Residues of Dibromochloropropane in Root Crops Grown in Fumigated Soil

Dibromochloropropane (DBCP) was found in radish and carrot crops after application to soil at a rate of 12.26 lb/acre. Residues were highest in carrots (1.5 ppm) and persisted for 16 weeks when applied at seeding. DBCP dissipated from carrot more rapidly than from soil. Foliage of both crops contained smaller amounts of DBCP than the root. Most (78%) of the DBCP in carrot root was contained in the pulp. Approximately two-thirds of the residue in carrot root was removed by boiling.

1,2-Dibromo-3-chloropropane (DBCP) is a soil fumigant effective in the treatment of nematode infestation of a variety of crops. DBCP has also been found mutagenic in microbial assays (Rosenkranz, 1975) and carcinogenic in rats and mice (Olson et al., 1973). Earlier studies on beans and potatoes harvested 2 to 6 weeks after soil fumigation with DBCP have indicated that inorganic bromide levels were increased but that no organic bromide occurred (Guinn and Potter, 1962). Similar conclusions were reached with oranges (Castro and Schmitt, 1962) and with brussels sprouts and walnuts (Beckman and Bevenue, 1963).

The distribution and movement of DBCP in soil has been studied in detail (Hodges and Lear, 1973, 1974) and residues found to persist 36 weeks after application. Indirect evidence (Wu and Salunkhe, 1971) suggests that DBCP or its metabolites are absorbed by carrot root. Because of the ability of some root crops to absorb organochlorine compounds (Lichtenstein, 1959; Harris and Sans, 1967), the present study was conducted to determine the uptake and persistence of DBCP in radishes and carrots.

EXPERIMENTAL SECTION

1,2-Dibromo-3-chloropropane was obtained from the Fairfield Chemical Co., Blythewood, S.C. and was found to be 97.5% pure when assayed by GLC against a standard labeled as being 100% pure. Solutions for soil treatment were prepared by dissolving the DBCP in absolute ethanol to give a concentration of 383 mg/mL.

Field Study. Field experiments were conducted at the Ottawa Research Station, Agriculture Canada during the summer of 1976. The crops were radish (White Tip variety) and carrot (Danvers Half Long variety) which were grown in rows 30 ft long and 3 ft apart. Untreated control crops were planted at the same time as treated ones and were grown in an area adjacent to the treated soil. Soil was treated with the solution of DBCP by injection of 1 mL at a depth of 7 in. and at intervals of 1 ft using a modified Cornwall Pipettor. The soil received the recommended application rate of the equivalent of 12.26 lb of DBCP/acre by this procedure. Each crop received a single row application of DBCP at time of planting. In a second experiment, a postplant application was made in the same manner as already described to previously untreated soil as soon as the crops began to mature. For the application at planting, the soil temperature at a depth of 7 in. was 15 °C with a moisture content of 20.6%. For the postplant application, the soil temperature was 20 °C for both radish and carrot crops. Soil moisture was 15.7% for radish and 14.2% for carrot.

Sampling. Samples were taken from six different locations in each treatment with the exception of the postplant treatment of carrots which were sampled in four locations. The material was placed in plastic bags and transported to the laboratory where the tops were removed, rinsed with water, and frozen pending analysis. The root portion was washed by scrubbing with a brush under a flow of water, trimmed, and homogenized in a Waring Blendor. Subsamples were frozen in glass jars at −18 °C until analyzed.

Soil samples were taken from the same locations as the plants using a soil auger (Cenco No. 28205). Cores were removed to a 6 in. depth from points 6 in. from the center of the row and equidistant from the injection sites. Samples were placed in glass jars and frozen prior to analysis for DBCP and moisture content.

