Removal of 2,4-Dichlorophenoxyacetic Acid (2,4-D) Formulations from Noncombustible Pesticide Containers

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Retained pesticides in discarded used containers can be a serious environmental pollution problem. If 1, 5, 30 and 55 gal[1] metal pesticide drums are defined as noncombustible packaging materials, then the large number of these containers that accumulate yearly entail special disposal considerations.

Published reports have discussed the decontamination of organophosphorus insecticides on and around aircraft and spray equipment (WOLVERTON et al. 1970); edaphic aspects of the disposal of unused pesticides, pesticide wastes, and pesticide containers (STOJANOVIC et al. 1972); chemical and thermal aspects of pesticide disposal (KENNEDY et al. 1972); engineering aspects of the disposal of unused pesticides, pesticides wastes, and pesticide containers (SHUMAN et al. 1972); and decontamination of noncombustible agricultural pesticide containers (HSIEH et al. 1972 and ARCHER and HSIEH 1973).

The previous investigations, particularly in regard to detoxication of metal drums, were directed toward organophosphorus insecticides. The present work was undertaken to investigate procedures for the removal of retained amounts of formulations of 2,4-dichlorophenoxyacetic acid in a water miscible (non-volatile weed killer) and a paraffinic (low-volatile weed killer) solvent base from 5, 30, and 55 gal metal drums so that the detoxified metal containers could be disposed by conventional methods or reclaimed for non-food usage.

Materials and Methods

Pesticide formulations. (1) Dow Esteron^{R} 99^{R} Concentrate Low-Volatile Weed Killer containing propylene glycol butyl ether esters of 2,4-D; acid equivalent: 4 pounds per gallon; active ingredient: 2,4-dichlorophenoxyacetic acid, propylene glycol butyl ether esters, 72.8%, 2,4-dichlorophenoxyacetic acid equivalent 44.9%; inert ingredients, 27.2%. (2) Dow Formula 40 Non-Volatile Weed Killer containing alkanolamine salts of 2,4-D; acid equivalent: 4 pounds per gallon; active ingredients: alkanolamine salts (of the ethanol and isopropanol series) of 2,4-dichlorophenoxyacetic acid, 59.7%,

[1] Throughout this paper 1 gal = 3.8 ℓ.

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2,4-dichlorophenoxyacetic acid equivalent 38.6%; inert ingredients, 40.3%.

Containers. The containers were flat-head steel drum types commonly used for agricultural pesticides and represented 5, 30, and 55 gal sizes.

Washing solvents. The aqueous solvent was deionized water, and the ethanol was freshly distilled absolute ethyl alcohol.

Diazomethane preparation. Diazomethane was prepared by the method of ZWEIG et al. 1964, and the etheral solution was adjusted to 25 ml volume. One ml of this solution was added to 1 ml of the drum wash extracts and allowed to stand at room temperature for 15 min. The excess reagent and solvent were evaporated by a warm air stream to dryness, the volume adjusted and an aliquot injected into the gas-liquid chromatograph (GLC) for analytical measurement of the 2,4-dichlorophenoxyacetic acid equivalent.

Container retention volume. Excess spray formulation was added to empty, dry, weighed containers. The containers were closed, shaken, and swirled so that the inner surfaces were wetted with the formulation. The containers were opened, inverted, and the excess formulation allowed to drain into a graduated cylinder until dripping stopped (at least 5 min), and the containers were reweighed. The formulation retention in the container was expressed as net retention volume or weight of active ingredient. The retention volumes were determined in triplicate for each container size and the mean retention volumes were added to the containers for the washing experiments.

Container washing. Adequate volumes of washing solvents, determined by visual observations, were added to each size container to result in efficient washing of the inner surfaces. These volumes were 250 ml for the 5 gal, 750 ml for the 30 gal, and 1000 ml for the 55 gal containers. The washing solvent was added to the container, the container was closed, and it was shaken, swirled, and tumbled repeatedly. The container was opened, the wash mixture was drained into a graduated cylinder until dripping stopped (at least 5 min), and the solution was measured and stored for extraction and analysis. Each container was washed repeatedly with each wash solvent, and the data are shown in Tables II through V.

