Dibromochloropropane Residues in Peaches following Fall Orchard Fumigation

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1,2-Dibromo-3-chloropropane (DBCP) residues were measured in peach fruits from trees growing in fall-fumigated or nonfumigated soil. No DBCP residue was detected in peaches from trees growing in nonfumigated soil or in soil fumigated at or below the previously recommended rate of 46.8 L/treated ha. Fruit was harvested between 183 and 217 days after fumigation. An average application rate of 58 L/treated ha resulted in residues of 0.19 ppb of DBCP, while 115 L/treated ha resulted in residues of 0.43 ppb of DBCP. DBCP residue levels were higher in samples collected from the Piedmont area of South Carolina than in samples from either the Sandridge or Coastal area. Possible mode of contamination is discussed.

The presence of ring (*Criconemella xenoplax*) or root-knot (*Meloidogyne* sp.) nematodes or both is important to peach growers in South Carolina because these organisms increase the susceptibility of peach trees to cold injury and certain diseases that cause sudden collapse and death of trees. The entire complex of factors that leads to premature death of peach trees has been given the name "peach tree short life". The importance of nematode control in the prevention of peach tree short life has been described previously (Zehr et al., 1982).

1,2-Dibromo-3-chloropropane (DBCP), the active ingredient in nematicides registered for postplant application in peach orchards, was used until its suspension pending cancellation in Oct 1979. DBCP registrations were voluntarily canceled in March 1981 for all uses except on pineapples in Hawaii. Voluntary cancellation of products containing DBCP was based on the toxic and carcinogenic nature of DBCP and on preliminary findings that DBCP use could result in potential exposure from drinking water, food residues, or occupational exposure (Babich et al., 1981).

Since research in South Carolina had failed to identify an alternative effective postplant nematicide that would reduce losses to peach tree short life (Zehr et al., 1982), research was conducted in 1979–1982 to determine if DBCP use would result in contamination of water and food products. Results of the water contamination study have been reported previously (Carter and Riley, 1981). The purpose of the present study was to determine if DBCP residues were present in peaches harvested from orchards fumigated postharvest the previous autumn.

MATERIALS AND METHODS

Field Plots. Three plots selected in each of the three peach growing areas found in South Carolina ranged in size from 0.16 to 0.28 ha. Soils were sandy loam in the Coastal and Sandridge area and sandy loam over clay in the Piedmont area of South Carolina. Plots were fumigated with Nematocide EM 12.1 containing 1.45 kg of DBCP/L (hereafter referred to simply as DBCP) under EPA experimental use permit no. 5481-EUP-1. DBCP was applied at concentrations that bracketed label rates (28.1–74.8 L/treated ha) and at twice these rates (66.4–148.7 L/treated ha). Application was by shank injection in a 1.04-m band within 1 m of the trunk on each side of the tree row. DBCP was applied between Nov 5 and 11, 1981. Treatments consisted of three adjacent rows of 10 trees each. Peaches were harvested at maturity of the cultivar between May 13 and June 14, 1982 (183–217 days after fumigation). Ten peaches were randomly selected from each of the center two trees of a given treatment and placed in a galvanized steel, ethyl acetate rinsed container used only for that treatment. Four ethyl acetate rinsed, 0.95-L sampling jars were filled with three or four randomly selected peaches from each treatment and capped with ethyl acetate rinsed aluminum foil, seals, and screw rings. Controls were selected from two trees at least four rows from the treated area. Samples were placed on ice immediately after collection.

Extraction Procedure. The procedure used for the extraction of DBCP has been described previously (Carter and Riley, 1982). Two samples were extracted initially and analyzed by gas chromatography. A third sample was extracted and analyzed if the two initial samples gave significantly different results. The fourth sample was stored.

Gas Chromatography. Concentration of DBCP residues in peach samples was determined in a Varian 3700 gas chromatograph connected to a CDS 111 chromatography data system and recorder. The gas chromatograph was equipped with a ^{63}Ni electron capture detector and a 2 m × 2 mm (inner diameter) glass column packed with 10% OV-101 on 80–100-mesh Chromosorb W-HP. The column, injector, and detector temperatures were 90, 260, and 300 °C, respectively. The nitrogen carrier gas flow rate was maintained at 60 mL/min. The retention time for DBCP was 3.5 min under these conditions, and the set detection limit was 0.1 ppb. This detection limit eliminated low-level background residues from being reported (Carter and Riley, 1981). The average recovery percentage was determined to be 77%. Levels of DBCP were calculated by the external standard method, corrected for recovery percentage.

