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Breakdown of the Herbicide Dicamba and Its Degradation Product 3,6-Dichlorosalicylic Acid in Prairie Soils

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The degradation of ^{14}C-ring- and ^{14}C-carboxyl-labeled dicamba was studied in moist nonsterile heavy clay at 25 ± 1° in Pramer and Bartha (1965) flasks. Gas chromatographic and radiochemical analytical techniques were used to monitor the breakdown. Over 50% of the dicamba was lost within 4 weeks, radioactive carbon dioxide and 3,6-dichlorosalicylic acid being the sole degradation products detected. Decomposition of ^{14}C-ring-labeled dicamba was compared in moist nonsterile silty clay, heavy clay, and sandy loam soils at 25 ± 1°. In all soils loss was rapid and complete in 3 weeks. A build-up of 3,6-dichlorosalicylic acid was followed by a slow loss which was complete within 9 weeks. Negligible breakdown of dicamba occurred in steam sterilized soils. Soil slurry adsorptive studies with 3,6-dichlorosalicylic acid indicated at least 30% adsorption to all soil types.

Dicamba (2-methoxy-3,6-dichlorobenzoic acid) is used as a postemergence herbicide for the selective control of weeds of the buckwheat family in cereals. The chemical is also applied for the control of broadleaved weeds in pastures and rangeland grasses.

Studies have shown that dicamba is degraded in moist soils (Burnside and Lavy, 1966; Corbin and Upchurch, 1967; Donaldson and Foy, 1965; Parker and Hodgson, 1966; Smith, 1973a,b). This breakdown is considered to be microbial in origin (Parker and Hodgson, 1966; Smith, 1973a), since degradation was inhibited in steam-sterilized soils.

Smith (1973b) using ^{14}C-carboxyl-labeled dicamba reported that in a warm moist heavy clay the herbicide was transformed into 3,6-dichlorosalicylic acid. Radioactive carbon dioxide was also liberated from the treated soils, indicating that dicamba or the salicylic acid, or both, underwent decarboxylation.

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In the present work the breakdown of ^{14}C-ring- and ^{14}C-carboxyl-labeled dicamba was studied in nonsterile heavy clay in Pramer and Bartha (1965) flasks to ascertain whether all the radioactivity applied to the clay could be accounted for after various time intervals. In addition, the isolation and identification of possible decarboxylated metabolites were undertaken. The decomposition of ^{14}C-ring-labeled dicamba in three different sterile and nonsterile soil types was investigated for comparative purposes in erlenmeyer flasks, to identify the metabolites and to study their persistence in the three soil types. Soil adsorption characteristics of the dicamba soil metabolite, 3,6-dichlorosalicylic acid, were also determined.

MATERIALS AND METHODS

Soil. The composition and physical properties of the soils used in these studies are presented in Table I.

Chemicals. ^{14}C-Carboxyl-labeled dicamba (2-[7-^{14}C]methoxy-3,6-dichlorobenzoic acid) and [^{14}C]dicamba labeled in the six ring carbon atoms were obtained from the Velsicol Chemical Corporation, Chicago, Ill., as were

Table I. Composition and Physical Characteristics of Soils

Soil type	Composition, %				pH	Field capacity moisture, %
	Clay	Silt	Sand	Org content		
Melfort, silty clay (SiC)	30	38	32	11.7	5.2	36
Regina, heavy clay (HvC)	69	26	5	4.2	7.7	40
Jameson, sandy loam (SL)	6	9	85	3.2	7.5	11

the nonradioactive 5-hydroxydicamba (5-hydroxy-2-methoxy-3,6-dichlorobenzoic acid) and 3,6-dichlorosalicylic acid. Each of the ^{14}C-labeled compounds was diluted with nonradioactive herbicide and methanolic solutions were prepared. In the case of the ^{14}C-carboxyl-labeled herbicide the solution had a total dicamba content of 1.13 mg/ml as determined by gas chromatography, following methylation of 100-μl aliquots with diazomethane, while the ^{14}C-ring-labeled dicamba solution contained 1.38 mg/ml. The specific activities of the carboxyl-labeled and ring-labeled dicamba solutions were 1.12 and 5.63 μCi/ml, respectively.

