

Removal of DDT and Related Chlorinated Hydrocarbon Residues from Alfalfa Hay

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Oven heat removed approximately 34% of the residues of DDT and related chlorinated hydrocarbon insecticides from alfalfa feeds containing 16.5% moisture. When the samples were saturated with water, removal increased to 86%, while more than 50% of initial DDT residues on alfalfa green

chop were removed by commercial dehydration processes. The same residues were removed almost completely by the vapors of various common solvents (water, 86%; isopropyl alcohol, 93%; benzene, 97%; and pentane, 73%).

Many commercial feeds contain residues of DDT and related chlorinated hydrocarbon insecticides (DDT-RCH) in the low parts-per-million range. Pesticides pass rapidly from feeds into milk, eggs, and other animal products and, once established, cannot be eliminated immediately simply by withdrawing the contaminated feed. Various workers have demonstrated the uptake of DDT and other chlorinated hydrocarbon pesticides from feed by dairy animals and the subsequent appearance of the pesticides in the milk fat (Brown *et al.*, 1966; Crosby *et al.*, 1967; Laben *et al.*, 1966 a, b; Williams *et al.*, 1964). Archer and Crosby (1967) reported the characteristics of the extraction, nature, and location of DDT-RCH residues in alfalfa hay. The effect of dehydration upon residues in alfalfa of aldrin, chlordan, parathion, toxaphene (Stansbury and Dahm, 1951), and malathion (Rai *et al.*, 1957) has been discussed.

The purpose of the present work was to find means by which DDT-RCH residues on common alfalfa feeds might intentionally be removed or detoxified. Such methods, where economical, would improve both the value of the feed as a marketable commodity and the potential marketability of animal products containing residues from this source; they would be of particular value in instances of accidental overapplication or drift contamination. The observations that DDT is relatively volatile, especially in the presence of water (Bowman *et al.*, 1959) and remains near the plant surfaces in alfalfa (Archer and Crosby, 1967), might provide the basis for effective practical removal of its residues.

METHODS AND MATERIALS

Detection and Determination of Pesticides. Thin-layer chromatography (TLC) and gas-liquid chromatog-

raphy (GLC) procedures were employed routinely, either separately or in combination. The GLC method of Crosby and Archer (1966) was used, except that a 6-foot \times $\frac{1}{8}$ -inch stainless steel column packed with 10% DC-200 silicone grease on 100- to 200-mesh Gas Chrom Q was used occasionally instead of the one specified. Samples were analyzed both with and without alkaline dehydrohalogenation, and the results are reported on a dry-weight basis. Recovery was essentially quantitative.

Thin-layer chromatography was employed for screening and, in combination with GLC, as an analytical tool. Silica gel H absorbent, pentane solvent, and the silver nitrate-2-phenoxyethanol color test (Mitchell, 1958) were preferred. For quantitative work, chromatogram areas containing the unknowns were extracted from the silica gel with benzene or pentane after comparing R_f values (0.41, DDE; 0.26, DDT; 0.14, DDD) with those of parallel standard pesticide tracers, and the extracts were analyzed by GLC.

Hay Samples. Hay samples were obtained from fields in Yolo County, Calif. The fields had not received intentional treatment with pesticides during the previous season, so the existing residues represent accidental contamination. Sampling and extraction methods were described by Archer and Crosby (1967). Moisture content was determined at the time of treatment (immediately after harvest in the case of fresh alfalfa); field-cured hay contained 16.5%, air-dried green-chop 9.5%, commercially dehydrated hay 5%, and alfalfa pellets 5.8% moisture. Chopped, mixed, composited hay samples were subsampled for use in the various experiments.

