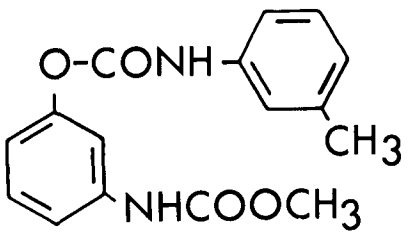
Phenmedipham and *m*-Aminophenol Decomposition in Alkaline Soil[1]

by BABASAHEB R. SONAWANE and CHARLES O. KNOWLES
Department of Entomology
University of Missouri
Columbia, Mo. 65201

Phenmedipham, the active component of Betanal®, is a post-emergence herbicide used for weed control in sugar beets (1). Kossmann (2) using nonradioactive phenmedipham reported that the compound was continuously decomposed in slightly acid soils of low humus content, and half-lives of 28-55 days were noted, depending on the experimental conditions and soil type. This paper describes the behavior of phenmedipham-^{14}C and one of its hydrolysis products, m-aminophenol-^{14}C, in an alkaline soil.

MATERIALS AND METHODS

Phenmedipham (shown below) uniformly labeled with radiocarbon in the m-aminophenol moiety (specific activity 5.5 mCi/mmole) and uniformly ^{14}C-ring-labeled m-aminophenol (specific activity 1.95 mCi/mmole) were provided by NOR-AM Agricultural Products, Inc., Woodstock, Ill. Both compounds were purified by thin-layer chromatography (TLC) prior to experimental use. NOR-AM also provided nonradioactive samples of phenmedipham, m-aminophenol, methyl-N-(3-hydroxyphenyl)-carbamate (MHPC), and 3,3'-dihydroxyazobenzene.



The radiocarbon-containing compounds extracted from phenmedipham- or m-aminophenol-treated soil were separated by TLC on silica gel GF_{254} coated glass plates. The solvent system was isooctane: n-butanol (4:1) (3), and average R_f values for authentic standard compounds were 0.46 for phenmedipham, 0.19 for m-aminophenol, 0.34 for MHPC, and 0.52 for 3,3-dihydroxyazobenzene. Following chromatography radioautographs were

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prepared, and the radioactivity in the silica gel corresponding to the darkened images on the film was measured with a Liquimat 220 liquid scintillation spectrometer. The composition of the counting solution has been described (4).

Soil was collected near Hartsburg, Mo. and had a pH of 8.0 (pH 7.4 under salt); the organic matter content was low (0.9%).

Air dried soil samples (200 g) were placed in 12-oz. Mason jars; the moisture level was adjusted to 20% by the addition of distilled water. Phenmedipham-^{14}C ($\sim 10^6$ counts/min) and 4 mg of nonradioactive phenmedipham were added to each jar in 3 ml of chloroform, and the compound was thoroughly mixed with the soil by gently shaking the jar. Soil was also treated with m-aminophenol in a manner similar to that described above. Soil samples were analyzed at 0, 4, 8, 16, and 32 days posttreatment; duplicate analyses were conducted and the results were averaged.

After the appropriate incubation period the soil was extracted 6 times with 50-ml aliquots of methanol. The methanol extracts were combined and concentrated on the rotary evaporator. The remaining water fraction ($\sim$30-35 ml) was extracted 6 times with 25-ml aliquots of ethyl acetate. The ethyl acetate extracts were combined, dried over anhydrous sodium sulfate, and concentrated to approximately 5 ml on the rotary evaporator. Duplicate 1-ml aliquots were radioassayed, and the remainder of the material was subjected to TLC and radioautography.

The total radioactivity in the aqueous fraction was determined by adding a 0.2-ml aliquot to a scintillation vial containing 15 ml of the regular cocktail plus 10% BIO-SOLV (5).

