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Residues in Crops Irrigated with Water Containing Trichloroacetic Acid

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Ten field and vegetable and three fruit crops were irrigated with water that contained about 0.1 and 0.5 ppm of trichloroacetic acid (TCA). Grapes were treated at 0.17 and 1.39 ppm. TCA residues were not detected in peaches, sugar beets, wheat, or tomatoes. Minute amounts of TCA (0.01–0.04 ppm) were detected in alfalfa, corn, garden peas, potatoes, and watermelon treated at 0.5 ppm. Slightly higher residues of TCA, ranging from 0.13 to 0.43 ppm, were detected in field-bean pods and seed, and snapbean herbage treated at 0.5 ppm. Apples treated at 0.1 ppm contained 0.19 ppm of residue, and grapes contained 0.03 and 0.20 ppm when treated at lower and higher rates, respectively. Of the two crops that were sprinkler and furrow irrigated with TCA-treated water, the only difference was in pods of furrow-irrigated field-beans, which contained maximum TCA residues of 0.19 ppm, compared to pods of sprinkler-irrigated beans, which contained 0.03 ppm. At harvest, residues had disappeared from most crops, except apples, field-bean pods and seed, garden peas, and grapes, which contained 0.19, 0.19, 0.13, 0.02, and 0.20 ppm of TCA, respectively.

Under favorable moisture conditions, fall applications of the sodium salt of trichloroacetic acid (TCA) effectively retard the growth and reduce the stand of reed canarygrass (*Phalaris arundinacea* L.) on canal banks (Comes, 1970; Bruns, 1973). This grass may develop from above or from below the waterline; consequently, the swath of a TCA treatment may cover an area from 1 to 2 m above to about 1 m below the normal waterline. Because of minimal absorption of TCA by the mature vegetation and the likelihood of limited leaching and degradation of TCA during the winter, the authors were concerned with any significant contamination of the water, and consequently of irrigated crops, which would occur in the spring when water was introduced into the canals. To determine the significance of possible residues from fall applications of TCA on canal banks, Comes *et al.* (1972) monitored the first water used for priming the canals in the spring. During the first hour of flow, the average levels of TCA in the water of six canals were usually in the range of a few ppb up to 100 ppb. In one instance, the average level of TCA during the first hour of water flow was 142 ppb. Less than 1 ppb of TCA was detected in any of these canals 8 hr after water flow had commenced. While these concentrations of TCA found in the water were quite low, the possible uptake of residues by the crops was of concern. A study was initiated to determine the amount of TCA that might be taken up by crops from irrigation water and to evaluate the potential for damage.

METHODS AND MATERIALS

Field-Scale Treatments. The water in eight small laterals or head ditches was treated with the sodium salt of TCA to provide about 0.1 and 0.5 ppm of TCA. These treatments simulate 1 and 5 times the maximum concentration of this herbicide usually found in water turned into canals in the spring after an autumn ditchbank treatment with TCA at 82 kg/ha. The duration of each treatment was about 2 hr. Duplicate water samples were taken for analysis every 20 min, after the water and TCA had been uniformly mixed, usually at the farm turnout just before the treated water reached the crop land. The treated water was applied to ten field and vegetable crops on several farm units of the Columbia Basin during the 1971 growing season. In 1972, three fruit crops were similarly treated.

Normal irrigation flows preceded and continued after the application of TCA-treated water. Alfalfa was sprinkler irrigated; all other crops were furrow irrigated. Stages of crop maturity at the time of treatment were as follows: potato, blooming; alfalfa, blooming and about ready for cutting; garden peas, fully developed pods; snap beans, blooming stage, with a few immature pods; wheat, early heading; watermelon, vining; sugar beets, 3-cm diameter roots; and corn, about 46 cm high. The treatments were made to apples, grapes, and peaches during the early stage of fruit development.

Triplicate samples of the field and vegetable crops were collected 6–8 days after treatment and at harvest. Fruit crops were sampled only at harvest. An untreated control sample for each crop was collected on dates corresponding to those of early and late harvests. The crops collected are

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Table I. Crop Samples Collected for TCA Residue Analysis