Vapor Treatments. Vapor treatments of hay were performed in the apparatus shown in Figure 1. The vapors were generated in the 3-liter boiler and passed from the spreader through hay packed in the treatment column, and the condensed vapors were collected in 500-ml. fractions in the cold trap. Subsamples of hay (100 grams) were washed with vapor from 2 liters of solvent, condensation in the lines and treatment column

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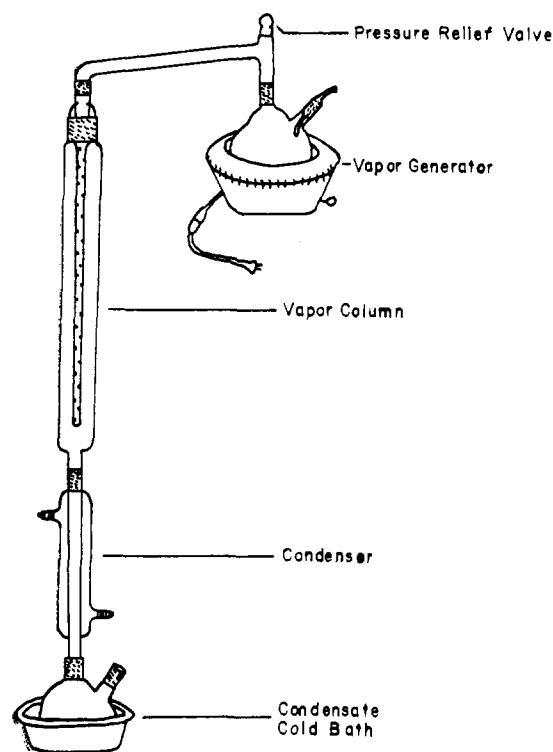


Figure 1. Apparatus for vapor-washing alfalfa hay with aqueous and organic solvents

being minimized by glass wool and aluminum foil insulation.

Dehydration. Alfalfa was dehydrated rapidly at inlet temperatures of 760° to 1000° C. and an outlet temperature of 127° C. for 3 to 5 minutes in a revolving drum-type dehydrator. Two to 3 tons of green alfalfa per hour were dehydrated under these conditions. Four types of samples were analyzed: green-chop containing 84% moisture; green-chop air-dried at room temperature for 5 days in a hood (10% moisture); commercially dehydrated hay obtained from the green-chop (5% moisture); and pelleted hay obtained from the same green-chop (6% moisture). The green-chop represented composited samplings of several acres of harvested alfalfa. Each dehydrated sample was extracted serially by two 1-hour treatments with each of benzene, acetonitrile, acetone, and ethanol to assure maximum recovery. The extracted plant solids were refluxed with ethanolic potassium hydroxide and analyzed to determine if any residue remained in them.

RESULTS AND DISCUSSION

Oven Heat. The effect of oven heat at 100° C. for 12 hours on residues in ordinary, field-cured hay is shown in Table I. At the highest residue levels (0.56 p.p.m. and 16.5% moisture), oven heating resulted in only 34% loss; when the residues were lower and the hay moisture was 5 to 6%, no residue loss could be detected. Fresh green-chop which contained approximately 84% moisture (but was not saturated with excess water) lost 57% of its residues on oven heating, while low-moisture samples—air-dried green-chop, commercially dehydrated alfalfa, and alfalfa pellets—exhibited no significant residue loss

Table I. Effect of Oven Heat on DDT-RCH Residues in Alfalfa Hay

Sample No.	Initial Residue, P.P.B.	Oven-Heated ^a Residue, P.P.B.	% Loss
1	560	370	34
2	153	153 ^b	0
3	16	66 ^b	0
4	42	62 ^b	0
5	81	81 ^b	0

^a 12 hours at 100° C.

^b Difference between data for room temperature and oven heating not statistically significant.

Table II. Effect of Oven Heat on DDT-RCH Residues in Fresh and Dried Alfalfa Feeds

Feed	Moisture, %	Initial Residue ^a , P.P.B.	Oven-Heated ^{a,b} Residue, P.P.B.	Residue Loss, %
Green-chop	84	99	43	57
Air-dried	10	53	52	0
Dehydrated	5	44	55	0
Dehydrated pellets	6	47	53	0

^a Average of five replicates.

^b 12 hours at 100° C.

on oven heating (Table II). Apparently residue loss was related to moisture content.