Degradation Studies Using Pramer and Bartha Flasks. To 48-g samples of moist heavy clay fresh from the field (40 g oven dry) in 250-ml capacity Pramer and Bartha flasks was added 0.1 ml of either [^{14}C]dicamba solution. After thorough mixing, 8.0 ml of distilled water was added to each flask to bring the moisture level to field capacity. Thus, the herbicide concentration was 2.8 ppm for the ^{14}C-carboxyl-labeled dicamba and 3.5 ppm in the case of the ^{14}C-ring-labeled material, based on oven dry heavy clay. For the absorption of carbon dioxide evolved during the study, 15.0 ml of 1 *N* sodium hydroxide solution was placed in the side arm of each flask. The flasks were stoppered and incubated in the dark at 25 ± 1°. Every 2 days the stoppers were removed for 10 min to permit air exchange. After a 24-hr equilibration period, and then at two weekly intervals, the radioactivity in 0.2-ml aliquots of the sodium hydroxide solution from duplicate flasks was determined; the soils were also extracted and analyzed.

Radioactive carbon dioxide evolution from ^{14}C-ring-labeled dicamba (138 μg) in the silty clay at field capacity moisture (40 g of soil on an oven dry basis) was also monitored, 0.2-ml aliquots of the sodium hydroxide solution from duplicate experiments being analyzed for radioactivity at weekly intervals.

Extraction Procedures. The soils were placed in 250-ml glass-stoppered flasks and 84 ml of methanol was added so that the combined volume of the methanol together with the water present in the soils was equivalent to 100 ml. The flasks were then shaken for 30 min on a wrist action shaker, after which the contents were filtered under suction and the filtrates retained. Aliquots (1.0 ml) of each filtrate were examined for radioactivity and the quantity of dicamba extracted calculated assuming that all the radioactivity was due to the respectively labeled [^{14}C]dicamba.

The soil cakes were washed with a further 50 ml of methanol, these washings being discarded. The soil was allowed to air dry to constant weight at room temperature.

Dicamba Analyses. A 25.0-ml aliquot of each methanolic extract in 150 ml of 1% aqueous sodium sulfate solution was acidified with 1.0 ml of 6 *N* hydrochloric acid and extracted four times with 20-ml volumes of ether to remove any dicamba present. The dried ether extracts were evaporated and methylated using diazomethane according to the procedure of Smith (1973b). The methylated extracts were taken up in 25.0 ml of *n*-hexane when 2- or 3-μl portions were examined by gas chromatography using an electron-capture detector (Smith, 1973a) and the methyl ester of dicamba present was determined. The radioactivity in the hexane solution was also determined and the dicamba content calculated, assuming that all the activity was due to [^{14}C]dicamba methyl ester.

Alkaline Soil Extraction. Samples (10.0 g) of the air-dried methanol extracted soils were shaken with 1 *N* sodium hydroxide solution and after suction filtration the filtrate was acidified and ether extracted as previously described (Smith, 1973b). The ether extracts were dried over sodium sulfate and evaporated to dryness using a rotary evaporator and the residue was dissolved in 10.0 ml of methanol. A 1.0-ml aliquot of each methanolic extract was examined for radioactivity while the remaining solution was evaporated to approximately 0.5 ml and subjected to thin-layer chromatographic examination.

Acidic Soil Extraction. Samples (10.0 g) of the air-dried methanol extracted soils were shaken with 50.0 ml of 2 *N* hydrochloric acid for 1 hr on a wrist action shaker. Following suction filtration, the soil cake was rinsed with a further 25-ml portion of the acid and the soil discarded. The filtrate was shaken three times with 60-ml volumes of ether and the combined extracts, after drying over sodium sulfate, were evaporated to dryness on the rotary evaporator. The residue was dissolved in 10 ml of methanol, 1.0-ml portions of which were checked for radioactivity.