Washing mixture extraction. Ten ml aliquots of the aqueous wash mixture containing the propylene glycol butyl ether esters of 2,4-D were acidified with 5 ml of 5N HCl and extracted four times in a separatory funnel with 25 ml diethyl ether. The ether extracts were filtered through a Whatman #1 filter paper, combined and adjusted to appropriate volumes. To 1 ml of the ether extracts was added 1 ml of the etheral diazomethane for methylating the 2,4-D present, and the excess reagent and solvents were evaporated to dryness after the solutions remained at room temperature for 15 min. Dilutions were made to approximate 1 ng methylated 2,4-D per µl hexane

and the samples were analyzed by GLC. The aqueous wash mixture containing the alkanolamine salts of 2,4-D were extracted as described above. Each total ethanol wash was concentrated in vacuo at 50-60°C to approximately 1 ml after the pH was adjusted to less than 2 with 10 ml of 5N HCl. The solution was adjusted to an appropriate volume with diethyl ether and 1 ml of this solution was added to 1 to 3 ml of the etheral diazomethane (until the color remained yellow) and allowed to stand at room temperature for 15 min. The excess reagents and solvent were evaporated by a warm air stream and the methylated 2,4-D was adjusted with hexane to approximate 1 ng/µl for analysis.

Detection and determination of the methylated 2,4-D. Gas-liquid chromatography (GLC) procedures were employed routinely. All chemicals used, with the exception of the pesticide, were reagent grade and the solvents were redistilled shortly before use. The gas chromatograph was a Varian Aerograph (Model 1200) equipped with an electron-capture detector and a Leeds and Northrup Speedomax W 1-mv recorder with a chart speed of 1/2-inch per min. Areas under the peaks were measured with a polar planimeter. The chromatographic column, made with a 6-foot x 1/8-inch glass tube packed with 60-80 mesh silylated Chromosorb W, acid washed, was coated with 5% SE-30 silicone gum rubber and 5% Dow 710 silicone fluid. Nitrogen carrier gas (50 p.s.i., 30 ml per min) and a column temperature of 190°C gave the best results and were used in these experiments.

Results

The retention volumes of emptied metal drums of various sizes are shown in Table I. Considerable amounts of 2,4-dichlorophenoxyacetic acid (2,4-D) equivalent in the formulation in terms of ml retention volumes were found actually retained in the drums when they were drained as completely as possible. However, these retention volumes represented approximately 0.12% of the 5 gal container volume and ranged from 0.05% to 0.07% for the 30 and 55 gal containers.

Tables II to IV and V to VI contain data on removal from the emptied containers by water and ethanol-acid or ethanol washing of the 2,4-D acid equivalent in the formulations containing the alkanolamine salts of 2,4-D and the propylene glycol butyl ether esters. The initial high removal efficiency for water washing is probably due to the presence of emulsifiers or other adjuvants in the formulations which were diluted rapidly during the repeated container washings. The remaining 2,4-D was removed by the ethanol-acid or ethanol washings in which the 2,4-D in the respective formulations is soluble. Washing the various sized containers with eight water washings followed by three ethanol-acid or ethanol washings (Tables II to V) removed 95 to 99% of the retained formulations in the supposedly empty containers. When the 55 gal drum containing 83.6 g of the 2,4-D acid equivalent of the propylene glycol butyl ether esters formulation of 2,4-D (Table VI) was washed with four water washings followed by three ethanol washings, approximately 96% of the 2,4-D contaminants were removed from the container.