Five replicate subsamples of hay (Table III) were analyzed for DDT, DDD, and DDE as individual residues and the total was checked by dehydrohalogenation. The mean residue was 434 ± 67 p.p.b. Five replicate subsamples of similar hay were soaked in excess distilled water until the hay was thoroughly saturated, water was added to cover the plant material, and the samples were heated at 100° C. for 12 hours in an oven, during which the water evaporated. The mean residue value obtained after analysis with and without dehydrohalogenation was 61 ± 12 p.p.b., indicating an 86% loss of residue. Three successive treatments, identical with the first, did not further reduce the residue level in these samples. The presence of excess moisture in the sample was essential for the effective removal of DDT and DDD residues by dry heat sources at temperatures of 100° C. or less, but DDE levels were little affected by such treatment.

Vapor Washing. The dependence of residue loss on the presence of an excess of water vapor suggested that some practical form of "steam distillation" with water or even organic solvents might facilitate pesticide removal. Table IV describes the results of an experiment in which alfalfa hay contaminated with DDT-RCH was treated by vapor washing with four solvents: pentane, benzene, isopropyl alcohol, and water. No liquid solvent was observed in the insulated treatment chamber. The loss of residue due to the vapor treatments with pentane was 73%; benzene, 97%; isopropyl alcohol, 93%; and water, 86%. The sum of the residues in the vapor-treated plant material and those in the condensates for each organic

Table III. Effect of Oven Heating on Residues of DDT, DDD, and DDE in Alfalfa Hay

Treatment	Mean ^a Residue, P.P.B.		% Deviation		% Residue Lost
Initial sample (16.5% moisture)					
DDT	387 ± 77		20		...
DDE	34 ± 3		9		...
DDD	9 ± 3		33		...
Total		430 ± 85		20	...
DDT-RCH (by dehydrohalogenation)		438 ± 23		5	...
Mean of totals		434 ± 67		15	...
Oven-heated ^b (water-saturated)					
DDT	24 ± 8		32		...
DDE	31 ± 6		19		...
DDD	3 ± 1		33		...
Total		58 ± 13		24	86
DDT-RCH (by dehydrohalogenation)		64 ± 12		18	86
Mean of totals		61 ± 12		20	86

^a Five replicates.
^b 12 hours at 100° C.

Table IV. Removal of DDT-RCH Residues from Alfalfa Hay by Solvent Vapor Washes

Sample	Mean Residue, P.P.B.			
	Pen- tane	Ben- zene	Iso- propyl alcohol	Water
Alfalfa hay				
Before treatment	560	560	560	560
Vapor-washed	153	16	42	81
Loss of residue, %	73	97	93	86
Condensates				
1	217	376	247	17
2	134	65	143	9
3	51	52	55	5
4	25	22	33	...
Total condensate residue	427	515	478	31
Total residue recovered	580	531	520	112
Recovery, %	103	95	93	20

solvent were essentially equal to the residues on the starting material. The condensate from the water vapor which had passed through the hay was analyzed, but very little pesticide was found. Other workers (Bowman *et al.*, 1959) have found that DDT very readily codistills with water, and loss from the receiver despite its low temperature may account for the poor recovery of DDT in the water-vapor experiments.

The individual residue losses of DDT, DDE, and DDD and their total recovery in each solvent treatment of another sample of hay are shown in Table V. The quantitative determination of the residues was accomplished by a combination of thin-layer and gas-liquid chromatography; the samples were not dehydrohalogenated before analysis. The steam condensate fractions could not be analyzed by these techniques, as the amounts of pesticides present were too low to be recovered from TLC plates. The residue removal was very satisfactory and represented a loss of 96% in the case of steam. However, recoveries declined with increasing polarity of solvent as expected. DDE totals were very high, indicating that

some dehydrohalogenation of DDT had occurred during vapor treatment.

The total DDT-RCH residues from the vapor-treatment experiments were measured by three separate analytical techniques: GLC without dehydrohalogenation, the same technique in combination with thin-layer chromatography, and GLC with prior dehydrohalogenation. The data were subjected to statistical analysis by the Student's *t*-test, and results from the three methods agreed closely at the 0.05 level of significance, as seen from the standard deviations and per cent deviations of the mean values. The water condensate values were not statistically analyzed because of the very low recoveries mentioned above.