Radioactivity. The ^{14}C in the various solutions was measured using a Picker Nuclear Liquimat 200 liquid scintillation spectrometer as described earlier (Smith, 1973b).

Thin-Layer Chromatography. Precoated tlc plates SILG-25 UV254 were used (Macherey-Nagel and Co., Darmstadt, Germany) and developed using chloroform–acetic acid (19:1) or benzene–hexane–acetic acid (5:10:2) or benzene. After development, the plates were air-dried at room temperature and autoradiograms prepared by placing the plates in contact with X-ray film (Kodak RP Royal X-OMAT) for 3 weeks.

The R_f values of the compounds studied are shown in Table II. These compounds were added to all chromatograms as reference compounds, and their positions on the developed chromatograms were detected by viewing under a short-wavelength ultraviolet lamp.

Comparative Degradation Studies in Three Soil Types. Samples of moist silty clay, heavy clay, and sandy loam fresh from the field, and equivalent to 40.0 g of oven-dried soil, were weighed into 250-ml capacity erlenmeyer flasks. To each flask was added 0.1 ml of the ^{14}C-ring-labeled dicamba solution representing 138 μg of the herbicide. After thorough mixing, sufficient distilled water was added to moisten all soils to their field capacity levels. The flasks were loosely stoppered with cotton wool plugs to permit circulation of air and incubated in the dark at 25 ± 1°. Distilled water was added every few days to maintain the moisture level. Duplicate samples were analyzed at regular intervals for 9 weeks.

To compare the persistence in sterile soils, samples of the three soil types, equivalent to 40.0 g of oven-dried soil, in 250-ml capacity glass-stoppered erlenmeyer flasks were steam sterilized twice for 2 hr at 120° with an interval of 24 hr. ^{14}C-Ring-labeled dicamba (138 μg) was added to each flask together with sufficient sterile distilled water to yield samples at field capacity. The flasks were stoppered

Table II. R_f Values of Compounds Studied

Compound	R_f a	R_f b	R_f c
Dicamba	0.66	0.63	0.00
5-Hydroxydicamba	0.29	0.22	0.00
3,6-Dichlorosalicylic acid	0.50	0.54	0.00
2,5-Dichloroanisole	1.00	1.00	1.00
2,5-Dichlorophenol	0.90	0.61	0.64

[a] Chloroform–acetic acid (19:1). [b] Benzene–hexane–acetic acid (5:10:2). [c] Benzene.

and incubated in the dark at 25 ± 1° and duplicate samples analyzed after 9 weeks.

All soils were extracted with methanol as described above, the combined methanolic and aqueous content being 100 ml, and the dicamba recovered was determined by direct measurement of the radioactivity in 1.0 ml of the methanolic solution. To confirm the absence of significant amounts of any methanol-soluble radioactive degradation products, 25.0-ml portions of the methanolic solutions were further extracted and examined using thin-layer chromatography as described.

Following methanolic extraction, the soils were air-dried and 10.0-g portions subjected to both acidic and alkaline soil extraction and thin-layer chromatographic analysis as described above.

Adsorption Studies with 3,6-Dichlorosalicylic Acid. Soil samples from the persistence studies known to contain this metabolite were pooled and extracted with 1 *N* sodium hydroxide solution. After filtration, acidification, and ether extraction, the evaporated residue was taken up in a small volume of methanol and the [^{14}C]salicylic acid present separated from [^{14}C]dicamba using thin-layer chromatography. Autoradiography was used to locate the position of the radioactive compounds. The silica gel area corresponding to the acid was carefully removed and eluted with methanol. The residue, after evaporation of the methanol, was taken up in 100 ml of distilled water. By measuring the total radioactivity in this aqueous solution, and knowing the specific activity of the original ^{14}C-ring-labeled dicamba, it was calculated that 17 μg of radiochemically pure ^{14}C-ring-labeled 3,6-dichlorosalicylic acid had thus been obtained.

To this solution was added 0.38 mg of nonradioactive 3,6-dichlorosalicylic acid to give a 4-ppm solution of the acid. Solutions containing acid concentrations of 0, 1, and 2 ppm were also prepared by dilution.

