Fate of Dicamba in a Model Ecosystem

by CHING-CHIEH YU[1], DALE J. HANSEN[2], and GARY M. BOOTH[3]
Illinois Natural History Survey and
Illinois Agricultural Experiment Station
Urbana, Ill. 61801

Dicamba (2-methoxy-3,6-dichlorobenzoic acid) is used to control both annual broad-leaved and grassy weeds. The metabolism of this compound in several species of plants has been described (Broadhurst et al. 1966; Chang and Vander Born 1968, 1971a, 1971b; Hull and Weisenberg 1967; Hurtt and Foy 1965; Ray and Wilcox 1969). Transformation of dicamba in soil has been reported (Smith 1973; Schweizer and Swink 1971). However, its fate in the food chain is not known. A simple model ecosystem recently developed by Metcalf et al. (1971) is useful for studying the behavior of pesticides in the environment. This model ecosystem has been used to evaluate the biodegradibility and magnification of several pesticides in a food chain (Yu et al. 1974; Sanborn and Yu 1973; Booth et al. 1974). This paper reports the results of dicamba in this model ecosystem.

MATERIALS AND METHODS

Model Ecosystem: Overall procedures described by Metcalf et al. (1971) were followed with some modifications (Sanborn and Yu 1973).

Labeled compound: Fifty μCi (5.85 mg, specific activity 1.89 mCi/mmole) of carboxyl-^{14}C-labeled dicamba (New England Nuclear, radiochemical purity greater than 99%) in 0.5 ml of acetone was applied to the leaves of 7-day-old sorghum plants.

Sample preparation: Ether extraction of water and acetone extraction of organisms have been described previously (Yu et al. 1974). The insoluble residues after acetone extraction from organisms were solubilized (Yu et al. 1974) and counted in a liquid scintillation counter.

Paper chromatography: Solvent extracts from water and

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[1] C. C. Yu's Present Address: Department of Entomology, NYS Agricultural Experiment Station, Geneva, New York 14456

[2] D. J. Hansen's Present Address: Agricultural Division, Monsanto Company, St. Louis, Missouri 63166

[3] G. M. Booth's Present Address: Department of Zoology, Brigham Young University, Provo, Utah 84601

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organisms were chromatographed on Whatman No. 1 paper and developed in a solvent system of benzene-acetic acid-water (2:2:1 V/V) according to Broadhurst et al. (1966).

RESULTS AND DISCUSSION

Radioactivity in water was monitored throughout the experimental period (Table I). Concentrations of dicamba and its metabolites in the water reached a peak at the 6th day after application, and then the radioactivity decreased very slowly. This indicates that decarboxylation does not occur rapidly since dicamba was labeled in the carboxyl group. Broadhurst et al. (1966) also found that dicamba decarboxylation was not measurable in plants.

TABLE I

Concentration of dicamba and its metabolites in water.

Day	1	6	11	19	26	32
ppm	0.0012	0.2364	0.2269	0.1928	0.1742	0.1669

Table II summarizes the distribution of dicamba and its metabolites in solvent extracts and in residual fractions from water and organisms. Very small amounts (0.2%) of the radioactive materials could be extracted by ethyl ether from the unhydrolyzed water. However, after HCl hydrolysis (0.025 N HCl at 70°C for 20 hrs), 98.8% of the dicamba and its metabolites could be extracted by ether. This indicates that most of the dicamba and its metabolites are conjugated or are present in anionic forms in unhydrolyzed water and cannot be extracted by ether. The acetone-extractable fraction of the organisms consisted of 0% (in Daphnia) to 67% (in crab) of this total radioactivity (Table II).