Analytical Methods. The analytical prodecure for DBCP as described in the literature (Beckman and Bevenue, 1963) was found unsatisfactory when applied to root crops due to background interference, necessitating development of the following method. A sample of crop material (5.0 g) was extracted with absolute ethanol (25 mL) by blending at high speed for 1 min in a Sorvall Omni-Mixer. The homogenate was gravity filtered through Whatman No. 1 paper and an aliquot (10.0 mL) of the filtrate added to 1 M NaCl (40 mL) in a 125-mL separatory funnel. The aqueous phase was extracted with hexane (5.0 mL) and the hexane extract dried over sodium sulfate. An aliquot (4.0 mL) of the dried extract was added to a column (1.5 cm diameter) containing activated Florisil (2.0 g) in hexane. The Florisil had been washed extensively with chloroform and dried at 100 °C prior to activation by heating to 300 °C for 20 h. After adsorption of the extract, the column was washed with hexane (2 mL) and the eluate discarded. The DBCP was recovered from the column by elution with benzene (5 mL). The first milliliter of eluate was discarded and the remaining 4 mL retained for analysis by GLC.

Soil was analyzed for DBCP using the extraction procedure of Hodges and Lear (1973). DBCP in the extracts was analyzed by GLC. Soil moisture was determined by drying at 105 °C for 24 h. The concentration of DBCP in soil is expressed as μg of DBCP/g of dry soil.

Gas–liquid chromatography was performed on a Hewlett-Packard 5700A fitted with a ^{63}Ni electron-capture detector and a 6 ft × 4 mm i.d. glass column. The column was packed with 6% QF-1 and 4% SE-30 on 80–100 mesh Supelcoport and was run at 120 °C at a flow rate of 43 mL/min of argon:methane (95:5) carrier gas. The injection port was maintained at 150 °C and the detector at 300 °C. At routine working attenuation, the injection of 0.3 ng of DBCP produced a 50% full-scale response. Samples were quantitated by comparison of the peak height to that of a standard.

Recoveries of DBCP added to radish samples at levels from 0.005 to 0.500 ppm averaged 86% with a standard error of 1.1 as shown by the data in Table I. The corresponding value for carrot was 88 ± 1.3%. With both crops the minimum detectable limit, defined as twice background was 0.002 ppm. For soil, a mean recovery of 87 ± 2.1% was found for DBCP added at levels of 0.01 to 5.0 ppm.

RESULTS AND DISCUSSION

Both radish and carrot absorbed DBCP as shown by the data in Tables II to V. With radish after treatment at seeding (Table II), the initial amount of residue in the root

Table I. Recovery of DBCP Added to Radish, Carrot, and Soil

DBCP added, ppm	DBCP recovered, %		
	Radish	Carrot	Soil
0.005	88	87	
0.010	83	89	77
0.100	89	86	95
0.500	84	92	91
1.00			86
5.00			89

Table II. Residues of DBCP in Radishes and Soil after Treatment at Seeding

Time after treatment, weeks	DBCP found, ppm ± SE[a]		
	Root	Top	Soil
4	0.159 ± 0.010	0.073 ± 0.015	0.187 ± 0.116
5	0.194 ± 0.010	0.029 ± 0.003	0.544 ± 0.236
6	0.081 ± 0.007	0.044 ± 0.007	0.099 ± 0.012
7	0.119 ± 0.012	0.031 ± 0.004	0.080 ± 0.023

[a] Values are the mean of determinations on six samples. Soil data are expressed as ppm dry weight. Control samples showed no detectable residues at all sampling times.

Table III. Residues of DBCP in Radishes and Soil after Postplant Application

Time after treatment	DBCP found, ppm ± SE[a]		
	Root	Top	Soil
1 day	0.024 ± 0.012	0.003 ± 0	0
1 week	0.045 ± 0.023	0.006 ± 0.001	0.009 ± 0.005
2 weeks	0.056 ± 0.005	0.037 ± 0.009	0.024 ± 0.012
3 weeks	0.167 ± 0.044	0.020 ± 0.003	0.037 ± 0.022

[a] Values are the mean of determinations on six samples. Soil data are expressed as ppm dry weight. Control samples showed no detectable residues.