Adsorption Determination. To 1.0 g of soil, sieved to pass 0.5 mm in a 25-ml Corex centrifuge tube, was added 10 ml of the appropriate salicylic acid solution. The tube was then capped and shaken on an end-over-end shaker at 30 rpm for 24 hr at a constant temperature of 25 ± 1° to establish equilibrium. After shaking, the tubes were centrifuged at 10,000 rpm for 10 min when 2.0-ml samples of the supernatant were analyzed for radioactivity. Two replicates were analyzed for each acid concentration and soil type. The difference in 3,6-dichlorosalicylic acid concentration between the initial and final equilibrium solutions was assumed to be due to adsorption.

RESULTS AND DISCUSSION

The breakdown of dicamba in the Pramer and Bartha flasks (Tables III and IV), as determined by the gas chromatographic and radiochemical methods, was slower than previously reported (Smith, 1973a,b). In these latter experiments the degradation was conducted in cartons in which a loosely fitting lid allowed a good circulation of air. In the sealed Pramer and Bartha flasks an adequate air exchange was probably not achieved even though air was allowed to permeate into the flasks every 2 days.

Table III. Recovery of 113 μg of ^{14}C-Carboxyl-Labeled Dicamba with Time from Regina Heavy Clay Incubated at Field Capacity and 25 ± 1°, Using Methanol as Extractant

Time, weeks	Dicamba remaining[a] Gc analysis μg	Gc analysis %	Radiochemical analyses I[b] μg	I[b] %	II[c] μg	II[c] %
0	108	96	107	95	104	92
2	75	66	87	77	79	70
4	42	37	58	51	47	42
6	40	35	43	38	41	36
8	24	21	26	23	23	20
10	0	0	3	3	2	2

[a] Average from duplicate experiments. [b] From direct counting of the methanol extracts. [c] From the ^{14}C present in the *n*-hexane extracts used for the gas chromatographic analyses.

Table IV. Recovery of 138 μg of ^{14}C-Ring-Labeled Dicamba with Time from Regina Heavy Clay Incubated at Field Capacity and 25 ± 1°, Using Methanol as Extractant

Time, weeks	Dicamba remaining[a] Gc analysis μg	Gc analysis %	Radiochemical analyses I[b] μg	I[b] %	II[c] μg	II[c] %
0	132	96	132	96	128	93
1	87	63	98	71	95	69
2	75	54	90	65	80	58
4	55	40	70	51	63	46
6	35	25	44	32	40	29

[a] Average from duplicate experiments. [b] From direct counting of the methanol extracts. [c] From the ^{14}C present in the *n*-hexane extracts used for the gas chromatographic analyses.

In all cases the reproducibility of replicates as determined gas chromatographically or radiochemically was excellent. After each incubation period there was a close agreement between the amounts of ^{14}C-ring- or ^{14}C-carboxyl-labeled dicamba remaining as determined by the gas chromatographic method and the two radiochemical procedures (Tables III and IV). Within experimental error all the radioactivity recovered from the soils (Tables III and IV), using methanol as extractant, could be accounted for as dicamba by the gas chromatographic analysis which is specific for the herbicide. This would indicate the absence of significant quantities of methanol-soluble ^{14}C-labeled degradation products containing carbon atoms derived from either the aromatic ring or the carboxyl group of dicamba.

The absence of any radioactive degradation products was confirmed at each sampling date by thin-layer chromatographic examination of the methanolic extracts derived from ether extraction of the acidified methanolic solutions. The autoradiograms indicated the presence of only one radioactive compound with each of the chromatographic solvent systems, having an R_f value corresponding to that for dicamba (Table II). Cochromatography of the ^{14}C-labeled methanolic extracts with pure dicamba confirmed the identification.

Production of radioactive carbon dioxide was observed from both ^{14}C-carboxyl- and ^{14}C-ring-labeled dicamba treated soils (Tables V and VI), thus indicating that decarboxylation (Smith, 1973b) and ring-opening mechanisms occur during the degradation of the herbicide.

