9	36.8 (83.8%)	7.1 (16.2%)		
MMC-22	22.5	41.2	33.9 (82.3%)	7.3 (17.7%)		
FINAL ANALYSES,[b] AFTER 35 DAYS						
MMD-19	15.5	42.7 (93.6%)	34.5 (75.6%)	8.7 (19.1%)	2.2 (4.8%)	0.2 (0.4%)
MMD-20	12.2	43.8 (91.8%)	35.9 (75.3%)	8.2 (17.2%)	3.3 (6.9%)	0.3 (0.6%)
MMD-21	9.2	40.7 (92.7%)	33.4 (76.1%)	7.3 (16.6%)	3.0 (6.8%)	0.2 (0.5%)
MMC-22	14.0	35.4 (85.9%)	29.1 (70.6%)	6.6 (16.0%)	5.3 (12.9%)	0.2 (0.5%)

[a] All percentages are based on the total mercury of the initial analyses. [b] Values calculated as described under *Experimental*.

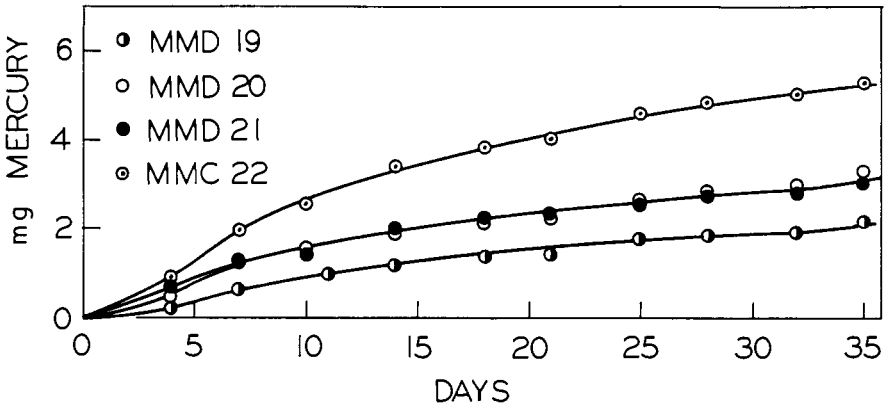

Figure 3. Cumulative methylmercury vapor from MMD- and MMC-treated soil in relation to elapsed days

MMD pots 19, 20, and 21 contained unautoclaved MMD-treated soil of varying initial moisture; MMC pot 22 contained unautoclaved MMC-treated soil with approximately the same initial moisture as MMD pot 20

8, 9 in the order of increasing initial moisture and 0.2 mg. Hg for PMA-6. Analyses of the pots by 1-inch layers indicated the greatest loss generally to be from the surface (Table I). Where unglazed clay pots were employed, as in the PMA and EMA series, the next greatest loss was from the bottom, indicating diffusion through the unglazed clay pots. The zone of heaviest concentration of the residual mercurial was at the 1- to 2-inch depth. In the MMC and MMD series, where glass pots were used, concentration of mercurials below the 1-inch depth was very close to the original. Table II shows that 14 to 16% of the original PMA mercury applied was lost as mercury vapor. Of the original mercury, 60 to 70% was extractable as the intact phenylmercury compound at the end of the experiment. About 20% of the original mercury, although recovered as part of final total mercury, was not characterized. This portion may consist of irreversibly bound or physically unavailable PMA, small amounts of unvolatilized metallic mercury, and sulfide.

EMA soil treatment series EMA-11, 12, and 13 were prepared in a manner similar to the PMA series with initial moistures of 5.7, 12.9, and 24.9%, respectively. A pot containing autoclaved soil, EMA-10, with 12.0% initial moisture was included. As degradation progressed, the vapor from these pots included both metallic mercury and the organic mercury compound (Figure 2) in contrast to the PMA series, which produced almost entirely metallic mercury. The loss of ethylmercury compound from soil was nearly a linear function of time for a given surface. Moisture appeared to affect this by determining the manner in which the soil was packed and by reducing the EMA vapor pressure. Figures 2*A* and *B* show that EMA-10 and 12, while giving up differing amounts of the metallic vapor, gave almost identical amounts of the EMA vapor throughout the experimental period, their moisture values being nearly identical. EMA-11, being rather dry and loosely packed, gave the most EMA vapor, while EMA-13, which contained moisture in excess of the soil capacity, gave the least EMA vapor. The autoclaved EMA-10 (Figure 2*A*), unlike the autoclaved PMA-6, showed no period in which elemental mercury was not evolved although the process of mercury production seemed impaired in comparison to its non-autoclaved equivalent, EMA-12. Also, Figure 2*A* appears to indicate that moisture facilitates EMA decomposition. Decomposition in EMA-11 with 6% initial moisture began slowly, but in EMA-12 with double the moisture, decomposition was more rapid. With EMA-13, the moisture capacity of the soil being exceeded, the soil was tightly packed and time apparently was required for mercury to diffuse to the outer surface. Thus an increase in the rate of mercury evolution over the other pots can be seen after 3 weeks.