Solvent extracts of water and crab which had higher radioactivity were analyzed by paper chromatography and radioautography. There were 3 spots on the radioautogram in hydrolyzed water (Table III). Co-chromatography with standard dicamba revealed that spot I (Rf 0.86) was the parent dicamba. Spots II and III (Rf 0.38 and 0.04, respectively) were very similar to those previously reported as 5-hydroxy-dicamba (5-hydroxy-2-methoxy-3,6-dichlorobenzoic acid) and conjugated products, respectively (Broadhurst et al. 1966). Unchanged dicamba constituted the major component in both unhydrolyzed and hydrolyzed water (Table III). Schweizer and Swink (1971) also reported that dicamba was quite persistent in soil.

TABLE II

Concentration of dicamba and its metabolites in solvent extracts and in residues of water and various organisms.

Sample	ppm Equivalent		
	Solvent Extract	Residue	Total
UHy-H_2O	0.0002 (0.2%)	0.1628 (99.8%)	0.1631
Hy-H_2O	0.1608 (98.8%)	0.0020 (1.2%)	0.1628
Algae	0.2279 (14.1%)	1.3903 (85.9%)	1.6182
Clam	0.01285 (46.8%)	0.1439 (53.2%)	0.02724
Crab	0.7432 (66.6%)	0.3740 (33.4%)	1.1172
Daphnia	0	0.1671 (100%)	0.1671
Elodea	0.3253 (35.4%)	0.5929 (64.6%)	0.9182
Fish	0.006648 (35.3%)	0.01216 (64.7%)	0.01881
Mosquito	0.07359 (20.7%)	0.2815 (79.3%)	0.3551
Snail	0.07205 (22.2%)	0.2518 (77.8%)	0.3239

In contrast, there was no detectable parent dicamba in the crab extract. There was also no detectable 5-hydroxy dicamba in the crab or hunhdrolyzed water extracts. However, the hydrolyzed water extract contained 10.2% of the 5-hydroxydicamba (Table III). Therefore, it appears that the acetone extract from the crab contained conjugated products.

TABLE III

Percent distribution of solvent-extractable metabolites after paper-chromatographic analyses.

Sample	Metabolites		
	I	II	III
UHy-H_2O	96.2%	0	3.8%
Hy-H_2O	89.7%	10.2	0.1%
Crab	0	0	100%

Total radioactivity in the water and organisms was compared (Table II). There was no evidence that dicamba and its metabolites magnified in the food chain. For example, the total equivalent of the radioactivities in a food chain from algae → mosquito → fish decreased from 1.6 ppm (in algae) to 0.02 ppm (in fish).

In summary, dicamba persisted in water in conjugated or in anionic forms. It slowly transformed to 5-hydroxydicamba in water (about 10% after 32 days) and was very slowly decarboxylated. Dicamba did not magnify in food chain organisms.

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REFERENCES

BOOTH, G. M., C. C. YU and D. J. HANSEN: J. Environ. Qual. 2, 408 (1971).

BROADHURST, N. A., M. L. MONTGOMERY and V. H. FREED: J. Agr. Food Chem. 14, 585 (1966).

CHANG, F. Y. and W. H. VANDER BORN: Weed Sci. 16, 176 (1966).

CHANG, F. Y. and W. H. VANDER BORN: Weed Sci. 19, 107 (1971a).

CHANG, F. Y. and W. H. VANDER BORN: Weed Sci. 19, 113 (1971b).

HULL, R. J. and M. R. Weisenberg: Plant Physiol. 42, S 40 (1967).

METCALF, R. L., G. K. SANGHA and I. P. KAPOOR: Environ. Sci. Tech. 5, 709 (1971).

RAY, B. and M. WILCOX: Physiol. Plant 22, 503 (1969).

SANBORN, J. R. and C. C. YU: Bull. Environ. Contam. Toxicol. 10, 340 (1973).

SCHWEIZER, E. E. and J. F. SWINK: Weed Sci. 19, 717 (1971).

Smith, A. E.: J. Agr. Food Chem. 21, 708 (1973).

YU, C. C., G. M. BOOTH, D. J. HANSEN and J. R. LARSEN: J. Agr. Food Chem. 22, 431 (1974).