Table V. Radioactivity Recovered from the Breakdown of 113 μg of ^{14}C-Carboxyl-Labeled Dicamba in Regina Heavy Clay at Field Capacity and 25 ± 1°

	% of the applied ^{14}C present as[a]				
Time, weeks	Dicamba–methanol extraction	Dicamba–NaOH extraction	3,6-Dichlorosalicylic acid–NaOH extraction	Carbon dioxide	Total % recov.
2	70	5	12	8	95
4	42	7	25	15	89
6	36	8	31	18	93
8	20	3	31	24	78
10	2	1	24	42	69
13	0	1	19	41	61
17	0	<1	16	45	61

[a] Average from duplicate experiments.

Table VI. Radioactivity Recovered from the Breakdown of 138 μg of ^{14}C-Ring-Labeled Dicamba in Regina Heavy Clay at Field Capacity and 25 ± 1°

	% of the applied ^{14}C present as[a]				
Time, weeks	Dicamba–methanol extraction	Dicamba–NaOH extraction	3,6-Dichlorosalicylic acid–NaOH extraction	Carbon dioxide	Total % recov.
1	69	5	11	2	87
2	58	9	13	4	84
4	46	4	17	5	72
6	29	2	23	9	63

[a] Average from duplicate experiments.

The methanol extract obtained from the acidic treatment of the air-dried soils following prior methanolic extraction contained insignificant amounts of radioactivity, and it was calculated that less than 2% of the original radioactivity could be removed from the soils using such means. By contrast, considerable activity was observed in the methanolic extracts derived from the alkaline soil extractions. No chromatographic separation from the origin was noted using benzene as solvent, but with both acidic solvent systems, the presence of two radiochemical compounds was noted. They appeared to be the same two products regardless of soil incubation time, or whether ^{14}C-ring- or ^{14}C-carboxyl-labeled herbicide had been used. The silica gel areas corresponding to the positions of these two radioactive compounds were removed from the chromatograms and extracted with methanol and subsequently identified and confirmed (Smith, 1973b) to be [^{14}C]dicamba and 3,6-[^{14}C]dichlorosalicylic acid. Knowing the relative proportion of ^{14}C in each of the above methanolic extracts (corresponding to the herbicide and breakdown product) and knowing the amount of radioactivity in the methanolic extracts obtained from the alkaline extraction, the amounts of [^{14}C]dicamba and 3,6-[^{14}C]dichlorosalicylic acid recovered by the sodium hydroxide solution were calculated (Tables V and VI).

Tables V and VI summarize the percentages of identifiable radioactivity recovered from the treated soils after various time intervals. These indicate a steady loss of the original dicamba with a subsequent build-up of salicylic acid and a steady evolution of $^{14}CO_2$. The 3,6-dichlorosalicylic acid also appeared to slowly disappear from the moist heavy clay with time (Table V). Some dicamba remained adsorbed to the soil and was not extracted with methanol, but was subsequently removed by the alkali (Tables V and VI). This alkali extractable dicamba decreased in quantity with time.