Crop	Commodity group	Days after treatment
Crops Grown on a Field Scale		
Potato	Root-crop vegetable	8, 78
Alfalfa	Forage legume	6, 65
Garden pea	Seed and pod vegetable	8
Garden pea, dry	Stored commodity	28
Snap-bean herbage	Forage legume	7
Snap-bean seed	Stored commodity	45
Wheat straw	Forage grass	8
Wheat grain	Grain crop	37
Watermelon vine	Not classified	7
Watermelon	Cucurbit	54
Sugar beet	Root-crop vegetable	97
Sugar beet top	Leafy vegetable	8
Corn plant	Forage grass	7
Corn grain	Grain crop	114
Apple	Pome fruit	130
Grape	Small fruit	100
Peach	Stone fruit	70
Crops Grown on Experimental Plots		
Tomato	Fruiting vegetable	14, 63
Field-bean pod	Seed and pod vegetable	2–7
Field-bean seed	Stored commodity	56

shown in Table I. The crops represent groupings published for the establishment of tolerances of pesticide chemicals in raw agricultural commodities (U. S. Department of Health, Education, and Welfare, 1967).

Soil cores were collected 6–8 days after treatment from the surface 15-cm layer of soil wetted by the treated water during the 1971 season. Several subsamples were composited, and replicate composites were obtained for each treatment level. Untreated soils were collected in the same manner.

Experimental Plot Treatments. In 1972, TCA was applied at 0, 0.1, and 0.5 ppm in irrigations of 1.7 cm of water to field beans and tomatoes. Immediately afterward, 5.9 cm of untreated water was added to each plot (total of 7.6 cm). The plots were 3.0 m wide and 4.6 m long. The treatments were made in triplicate by furrow and sprinkler irrigation as previously described (Bruns *et al.*, 1964, 1975). Each furrow and sprinkler irrigation treatment was made in 2 and 12 hr, respectively.

For residue analyses, bean pods were collected 2 and 7 days after the sprinkler and furrow irrigation treatments, respectively, and mature seeds were collected 8 weeks after treatment. Tomatoes were collected as green fruit 2 weeks after the treatments and as ripe fruit 9 weeks after treatment.

Analytical Procedures. The analysis for TCA in water used the same procedure as that developed for 2,2-dichloropropionic acid (dalapon) and was sensitive to less than 1 ppb of TCA (Frank and Demint, 1969) in 1 l. of water. Water samples were acidified and extracted with ether; then they were partitioned into buffer and back to ether and analyzed by electron-capture gas chromatography. Recoveries of TCA from fortified water averaged 87%. Soil samples were slurried with water and acidified to a pH of 0.9 with hydrochloric acid. The slurries were shaken for 1 hr, and the acid extracts were then analyzed by a procedure similar to the water analysis. Recoveries of TCA from fortified control soils were 86 and 77% at the 0.1- and 0.05-ppm levels, respectively. All water and soil analyses were corrected for recovery.

The analytical method used for TCA in crops was based on a procedure developed for TCA in wheat grain (Chiba and Morley, 1966). The method was subsequently modified for the determination of TCA in sugar beets and various by-products of the beet-sugar industry (Hanzas, 1971). The modifications of Hanzas consisted of the use of an electron-capture detector instead of a microcoulometric detector, and toluene in lieu of xylene as the chloroform collection solvent. The procedure consisted of a digestion of the crop with 0.005 N H_2SO_4, which converted the TCA present into chloroform. The chloroform was distilled and swept into a toluene trap by a stream of nitrogen. The chloroform was then quantitated by a gas chromatograph with an electron-capture detector.

Table II. Chromatographic Columns and Conditions Used for TCA Residue Analysis in Crops

Parameter	Col. 1, 1971 crops	Col. 2, 1972 crops
Stationary phase	20% QF-1	30% DC 200
Support	Chromosorb W-AW	Gas-Chrom Q
Mesh	60–80	60–80
Column	8 ft × 1/8 in. stainless steel	6 ft × 1/8 in. stainless steel
Oven	85°	70°
Inlet	115°	115°
Detector	115°	115°
Carrier-gas flow	20 ml/min	35 ml/min
Retention time	2 min	2.25 min

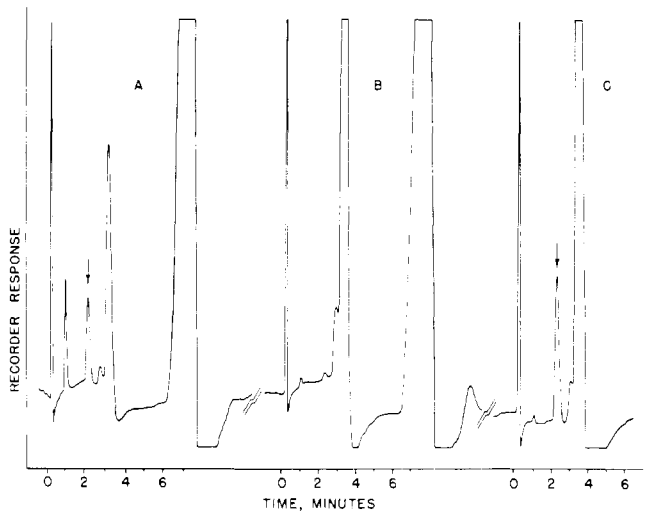

Figure 1. Gas chromatograpic spectra: (A) chloroform standard, 0.02 ng of chloroform (equivalent to 0.0274 ng of TCA); (B) untreated peach; (C) untreated peach fortified with 0.1 ppm of TCA (distillate diluted twofold before analysis).