The soil residue remaining after extraction with methanol was extracted 6 times with 50-ml aliquots of hydrochloric acid (pH 5.2). The total radioactivity in the acid fraction was determined by radioassaying 0.2-ml aliquots in the BIO-SOLV cocktail. Following acid extraction the soil residue was refluxed for 5 hr with 150 ml of 5N sodium hydroxide. The alkaline solution was separated from the soil by filtration and concentrated on the rotary evaporator. A 0.1-ml aliquot was radioassayed as described above.

Finally the soil residue was dried, and a 50-mg aliquot was combusted. The radioactivity in an aliquot of the trapping solution was measured (6).

RESULTS AND DISCUSSION

Table 1 gives the results of fractionation of soil samples incubated with phenmedipham-^{14}C. The majority of the radioactive material in the methanol extract partitioned into ethyl acetate; the maximum amount detected in the aqueous fraction was only 2.6% (Table 1). The ethyl acetate-soluble radioactive material

decreased from 89.6% at "zero" time to 22.5% by 32 days.

TABLE 1
Results of fractionation of soil samples incubated with phenmedipham-^{14}C

Fraction	% Applied phenmedipham-^{14}C equivalents at indicated days				
	0	4	8	16	32
Methanol Extract					
Ethyl acetate	89.6	72.3	62.0	39.1	22.5
Aqueous	2.3	2.6	2.1	1.4	1.7
Residue					
Hydrochloric acid	2.4	7.9	11.9	17.5	16.0
Sodium hydroxide	1.9	5.3	9.0	16.3	15.7
Unextractable	0.3	2.0	6.5	11.5	26.1
Total Recovery, %	96.5	90.1	91.5	85.8	82.0

The nature and relative concentration of these materials are given in Table 2. Phenmedipham and MHPC combined comprised a minimum of 96.8% of the ethyl acetate-soluble radioactive material (Table 2). The remainder of this fraction consisted of low levels of m-aminophenol, an unknown, and radioactive material(s) at the TLC origin. Phenmedipham decreased from 87.4% at "zero" time to 64.3% by 4 days and remained relatively constant at 49% from 8 through 32 days. Concurrently, there was an increase in levels of MHPC from 10.8% at "zero" time to 50% at 8 days where a plateau was reached that continued through the 32-day period.

TABLE 2
Nature and relative concentration of ethyl acetate-soluble radioactive materials isolated from soil incubated with phenmedipham-^{14}C

Compound	R_f value for TLC	% Ethyl acetate-soluble radioactive material at indicated days				
		0	4	8	16	32
Phenmedipham	0.46	87.4	64.3	47.9	49.6	48.8
MHPC	.34	10.8	33.1	50.0	48.9	48.0
m-Aminophenol	.19	0.2	0.5	0.7	0.6	0.5
Unknown I	.50	1.1	1.6	1.2	0.6	2.3
Origin	.00	0.5	0.5	0.2	0.3	0.4

Although the total ethyl acetate soluble radioactivity was decreasing with time (Table 1), there was an apparent equilibrium between phenmedipham and MHPC after 8 days (Table 2). An infrared spectrum of MHPC isolated from phenmedipham-treated soil was identical to that of the authentic standard (Fig. 1).

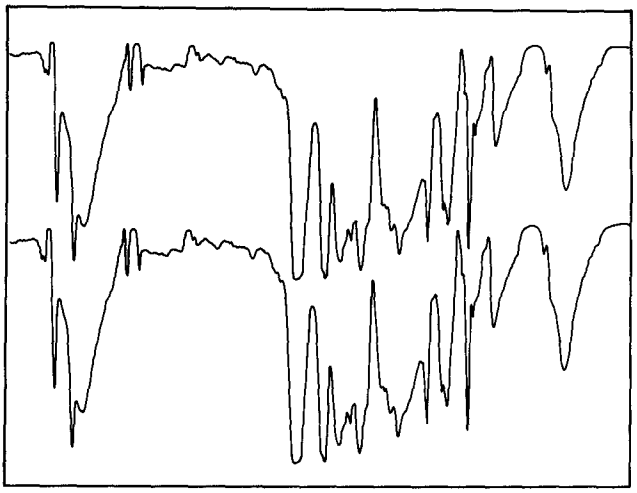

Figure 1. Comparison of infrared absorption spectrum (chloroform solution) of authentic MPHC (top) with a phenmedipham decomposition product isolated from soil (bottom).