It has previously been noted (Smith, 1973b) that the $^{14}CO_2$ liberated from moist heavy clay, treated with ^{14}C-carboxyl-labeled dicamba, could have been a result of decarboxylation of either dicamba, or 3,6-dichlorosalicylic acid, or both. Decarboxylation of the former would be expected to yield 3,6-dichloroanisole, while loss of carbon dioxide from the latter would give 3,6-dichlorophenol. By using ^{14}C-ring-labeled herbicide such degradation products, if present, should be identifiable. In the present experiments methanol was used for the extraction of dicamba from the soils instead of the aqueous calcium chloride used previously (Smith, 1973b). The methanol was used in the hopes of recovering any anisole formed, as this product would not be appreciably soluble in aqueous medium. Any anisole or phenol formed would only be in minute quantities as the gas chromatographic and radiochemical analyses (Table IV) had precluded the presence of significant amounts of any methanol-soluble degradation products. No trace of any [^{14}C]anisole or [^{14}C]phenol, or any other product, was ever detected on any of the autoradiograms. It was considered possible that traces of both the anisole and phenol, being relatively volatile, could have evaporated from the tlc plates during the preparation of the autoradiograms. To overcome this shortcoming nonradioactive 3,6-dichloroanisole and phenol were added to the various soil extracts prior to chromatographic examination, as markers. After development with the three solvent systems the chromatograms were air-dried and the silica areas corresponding to the positions of the anisole and phenol were removed and eluted with 5.0 ml of methanol, which was then checked for radioactivity. In every case less than 1% of the original soil-applied ^{14}C could be attributed to either of these suspected metabolites. Thus $^{14}CO_2$ and 3,6-[^{14}C]dichlorosalicylic acid were the only identifiable degradation products. No trace of any 5-hydroxydicamba was found in any of the treated soils, thus confirming earlier findings (Smith, 1973b). However, it is possible that either 3,6-dichloroanisole or 3,6-dichlorophenol, or both, could have been formed as intermediates, which then underwent further breakdown before sufficient amounts could be concentrated in the soil to allow detection.

As radioactive carbon dioxide was evolved from the ^{14}C-ring-labeled dicamba treated heavy clay (Table VI), fission of the aromatic nucleus must have occurred. With the silty clay radioactive carbon dioxide evolution was much more rapid, with 35% of the applied ^{14}C-ring-labeled herbicide being liberated in this form in 7 weeks. Thus, it is also possible that the dicamba or 3,6-dichlorosalicylic acid (or both) could have undergone direct ring fission with subsequent decarboxylation, without the formation of such products as the anisole and phenol.

The total radioactivity recovered and identified at each time interval (Tables V and VI) did not account for all of that applied. Approximately 40% of the applied ^{14}C could not be accounted for from the ^{14}C-carboxyl-labeled herbicide treated soils after 17 weeks (Table V), while a similar amount was nonrecoverable after 7 weeks from the experiments with the ^{14}C-ring-labeled material (Table VI). Little is known regarding this unaccountable radioactivity. Any radioactivity not recovered from the soil must be insoluble in acidic and basic solutions and methanol. Some radioactivity from small carbon fragments could have been incorporated into constituents of soil microorganisms, while a portion of the lost activity may have remained in the acidic solution following ether extraction of the acidified alkaline soil treatments. Some ^{14}C complexing to soil colloids may also have occurred.

The comparative breakdown of ^{14}C-ring-labeled dicamba on moist nonsterile silty clay, heavy clay, and

Table VII. Radioactivity Recovered from ^{14}C-Ring-Labeled Dicamba Treated Soils by Methanol and 1 *N* Sodium Hydroxide following Incubation at 25 ± 1° and Field Capacity

Time, weeks	% of the applied ^{14}C present as[a]								
	Dicamba–methanol extraction			Dicamba–NaOH extraction			3,6-Dichlorosalicylic acid–NaOH extraction		
	SiC	HvC	SL	SiC	HvC	SL	SiC	HvC	SL
1	28	65	35	7	10	7	45	20	19
2	13	20	26	2	2	1	46	33	29
3	3	3	2	1	1	1	32	31	24
5	0	0	0	<1	1	<1	9	27	7
7	0	0	0	<1	<1	<1	7	12	5
9	0	0	0	<1	<1	<1	4	7	3

[a] Average from duplicate experiments.

sandy loam at 25 ± 1° is summarized in Table VII. In the erlenmeyer flasks the breakdown of the herbicide was much more rapid than in the Pramer and Bartha flasks, presumably because of better air circulation through the cotton wool plug. In all three soil types breakdown of the herbicide was rapid and complete in 3 weeks which compares well with previous observations (Smith, 1973a). In the present experiments the dicamba was assayed by direct counting of the methanolic solution following soil extraction. Autoradiograms, following thin-layer chromatographic examination, indicated the absence of any detectable degradation products, only ^{14}C-ring-labeled dicamba being detected.