The two columns and sets of instrument-operating conditions used in the analysis of crops for TCA are shown in Table II. The second column was superior in separating chloroform from carbon tetrachloride and other interfering gases, which were present occasionally in the atmosphere. Typical chromatograms for the analysis of TCA in peaches are shown in Figure 1. Chromatogram A is the chloroform standard. The major peaks shown, from left to right, are the air peak, a peak from freon gas in the room atmosphere, the chloroform peak, a carbon tetrachloride peak, and toluene shown as a broad band. Sensitivity of the procedure was 0.01 ppm of TCA when 10-g samples of the crops were analyzed. Recoveries of TCA from a series of 12 crop controls, fortified with TCA at levels from 0.05 to 1.0 ppm, are shown in Table III. Recoveries ranged from a low of 77% for corn plants to a high of 106% for potatoes, with an average of 94% for all crops. All crop data were corrected for recovery.

Table III. Recovery of TCA from Fortified Crops

Crop	Level added, ppm	Recovery, %
Potato	1.0	99
Potato	0.5	106
Potato	0.1	104
Snap-bean seed	0.1	84
Snap-bean plant	0.5	84
Alfalfa	0.1	90
Garden pea (dry)	0.1	96
Watermelon	0.05	85
Watermelon vine	0.05	86
Sugar beet	0.05	92
Corn plant	0.05	77
Corn grain	0.1	92
Wheat grain	0.1	97
Tomato	0.1	100
Apple	0.2	101
Grape	0.2	101
Peach	0.1	102
Av recovery from all crops		94

Table IV. Concentration (ppm) of TCA Found in Water Applied to Crops

Crops	Rates applied	
	0.1 ppm	0.5 ppm
Potatoes, sugar beets, garden peas, and wheat	0.11[a]	0.37
Alfalfa	0.10	0.30
Beans	0.09	0.50
Corn	0.09	0.47
Watermelon	0.09	0.66
Peaches	0.06	0.49
Apples	0.08	0.46
Grapes	0.17	1.39

[a] Average of two chromatograms and the mean of triplicate samples.

RESULTS AND DISCUSSION

Irrigation Water. The TCA concentrations found in water samples taken from the treated laterals or head ditches are shown in Table IV. In general, the TCA concentrations found in the water were within the desired range, except for those in water used for irrigation of grapes. These were considerably higher than desired and probably resulted from a miscalculation of the volume of water flow. TCA concentrations in the irrigation water applied to experimental plots were assumed accurate, because TCA solutions were carefully formulated in the laboratory and diluted in calibrated tanks with thorough mixing.

Field-Scale Treatments. The residues found in field and vegetable crops after irrigation with water containing TCA are shown in Table V. Average TCA residues of 0.01 ppm were found in potatoes collected 8 days after the 0.5-ppm treatment; however, TCA was not detected in potatoes harvested 78 days after treatment. In the alfalfa samples collected 6 days after sprinkler irrigation treatment, 0.01 and 0.04 ppm of TCA were found at the lower and higher rates, respectively. At 65 days after treatment of the alfalfa, residues of TCA were not detected. Average values of 0.01 ppm of TCA were found at both treatment rates in fresh garden peas collected 8 days after treatment. An apparent increase was noted in the mature seeds at the 0.5-ppm rate and may have been caused by a reduction in moisture content. Whole snap bean plants (minus the roots), collected 7 days after treatment, showed 0.4 ppm of TCA at the higher treatment rate; however, TCA was not detected in the harvested dry bean seeds. A slight uptake of TCA was noted in corn fodder collected 7 days after treatment at the higher rate. Residues were not detected in the harvested kernels. No measurable residues were found in sugar beet foliage or roots. Beet tops are known to take up TCA (Hanzas, 1971) when treated at normal rates of 7–10 kg/ha of TCA (13–20 ppm in 0.3 ha-cm of water). The 0.5 ppm (0.28 kg/ha) of TCA in irrigation water no doubt resulted in concentrations that were considerably below the level of detection. Watermelon vines contained 0.04 ppm of TCA at the higher treatment rate, but residues were not detected in edible portions of melon. No measurable residues were detected in immature (dough stage) or mature grain.