DBCP standards were prepared in redistilled ethyl acetate from a 99.6% analytical standard (AMVAC Chemical Corp.). Standards were kept in a freezer separate from the sample extracts. Caution should be exercised in preparing DBCP standards since DBCP is a potential carcinogen and mutagen (Babich et al., 1981). The gas chromatograph was calibrated with a 5 pg/μL DBCP standard as the first sample each day. Ethyl acetate blanks were run after each sample containing DBCP residue.

The presence of DBCP was confirmed by GLC on a 2 m × 2 mm (inner diameter) glass column packed with 3% OV-210 on 80–100-mesh Chromosorb W-HP with column, injector, and detector temperatures of 75, 270, and 250 °C, respectively. The DBCP retention time was 2.1 min. The nitrogen carrier gas flow rate was 30 mL/min and the set detection limit was 0.1 ppb.

RESULTS AND DISCUSSION

Peaches from trees growing in nonfumigated soil (control) contained no detectable DBCP residue (Table I). An average application rate of 58.0 L/treated ha resulted in

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Table I. DBCP Residues in Peaches Harvested from Orchards Treated with DBCP

location	DBCP treatment, av no. of L/treated ha	no. sites	mean DBCP concn, ppb (3 replicates/site)
Coastal area	control	3	n.d.[a]
	50.5	3	n.d.
	101.0	3	0.27
Sandridge area	control	2[b]	n.d.
	51.4	2	0.13
	102.9	2	0.24
Piedmont area	control	3	n.d.
	69.2	3	0.41
	137.5	3	0.72
overall	control	8	n.d.
	58.0	8	0.19
	115.1	8	0.43

[a] n.d. = none detected. [b] No residue data to report for one site because entire peach crop was destroyed by freeze.

residues of 0.19 ppb of DBCP while an average application rate of 115.1 L/treated ha resulted in residues of 0.43 ppb of DBCP (Table I).

DBCP residues were higher in samples collected from the Piedmont area of South Carolina (Table I) than from samples collected from either the Sandridge or Coastal area. This may have resulted from higher application rates in this area. Additionally, the presence of clay in these soils may have affected adsorption and subsequent uptake and/or volatilization of DBCP. However, this is speculative since factors other than application rates that might affect fruit residue were not examined.

Previous suppositions that DBCP volatilizes and becomes adsorbed onto the developing peach or that contaminated dust settles on the fruit (K. Maddy, personal communication) seem less credible by the appearance of DBCP residues in fruit following a postharvest, fall fumigation treatment. Contamination by uptake, translocation, and accumulation of DBCP in the developing peach appears to ensue. Earlier pilot studies indicated that DBCP residues can be found in the peach pit and conductive tissues of the tree (G. Carter, unpublished experiments).

In individual plots where application rates were 46.8 L/treated ha or less residues of DBCP were not found in the fruit, an observation not reflected by the reporting of average values. This is a key point since 46.8 L/treated ha was the recommended application rate prior to cancellation. Potential for residues in fruit, therefore, would probably not limit the use of an effective concentration of DBCP in peach orchards if other problems, such as the tendency of DBCP to contaminate shallow wells, could be resolved.

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Metabolism of the Herbicide Hoe 33171 in Soybeans

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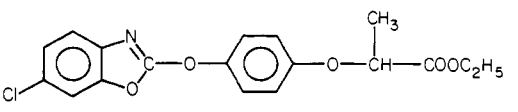
Soybean plants were treated with formulated ^{14}C-labeled Hoe 33171, ethyl 2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propanoate. At the end of a 15-day degradation period 75% of the radioactivity in/on the leaves was characterized as water-soluble metabolites apart from 25% unchanged parent compound present mainly on the leaf surface. The free carboxylic acid of Hoe 33171 (5%) did not accumulate because of rapid conversion to bound residues (30%) and more than 10 polar conjugates, some of which contained the structural elements of hydroxylated (4-hydroxy and 5-hydroxy isomer; 12.8%) and nonhydroxylated 6-chloro-2,3-dihydrobenzoxazol-2-one. The latter is the common structure of 43% of the total residue and is suitable to be quantified in routine residue analysis. For the identification of the hydroxylated metabolites 4-hydroxy-6-chloro-2,3-dihydrobenzoxazol-2-one was synthesized.

The plant protection compound designated Hoe 33171 is a selective herbicide to control a broad spectrum of grass weeds in dicotyledonous crops (Hoechst AG, 1976; Bieringer et al., 1982) and has the structural formula



ethyl 2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]-propanoate

Previously reported results on the mode of action by Köcher et al. (1982) indicate rapid destruction of plant

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