The total radioactive material extractable from the soil (ethyl acetate plus aqueous fractions) declined from 91.9% at "zero" time to only 24.2% at 32 days (Table 1). Although some of the loss was probably due to volatilization of certain of the radiocarbon-containing components, it was too great to be explained solely on this basis. Preliminary combustion analyses revealed that an appreciable amount of radioactive material still remained in the soil residue. Therefore, the soil residue was subjected to acid extraction and alkaline hydrolysis in an attempt to recover more of the radioactive material (Table 1). Levels of radioactivity in the hydrochloric acid and sodium hydroxide fractions generally increased with time after treatment reaching a maximum of 17.5% and 16.3% respectively, at 16 days posttreatment (Table 1). However, there still remained in the soil residue an appreciable amount of radioactive material as determined by combustion analysis (unextractable, Table 1); the maximum level was 26.1% at 32 days posttreatment.

Table 3 gives the results of fractionation of soil samples incubated with m-aminophenol-^{14}C. The ethyl acetate-soluble radioactive material rapidly decreased from 62.9% at "zero" time to 19.6% at 16 days. m-Aminophenol, the parent compound, comprised the vast majority of the organosoluble radioactive material during the 16-day period although several unidentified compounds were also present (Table 4). The maximum level of radioactivity in the aqueous fraction was 4.7% and occurred at 16 days (Table 3).

TABLE 3
Results of fractionation of soil samples incubated with m-aminophenol-^{14}C

Fraction	% Applied m-aminophenol-^{14}C equivalents at indicated days			
	0	4	8	16
Methanol Extract				
Ethyl acetate	62.9	22.1	18.7	19.6
Aqueous	4.4	2.6	3.5	4.7
Residue				
Hydrochloric acid	18.4	22.9	17.6	18.8
Sodium hydroxide	6.9	17.3	27.1	24.8
Unextractable	3.4	17.3	22.8	19.6
Total Recovery, %	96.0	82.2	89.7	87.5

TABLE 4
Nature and relative concentration of ethyl acetate-soluble radioactive materials isolated from soil incubated with m-aminophenol-^{14}C

Compound	R_f value for TLC	% Ethyl acetate-soluble radioactive material at indicated days			
		0	4	8	16
m-Aminophenol	0.19	69.6	58.4	51.7	43.9
Unknown I	.54	0.6	1.2	1.1	2.6
Unknown II	.48	1.7	3.1	2.0	3.3
Unknown III	.35	7.9	9.5	12.7	10.4
Unknown IV	.28	5.6	8.3	10.4	13.5
Unknown V	.09	2.3	1.9	3.2	3.0
Origin	.00	12.3	17.6	18.9	23.3

As expected from the phenmedipham study the soil residue contained the bulk of the radiocarbon-containing compounds, ranging from 28.7% at "zero" time to a maximum of 67.5% at 8 days (Table 3). The hydrochloric acid and sodium hydroxide fractions contained significant amounts of radioactive material as did the soil residue remaining after extraction with acid and alkali (Table 3).

Thus, it is concluded that in alkaline soil phenmedipham is hydrolyzed to m-aminophenol *via* MHPC. The free m-aminophenol then undergoes both physical adsorption and chemical complexation with various unidentified soil components. One possibility is the formation of a humus-m-aminophenol complex in an analogous

manner to that suggested for the 3,4-dichloroaniline moiety derived from propanil herbicide (7).

Unknown I from phenmedipham and m-aminophenol degradation chromatographed in a similar region with 3,3'-dihydroxyazobenzene in the single solvent system used. However, it seems unlikely that this symmetrical azo derivative was formed in the soil, since it was not detected when m-aminophenol was incubated in horseradish peroxidase-hydrogen peroxide and ferrous iron-hydrogen peroxide systems (8).

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