Residues of TCA found in fruit after irrigation with water containing TCA are shown in Table VI. Residues were not detected in peaches at any treatment level. Apples and grapes contained artifactual or background levels equivalent to 0.03 ppm of TCA. Grapes from the area treated at the highest level (above 3× the intended treatment of 0.5 ppm) contained 0.2 ppm of TCA residue. A similar level of TCA was found in apples at both treatment rates.

Experimental Plot Treatments. An apparent background level of 0.01 ppm of TCA was found in bean samples from the untreated experimental plots (Table VII). Green pods collected 7 days after the furrow irrigation treatments contained higher concentrations of TCA than

Table V. TCA Residues (ppm) in Field and Vegetable Crops after Irrigation with Water Treated with the Sodium Salt of TCA

Treatment rate, ppm	Potatoes	Alfalfa	Garden peas		Snap beans		Corn		Sugar beets		Watermelon		Wheat	
			Green	Mature seed	Green herbage	Mature seed	Green fodder	Mature kernels	Tops	Roots	Green vines	Mature fruit	Immature grain	Mature grain
6–8 Days after Treatment														
0	<0.01[a]	<0.01	<0.01		<0.01		<0.01		<0.01		<0.01		<0.01	
0.1	<0.01	0.01	0.01		0.02		<0.01		<0.01		<0.01		<0.01	
0.5	0.01	0.04	0.01		0.43		0.01		<0.01		0.04		<0.01	
At Harvest														
0	<0.01	<0.01		0.01		<0.01		<0.01		<0.01		<0.01		<0.01
0.1	<0.01	<0.01		<0.01		<0.01		<0.01		<0.01		<0.01		<0.01
0.5	<0.01	<0.01		0.02		<0.01		<0.01		<0.01		<0.01		<0.01

[a] Average of two chromatograms and the mean of triplicate samples.

Table VI. TCA Residues in Field-Grown Fruit after Irrigation with Water Treated with the Sodium Salt of TCA

Treatment rate, ppm	Peaches, ppm	Grapes, ppm	Apples, ppm
	At Harvest		
0.0	<0.01[a]	0.03	0.03
0.1	<0.01	0.03[b]	0.19
0.5	<0.01	0.20[b]	0.16

[a] Average of two chromatograms and triplicate samples. [b] Concentration of TCA found in the irrigation water applied to grapes was 0.17 and 1.4 ppm.

Table VII. TCA Residues (ppm) in Experimental Plot Grown Crops after Irrigation with Water Treated with the Sodium Salt of TCA

	Field beans		Tomatoes	
Treatment rate, ppm	Green pods	Mature seed	Green fruit	Ripe fruit
	Furrow Irrigation Treatments			
0.0	0.01[a]	0.01	<0.01	<0.01
0.1	0.04	0.06	<0.01	<0.01
0.5	0.19	0.13	<0.01	<0.01
	Sprinkler Irrigation Treatments			
0.0	0.01	0.01	<0.01	<0.01
0.1	0.02	0.03	<0.01	<0.01
0.5	0.03	0.12	<0.01	<0.01

[a] Average of duplicate chromatograms and mean of three replications.

those collected 2 days after the sprinkler irrigation treatments. This would be expected because plants take up TCA primarily through the roots (Crafts, 1961), and TCA would be carried into the root zone more readily by furrow irrigation than by sprinkler irrigation. Eight weeks after the treatments, the concentrations in the mature beans from comparable furrow and sprinkler irrigated plots were approaching equivalence. Sprinkler irrigations with untreated water, which followed treatments, undoubtedly carried the herbicide further into the soil where it could be picked up by the roots. Tomatoes, both green and mature, contained less than 0.01 ppm of residue at both treatment rates.

Soil Residues. A background of apparent TCA was present in some, but not all, of the soil control samples. The soils in which potatoes and watermelons were grown contained 0.03 (Shano silt loam) and 0.01 ppm (Timmerman sandy loam) of TCA, respectively. There appeared to be no correlation between the amount of TCA found in the soils and the amount of TCA taken up by the corresponding crops.

Crop Injury. No visible symptoms of injury were observed in any of the crops irrigated with water containing TCA at either 0.1 or 0.5 ppm. Wheat is known to be sensitive to TCA (Crafts, 1961), but no damage was noted at the 0.5-ppm level in irrigation water.

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