TABLE I

Retention Volume of 2,4-D Formulations in Various Sized Metal Containers

Drum Size (gal)	Retention Volume* (ml)	Grams Actual 2,4-D	% of Container Total Volume
	Alkanolamine Salts of 2,4-D		
5	24	11.5	0.12
30	83	39.8	0.07
55	146	69.9	0.07
	Propylene Glycol Butyl Ether Esters of 2,4-D		
30	72	55.5	0.06
55	109	83.6	0.05

*Rentention volumes were determined in triplicate for each sized container and mean values are reported.

TABLE II

Five Gallon Metal Drum Washed with 0.250 ℓ Solvent 2,4-D Removed Per Wash (g)*

Wash	Removed	Present Before Washed**	% Removed in Wash	Total Removed	% Total Recovered
Water					
1	10.200	11.500	88.6	10.200	88.6
2	0.624	1.300	48.0	10.824	94.1
3	0.060	0.676	8.8	10.884	94.6
4	0.025	0.616	4.0	10.909	94.8
5	0.008	0.591	1.3	10.917	94.9
6	0.007	0.583	1.2	10.924	94.9
7	0.008	0.576	1.3	10.932	95.0
8	0.007	0.568	1.2	10.939	95.1
Ethanol-Acid					
1	0.031	0.561	5.5	10.970	95.3
2	0.004	0.530	0.7	10.974	95.4
3	<0.001	0.530	<0.1	10.974	95.4

*2,4-D acid equivalent in alkanolamine salts of 2,4-D.

**Twenty-four ml (11.5 g 2,4-D) added to drum before washing.

TABLE III

Thirty Gallon Metal Drum Washed with 0.750 ℓ Solvent
2,4-D Removed Per Wash (g)*

Wash	Removed	Present Before Wash**	% Removed in Wash	Total Removed	% Total Recovered
Water					
1	34.900	39.760	87.7	34.900	87.7
2	3.200	4.860	65.8	38.100	95.8
3	0.682	1.660	41.0	38.782	97.5
4	0.175	0.978	17.8	38.957	97.9
5	0.089	0.802	11.0	39.046	98.2
6	0.067	0.714	9.3	39.113	98.3
7	0.039	0.647	6.0	39.152	98.4
8	0.028	0.608	4.6	39.180	98.5
Ethanol-Acid					
1	0.088	0.580	15.1	39.268	98.7
2	0.032	0.492	6.5	39.300	98.8
3	0.019	0.460	4.1	39.319	98.8

*2,4-D acid equivalent in alkanolamine salts of 2,4-D.

**Eighty-three ml (39.8 g 2,4-D) added to drum before washing.

TABLE IV

Fifty-Five Gallon Metal Drum Washed with 1 ℓ Solvent
2,4-D Removed Per Wash (g)*

Wash	Removed	Present Before Wash**	% Removed in Wash	Total Removed	% Total Recovered
Water					
1	59.900	69.940	85.6	59.900	85.6
2	8.520	10.040	84.8	68.420	97.7
3	1.070	1.520	70.3	69.490	99.3
4	0.150	0.450	33.3	69.640	99.5
5	0.041	0.300	13.6	69.681	99.6
6	0.021	0.259	8.4	69.702	99.6
7	0.012	0.238	5.0	69.714	99.6
8	0.009	0.226	3.9	69.723	99.6
Ethanol-Acid					
1	0.009	0.217	4.1	69.732	99.7
2	0.007	0.208	3.3	69.739	99.7
3	0.005	0.201	2.4	69.744	99.7

*2,4-D acid equivalent in alkanolamine salts of 2,4-D.