Insignificant amounts of radioactivity were removed from the air-dried soils (following methanol extraction) by acidic treatment, but basic extraction of such soils recovered considerable ^{14}C from all soils. Using thin-layer chromatographic techniques the presence of [^{14}C]dicamba and 3,6-[^{14}C]dichlorosalicylic acid was confirmed and quantitated. No detectable traces of any other radioactive degradation products were noted. In all three soil types 3,6-dichlorosalicylic acid was formed from dicamba and formation appeared to be greatest in the silty clay (Table VII). After an initial build-up, corresponding to the degradation of dicamba, there was a slow but steady loss of the metabolite (Table VII) with almost complete breakdown occurring within 9 weeks in all three soil types. Following methanolic extraction of all soils, small amounts of dicamba were recovered by alkaline extraction (Table VII) and traces of the herbicide could thus be detected after 9 weeks.

After 9 weeks in moist sterile silty clay, heavy clay, and sandy loam over 90% of the applied radioactivity was recovered by methanolic extraction and confirmed to be [^{14}C]dicamba using thin-layer chromatography. Between 5 and 10% of the applied ^{14}C was further recovered by subsequent alkaline extraction, and this radioactivity was also shown to consist entirely of [^{14}C]dicamba. Thus, no degradation was judged to have occurred in any of the sterile soils.

It was concluded that on the three soil types studied the ^{14}C-ring-labeled dicamba was microbially converted to ^{14}C-ring-labeled 3,6-dichlorosalicylic acid and that this metabolite could then undergo further degradation. This breakdown was slower than that for dicamba. No trace of any other ^{14}C-labeled degradation product was observed in any soil type.

The adsorption of 3,6-dichlorosalicylic acid was evaluated using the Freundlich relationship $\log Y = \log K + (1/n) \log C$, where Y is the amount of solute adsorbed by unit weight of adsorbent, C is the equilibrium solution concentration, and K and n are constants. Graphs of $\log Y$ *vs.* $\log C$ gave straight lines in all cases (Figure 1). The greatest adsorption occurred to the silty clay and the least to the sandy loam, approximately 55% of the chemical being adsorbed by the former at all three concentrations and 30% by the latter soil.

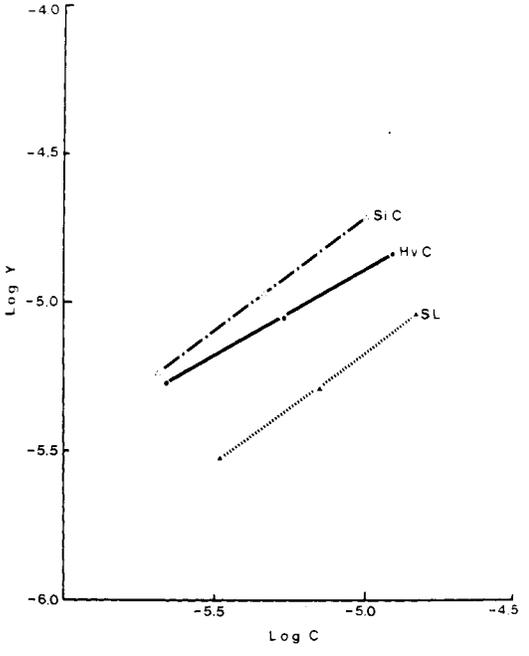

Figure 1. Freundlich isotherms for the adsorption of 3,6-dichlorosalicylic acid from aqueous solutions to a silty clay (SiC), a heavy clay (HvC), and a sandy loam (SL).

Dicamba is known to undergo negligible adsorption to a variety of soils (Burnside and Lavy, 1966) and Grover (1973) has observed that its adsorption to Regina heavy clay is minimal. The 3,6-dichlorosalicylic acid is thus adsorbed to a much greater extent than dicamba, which must explain why it is not extracted from soils by either methanol or aqueous calcium chloride (Smith, 1973b). The soil adsorptive characteristics of 3,6-dichlorosalicylic acid would presumably retard its leaching under field conditions.

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