Table IV. Residues of DBCP in Carrots and Soil after Treatment at Seeding

Time after treatment, weeks	DBCP found, ppm ± SE[a]		
	Root	Top	Soil
7	0.159 ± 0.001	0.201 ± 0.001	0.111 ± 0.007
8	1.13 ± 0.051	0.406 ± 0.023	0.917 ± 0.060
9	0.775 ± 0.015	0.231 ± 0.012	1.26 ± 0.284
10	0.286 ± 0.009	0.051 ± 0.001	1.61 ± 0.357
11	0.224 ± 0.010	0.052 ± 0.001	0.264 ± 0.062
12	0.103 ± 0.005	0.037 ± 0	0.373 ± 0.068
13	0.067 ± 0.003	0.034 ± 0.002	0.241 ± 0.021
14	0.033 ± 0.002	0.030 ± 0	0.267 ± 0.022
15	0.024 ± 0	0.010 ± 0	0.514 ± 0.031
16	0.019 ± 0.001	0.009 ± 0	0.250 ± 0.006

[a] Values are the mean of determinations on six samples and are uncorrected except for those in soil which are expressed as ppm dry weight. Values for control samples were 0.002 ± 0.001 ppm in the root, 0.003 ± 0.001 ppm in the top, and 0 in soil.

was less than that in soil, while with carrot (Table IV), the initial concentration in the root exceeded that in soil. A marked ability of carrots to absorb soil residues has been noted with other compounds such as DDT and lindane (Lichtenstein, 1959), aldrin (Harris and Sans, 1967), and heptachlor (Lichtenstein et al., 1965). The decrease of residues from carrot was greater than that from soil and did not correspond to the increase in plant weight due to growth, suggesting metabolism of DBCP by the plant.

The foliage of both crops contained residues of DBCP which were generally lower than those in the root or soil. It remains to be determined whether this residue results from translocation or absorption of vapor from the soil. Contamination from soil dust as suggested for chlorinated biphenyls (Iwata and Gunther, 1976) appears unlikely due to the relatively large amounts present.

Table V. Residues of DBCP in Carrots and Soil after Postplant Application

Time after treatment, weeks	DBCP found, ppm ± SE[a]		
	Root	Top	Soil
1	0.227 ± 0.037	0.556 ± 0.182	0.032 ± 0.008
2	1.01 ± 0.007	0.494 ± 0.016	0.207 ± 0.31
3	1.50 ± 0.047	0.166 ± 0.006	1.64 ± 0.423
4	0.633 ± 0.046	0.188 ± 0.016	0.686 ± 0.369
5	0.874 ± 0.063	0.620 ± 0.022	1.38 ± 0.156
6	0.358 ± 0.012	0.162 ± 0.010	0.774 ± 0.197
7	0.485 ± 0.035	0.163 ± 0.012	0.973 ± 0.092
8	0.335 ± 0.012	0.094 ± 0.006	1.07 ± 0.020
9	0.095 ± 0.004	0.039 ± 0.001	0.961 ± 0.034

[a] Values are the mean of determinations on four samples and are uncorrected except for those in soil which are expressed as ppm dry weight. Control data are given in Table IV.

The effects of peeling or cooking on the content of DBCP were examined with samples of carrot taken 9 weeks after treatment at seeding. Peels were found to contain 0.339 ± 0.006 ppm of DBCP while the pulp contained 0.607 ± 0.016 ppm. Thus, in contrast to findings with other organochlorine compounds (Hermanson et al., 1970; Iwata and Gunther, 1976), most of the residue is in the pulp. After boiling the unpeeled carrots in water for 5 min, analysis of the drained product showed a DBCP level of 0.251 ± 0.009 ppm. This reduction by two-thirds on cooking is consistent with the high vapor pressure of DBCP.

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