**One hundred forty-six ml (69.9 g 2,4-D) added to drum before washing.

TABLE V

Thirty Gallon Metal Drum Washed with 0.750 ℓ Solvent
2,4-D Removed Per Wash (g)*

Wash	Removed	Present Before Wash**	% Removed in Wash	Total Removed	% Total Recovered
Water					
1	30.500	55.500	54.9	30.500	54.9
2	9.800	25.000	39.2	40.300	72.6
3	5.540	15.200	36.4	45.840	82.5
4	3.540	9.660	36.6	49.380	88.9
5	1.500	6.120	24.5	50.880	91.6
6	1.040	4.620	22.5	51.920	93.5
7	0.390	3.580	10.8	52.310	94.2
8	0.380	3.190	11.9	52.690	94.9
Ethanol					
1	1.340	2.810	47.6	54.030	97.3
2	0.550	1.470	37.4	54.580	98.3
3	0.390	0.920	42.3	54.970	99.0

*2,4-D acid equivalent in the propylene glycol butyl ether esters of 2,4-D.

**Seventy-two ml (55.5 g 2,4-D) added to drum before washing.

TABLE VI

Fifty-Five Gallon Metal Drum Washed with 1 ℓ Solvent
2,4-D Removed Per Wash (g)*

Wash	Removed	Present Before Wash**	% Removed in Wash	Total Removed	% Total Recovered
Water					
1	58.850	83.600	70.3	58.850	70.3
2	12.200	24.750	49.2	71.050	84.9
3	4.110	12.550	32.7	75.160	89.9
4	1.650	8.440	19.5	76.810	91.8
Ethanol					
1	2.060	6.790	30.3	78.870	94.3
2	0.860	4.730	18.1	79.730	94.1
3	0.160	3.870	4.1	79.890	95.5

*2,4-D acid equivalent in the propylene glycol butyl ether esters of 2,4-D.

**One hundred nine ml (83.6 g 2,4-D) added to drum before washing.

Generally the 2,4-D in these formulations was more persistent against removal by the aqueous and organic solvent washing treatments than as previously discussed for emulsifiable concentrate formulations of parathion (ARCHER and HSIEH 1973). However, 95 to 99% of the retained formulations were apparently removed from the containers, and considering the low mammalian toxicity of 2,4-D, this is probably an adequate efficiency.

Discussion

Supposedly empty noncombustible metal containers retained as much as 24 to 146 ml of formulation for 5 and 55 gal sizes, respectively, after the containers were drained as completely as possible. Although 2,4-D is harmless to mammals at phytotoxic concentrations, it has been widely used as a herbicide toward most broad-leaved plants since it is relatively nontoxic to monocotyledonous plants. It has also been used for the prevention of preharvest fruit drop, the production of seedless fruit, and the regulation of the growth of plants.

These effects are useful when 2,4-D is applied to plants intentionally. However, what results would occur if 2,4-D were to appear in and pollute the environment by unintentional application such as contamination of surface and ground waters as well as soil? The improper disposal of noncombustible used metal containers which previously contained formulations of 2,4-D could contribute to such environmental pollution.

It has been shown by previous studies (HSIEH et al. 1972 and ARCHER and HSIEH 1973) that the efficiency of parathion removal from noncombustible used pesticide containers by solvent washing is independent of the chemical properties of the solvents, and this also appears to be true for 2,4-D formulations. The important factors to be considered are solubility of the pesticide in the solvent, or partition between the inner surface of the container and the solvent, and the presence of adjuvants or emulsifiers. The latter is particularly important when water is used. Formulations of 2,4-D can most efficiently be removed from a used noncombustible container, first by four water washes, followed by three washes with a water miscible organic solvent such as ethanol or ethanol-acid depending upon the formulation in the container. The aqueous and alcoholic washes can be added to the spray tank and disposed with the spray mixture provided that this does not adversely affect the properties of the spray liquid or constitute a flammability hazard. The decontaminated drums could then be disposed in a conventional manner or reclaimed for pesticide use if their condition warrants it.

This procedure is a convenient and economical method for removal of potentially hazardous pesticides remaining in emptied noncombustible metal containers, and is a practical solution for the disposal of the containers as well as for the prevention of environmental pollution with unwanted chemicals.

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