Transformation of the Herbicide Methyl-N-(3,4-dichlorophenyl)-carbamate (Swep) in Soil*

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Several 3,4-dichloroacylanilide herbicides were shown (1,2) to be degraded in soil with the release of 3,4-dichloroaniline (DCA) that was subsequently transformed in part to 3,3',4,4'-tetrachloroazobenzene (TCAB). A comparative study of the fate of 13 different anilines in soil revealed a dependence of chloroazobenzene formation on the number and distribution of chlorosubstituents of the aniline precursor (3). On the basis of these results it was predicted that other chloroaniline based herbicides, including some phenylcarbamates and phenylureas, may be trans-

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formed to azo compounds in soil. The experiments reported here were designed to test the validity of this prediction in the case of Swep, a phenylcarbamate herbicide that contains a DCA moiety.

MATERIALS AND METHODS

Technical grade methyl-N-(3,4-dichlorophenyl)-carbamate (Swep) was sublimed under high vacumm at 95°C, and the purity of the product was established by thin-layer chromatography, by gas chromatography and by its melting point (Table 1). For the isolation and identification of metabolites, 500 mg herbicide was mixed with 500 g (dry weight) of freshly collected Nixon sandy loam (pH 5.5). The soil sample was moistened to 60% of water-holding capacity and incubated at 28°C for 40 days in a beaker covered with polyethylene film. Periodic exposure to air and additions of water assured the system of a continuous supply of oxygen and moisture. At the end of the incubation period, the soil sample was extracted with 2 liters of acetone, and the extract was fractionated by procedures described previously for the isolation of DCA and TCAB (1). For quantitative analyses, 50 g soil samples treated with 25 mg of the herbicide were incubated under the conditions just described. Methods used to extract, identify and measure herbicide residues and metabolites included thin-layer chromatography and quantitative gas chromatography performed as reported previously (2). Infrared spectra were recorded using KBr pellets in a Perkin-Elmer Model 21 spectrograph.

RESULTS AND DISCUSSION

A quantity of Swep remained intact after 40 days in soil but thin-layer chromatograms indicated that a portion of the herbicide was transformed to a variety of products. Two of these were isolated and identified as DCA and TCAB by comparing their movement on thin-layer plates, retention times, melting points, and infrared spectra to those of authentic compounds (see Table 1).

TABLE 1

Some characteristics used for identification of Swep, DCA and TCAB

Compound	M.P. °C	R_f	Retention (Seconds) 200 °C	Retention (Seconds) 250 °C
Swep	109-111	0.46	130	29
DCA	71	0.65	38	
TCAB	158	0.95		140

Previous tests (2) established that the extraction procedures recovered DCA and TCAB completely. Recoveries from soil of added Swep averaged 80%. The latter value was used to correct analytical data obtained from a study of degradation of Swep with time in soil

(Table 2). The herbicide was decomposed and evidence was obtained for the production in soil of both DCA and TCAB. Only traces of DCA were detected but TCAB accumulated with time and accounted for 24% of the degraded herbicide after 28 days. Chin et al. (4) have reported previously that small amounts of DCA are produced from Swep in soil. Since DCA is an intermediate in the transformation of Swep to TCAB and other products, it does not accumulate. The DCA concentration did not exceed 1.0 mg/50 g soil at any time in the present study. Quantities below this level were not measured because the compound was partially lost from soil extracts during the concentration procedure (2).

TABLE 2

Swep degradation and metabolite accumulation with time in soil

Day	Compound (mg) Swep	DCA	TCAB
0	25.00	-	-
7	16.50	+	1.25
14	15.00	+	1.35
21	12.24	+	2.05
28	9.36	+	2.65

+ = less than 1.0 mg

Swep was not degraded and no DCA or TCAB was detected in soil samples that received the metabolic poisons NaN_3 and $HgCl_2$ in addition to Swep. It was concluded, therefore, that the transformation of Swep to DCA and TCAB was biological rather than chemical. It required about 21 days in Nixon sandy loam for 50% degradation of Swep. This is slower than the rate of decomposition of acylanilide herbicides (2).

The results obtained with Swep are consistent with the prediction that some chloroaniline based herbicides will give rise to DCA and TCAB on decomposition in soil. It should be noted, however, that no DCA or TCAB was detected in soil samples that received 500 ppm of 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron) or 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (Linuron) and were incubated for 40 days. These phenylurea herbicides remained unchanged, resisting completely degradation under the experimental conditions employed.

SUMMARY

In soil, the herbicide methyl-N-(3,4-dichlorophenyl)-carbamate (Swep) was transformed to 3,4-dichloroaniline, 3,3',4,4'-tetrachloroazobenzene and other unidentified compounds. The rate of Swep degradation was found to be slower than that of acylanilide herbicides. Under identical conditions 3-(3,4-dichloro-

phenyl)-1,1-dimethylurea (Diuron) and 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea (Linuron) remained unchanged for 40 days.

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