Commercial Dehydration. In cooperation with a commercial dehydrator company, laboratory and commercial samples were compared with respect to DDT-RCH residue loss from alfalfa green-chop during dehydration. As shown in Table VI, green-chop which initially contained 213 p.p.b. of DDT-RCH underwent approximately a 50% loss of residue when dehydrated commercially. The residue values, expressed as mean parts per billion in the air dried, dehydrated, and pelleted samples in comparison with the mean parts per billion values in the green-chop, all showed a significant loss due to dehydration as statistically analyzed with a level of significance of 0.01.

Green alfalfa will lose DDT residues if dehydrated under the commercial conditions investigated, apparently because of codistillation of the insecticide with water vapor. These observations provide a practical basis for the intentional removal of DDT-RCH residues from alfalfa hay which accidentally might be exposed to drift. If the level of pesticide contaminants was in the 1- to 2-p.p.m. range, the alfalfa could be dehydrated with the probable loss of sufficient residue to permit the product to be within the existing 0.5-p.p.m. DDT tolerance. Saturation with a small increment of water immediately prior to dehydration could be expected to result in even more effective removal. The excellent feed quality of dehydrated alfalfa has been amply demonstrated, and the product could provide a form in which a pesticide-contaminated crop could be salvaged economically.

Table V. Effect of Vapor Treatment on Residues of DDT, DDD, and DDE in Alfalfa Hay

Sample	Pentane			Benzene			Isopropyl Alcohol			Water		
	DDT	DDE	DDD	DDT	DDE	DDD	DDT	DDE	DDD	DDT	DDE	DDD
Residue, P.P.B.												
Alfalfa hay												
Before treatment	469	51	57	469	51	57	469	51	57	469	51	57
Vapor washed	137	23	N ^a	25	2	N	66	1	7	18	18	6
Loss of residue, %	71	55	100	95	96	100	86	98	88	96	65	90
Condensates												
Fraction 1	161	3	12	291	126	16	148	4	27
Fraction 2	77	54	N	65	53	2	92	6	32
Fraction 3	43	8	12	32	17	2
Fraction 4	49	5	N	13	16	4
Total condensate residue	330	70	24	401	212	24	240	10	59
Total residue recovered	467	93	24	426	214	24	306	11	66	18	18	6
Recovery, %	100	182	42	91	420	42	65	28	116	4	35	11

^a N = no detectable residue.

Table VI. Effect of Commercial Dehydration on DDT-RCH Residues in Alfalfa Feeds

Sample Treatment	Green Chop Alfalfa ^a	Laboratory-Dried Alfalfa	Dehydrated Alfalfa	Dehydrated Pellets
Benzene				
First extraction	65	44	47	53
Second extraction	17	12	14	11
Total	82	56	61	64
Acetonitrile				
First extraction	41	7	7	15
Second extraction	14	6	5	15
Total	55	13	12	30
Acetone				
First extraction	11	4	2	4
Second extraction	38	2	2	1
Total	49	6	4	5
Ethanol				
First extraction	11	8	4	6
Second extraction	7	6	6	1
Total	18	14	10	7
KOH extract				
Total	9	9	10	6
Grand total	213	98	97	112
Residue loss by dehydration, %	...	55	55	48
Standard deviation	±0	±5	±1	±10
Per cent deviation	0%	6%	1%	9%

^a 84% moisture, undehydrated starting material.

Admittedly, the use of organic solvents for residue removal might carry with it inherent complications of solvent recovery, expense, fire hazard, but not necessarily solvent residue, and possible loss of feed value due to loss of fat-soluble nutrients. However, the effectiveness of the well-known and widely accepted commercial dehydration, especially if a prior water spray were added, makes practical consideration of organic solvent extraction unwarranted for the removal of DDT residues. Water vapor treatment of contaminated hay with steam prior to dehydration may have some practical applications.

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