The extraction of EMA from soil is apparently more difficult than the extraction of PMA. Thus, only 81 to 83% of the EMA could be extracted after being in contact with soil for less than 24 hours (Table III). Since the degradation of an organic mercurial appears to be a very slow process, the conversion of 17 to 19% of the mercurial to mercury in such a short period would be unlikely. It is more reasonable to assume that the 17 to 19% of the mercurial was irreversibly bound or otherwise unavailable for extraction. After 53 days of aeration, the total mercury content of the soil had dropped to 68 to 79% of the original application. All of the loss can be accounted for as ethylmercury and mercury vapors caught in the absorbers. Of the mercury remaining in soil, a major portion was extractable as the ethylmercury compound. Here again the bulk of the uncharacterized mercury is quite probably the irreversibly bound or physically unavailable organic mercury compound.

In the methylmercury series, MMD was used in three pots, MMD-19, 20, and 21, with initial moisture contents of 25.8, 20.9, and 16.0%, respectively (Table IV). The autoclaved pot was omitted. For volatility comparison, an MMC pot containing 22.5% initial moisture, MMC-22, was included. In contrast to the PMA pots, which gave

primarily mercury vapor, and EMA pots, which gave both mercury and EMA vapors, the MMD and MMC pots gave primarily the methylmercury vapor. The minute amount of mercury vapor detected indicated that methylmercury compounds are quite stable to degradation in soil over a 35-day period. After the aeration period, 86 to 94% of the original mercury remained. All of the loss was recovered as the methylmercury compound captured in the carbonate absorbers. Comparison of the total mercury column with the extractable mercury column again suggested an absorption of the organomercury by the soil, especially when the insignificant amount of metallic mercury obtained during this period is considered.

The cumulative vapor (Figure 3) for methylmercury compounds appeared abnormally low. This was due to compacting of the soil surface by periodic watering to bring the pots to their original weights and also to impervious glass pots used. The compacted surface then acted as a vapor barrier. The ratio of the volatility of MMD to MMC was apparently about one to two.

The data, thus far, indicate gross differences in the tendencies of the three organomercurials toward degradation in soil and their mode of loss from soil. The nonvolatile PMA was degraded to mercury and was lost as mercury vapor. The volatile EMA was also degraded in soil to mercury, but its loss from soil occurred both as mercury vapor and the organomercury vapor. MMD and MMC gave no significant metallic mercury vapor and their loss from soil was due entirely to the volatility of the organomercury compound. If biological inactivation and mercury evolution are assumed to be intimately related, this would be inconsistent with the results of Spanis *et al.* (*8*), who found that Panodrench 4, a commercial preparation containing 0.6% MMD, was inactivated by soil microorganisms. Thus, one must assume that biological inactivation and mercury evolution do not necessarily occur together. Most of the mercurial remaining in soil could be extracted undegraded by using mild reagents, indicating that the mercurial fungicide, whether biologically active or inactive, persists in soil for a considerable time.

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FUMIGANT MEASUREMENT

Determination of Phosphine in Air by Gas Chromatography

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Phosphine was determined in air by gas chromatography of sample sizes of 0.05 to 1 ml. for concentrations of 10 mg. of PH_3 to less than 0.5 mg. of PH_3 per liter. Analysis took less than 4 minutes.

Hydrogen phosphide (PH_3), also known as phosphine, is highly toxic to insects infesting grain (*2*) and, by modern methods of application, may be safely used for control in such material. Several methods for phosphine analysis have been published: the method of White and Bushey (*5*) is not accurate with small samples at low concentrations; the colorimetric phosphorus determination by King (*3*) is more accurate but it is complicated and time consuming; the technique of Nelson and Milum (*4*) requires a sample of several liters. A rapid and simple method using small samples was required in view of the shortcomings of the above methods; therefore, gas chromatography was investigated.

Experimental

Apparatus. The Perkin-Elmer 154-D gas chromatograph with thermistor cell was used. The column was of stainless steel, 160 inches long and 1/4 inch diameter, and filled with firebrick 40-60 mesh as the solid phase and Apiezon L 30% as the liquid phase. Column temperature was 35° C., and the flow rate of helium carrier gas was 25 cc. per minute. A 1-mv. recorder was used with pen speed of 1 second for full 10-inch scale.

Reagents. For the generation of phosphine, Phostoxin tablets produced by Degesch Co., Frankfurt Am-Main, W. Germany, were used. Each tablet weighs about 3 grams and generates 1 gram of phosphine. The tablet composition was 70% aluminum phosphide, 26% ammonium carbamate, and 4% solid paraffin. To avoid ignition, phosphine is generated from a tablet of the above composition by reaction with water, which produces, in addition, ammonia and carbon dioxide.

The solid support packing in the column with Apiezon L was obtained from Wilkins Instruments and Research, Calif.

Procedure. Phosphine was generated in a 525-liter fumigation chamber by introducing Phostoxin tablets in a beaker and adding sufficient water to cover them. Subsequent to the generation of the phosphine gas, samples of the phosphine-air mixture were drawn from the fumigation chamber at various intervals of time by a gas syringe and