Pesticide Container Decontamination by Aqueous Wash Procedures

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A health and environmental hazard exists when so-called "empty" pesticide containers are disposed of improperly. The Working Group on Pesticides recommends that, "Contaminated non-returnable pesticide containers should be disposed of in well-designed and operated sanitary landfills or by adequate incineration" (PROCEEDINGS, 1970). An "empty" 55 gallon drum can retain as much as five liters of pesticide formulation. It does not take much imagination to realize that a few hundred such "empty" containers in a small area or landfill results in a concentration of chemicals similar to a small "spill" with its associated hazards, particularly to local wildlife.

WOLFE (1961) has reported parathion formulation residues in emptied four pound (1.8 kg) paper bags ranging between 0.25 and 1.20 g which when burned produced smoke containing a mean parathion concentration of 7.9 mg/m^3; a figure far in excess of typical air concentrations (0.03-0.09 mg/m^3) during orchard spraying (BATCHELOR and WALKER, 1954). Discarded 5 gallon drums, which these authors suggest could be used for other household purposes, contained between 1.25 g and 9.48 g residual technical parathion with an average of 2.73 g for 22 containers. Case histories have shown the tragedies that can result when the public, especially children, are exposed to these "empty" pesticide containers (GEHLBACH and WILLIAMS, 1975).

Because of these environmental health implications, some experimental work has recently been conducted by investigators for decontaminating "empty" pesticide containers. Various solvents including water have been shown to remove emulsifiable concentrate formulations of parathion from pesticide containers (WOLFE, 1961; ARCHER and HSIEH, 1973). Solubility of the formulation seems to be a criterion for decontamination efficiency. In the case of emulsifiable concentrates, water is frequently an adequate solvent. Similar findings have been reported for decontamination of 2,4-D formulations (ARCHER, 1975). In each case, a single aqueous wash has been reported to remove most of the pesticide; and with two or three additional water rinses, more than 90% of the pesticide is usually removed.

A procedure that has been used in the decontamination of parathion involves its oxidation to the more water soluble oxon analog by sodium hypochlorite (HSIEH et al., 1972). This proce-

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dure, however, may have a serious drawback because of the increased toxicity of the oxon intermediate.

Several papers have dealt with incineration of pesticide containers (KENNEDY et al., 1972; SHUMAN et al., 1972; STOJANOVIC et al., 1972). Noxious gases including CO, HCl, H_2S, and Cl_2 are formed from incinerated organophosphates and chlorinated hydrocarbons. As a result, this method will not necessarily reduce the environmental hazards without some additional scrubbing of the stack emissions. Incineration is thus not the most desirable single method for reducing the hazards from residues in pesticide containers.

The Oregon Insect Control Handbook (EVERY and CAPIZZI, 1970) outlines procedures for rinsing containers. A five gallon container should be washed with two quarts water to which two tablespoons detergent have been added. After intermittent agitation for fifteen minutes, it is drained and the cycle is repeated. The final draining is accomplished by inverting the drum for fifteen minutes. It is also recommended that glass and smaller metal containers be rinsed several times and the rinsings included in the spray (HSIEH et al., 1972). By adding the rinse to the spray tank, the decontamination procedure becomes economically feasible (WITT and CAPIZZI, 1970), since the rinsed pesticide goes onto the target crop rather than becoming a disposal problem itself.

This study was undertaken to determine how effectively pesticide containers are cleaned in the field by triple rinsing or by processing with detergents in a barrel cleaning installation. The results from other investigations are based on the amount of added hydrolyzable pesticides which is removed upon rinsing (ARCHER and HSIEH, 1973; ARCHER, 1975; HSIEH et al., 1972); or on the amount of removable pesticide (WOLFE, 1961) without measuring what remains in the container. The present studies have employed similar techniques in some cases, but also included an analysis of samples of the drum itself, with special efforts to include the residues left in the chime of the rinsed or washed containers. These studies have been concerned only with the residues in weathered drums and have not included added residues.

EXPERIMENTAL

Wash Process. Thirty and fifty-five gallon used pesticide barrels were processed at Van Barrel Company, Incorporated, in Portland, Oregon, using standard methods for reclaiming used barrels. A detailed description of this process is given in a report by GOULDING (1974). The barrels included had contained carbaryl, 2,4-D, 2,4,5-T, phorate, disulfoton, and chlordane. Experiments were carried out using triple rinse procedures for these pesticides, as well as several others, which included malathion and 2,4,5-T low volatile ester. Pennwalt 91 and Oakite were both tried as detergents in the washing process, although no effort was made to compare one over the other. The amount of detergent in solution was adjusted to make the wash solution 1 or 2% caustic.

Sampling, Extraction, and Analysis. Although barrels for several different types of pesticides were used, phorate was the only one for which an adequate number of barrels were available for cleaning and analysis in a systematic manner. Two different procedures were used in sampling these drums. One series of drums was sampled such that ten randomly selected drums were sampled before washing, ten sampled after rinsing three times with clean water (triple rinse), ten sampled after running through the cleaning plant process, and ten sampled after triple rinsing and plant processing. The second series involved sampling ten barrels before washing and resampling the barrels after rinsing and processing. Barrels containing other pesticides were randomly divided and washed by the various washing processes.

Four samples from each end of the barrels were cut so that each sample piece included a wedge cut from both the end and side of the barrel and the chime. Each sample had an area of 23.4 ± 1.4 in^2 and an average chime length of 3.66 ± 0.16 inches. From separate analyses of the chime and flat surfaces of the wedges, it was shown that 81% of the pesticide was contained in the chime. It was also determined that the weight of the wedge was proportional to the area of the wedge and chime. Taking these two factors into consideration, the total weight of pesticide was determined for each container using the weight of the wedges.

Extraction of the wedges was accomplished by placing them chime down in 4 l stainless steel beakers with sufficient solvent to cover them. The beakers were covered with aluminum foil and warmed on a steam bath for 18 hours. The solvent was decanted and the wedges were covered again with solvent and cooked an additional 18 hours. The solvent was then decanted and the wedges rinsed two times with a small amount of solvent. The solvents used for the various pesticides are shown in Table I.

Several of the experiments reported here using 2,4,5-T LV ester and malathion were done several years earlier on a laboratory scale, using different procedures. The tops of five gallon drums containing the residual pesticide of interest were cut out in order to provide easy access to the pesticide residues and facilitate its complete removal. The cans which had been rinsed with water or water and detergent were rinsed two times with 100 ml hexane. All of this was collected in a separatory funnel and extracted twice with additional hexane. Those cans that had had no water rinsing previously were rinsed with three 150 ml portions of hexane after all the free flowing pesticide was drained from them and measured.

The methods of analyses are shown in Table I. The extraction solvents were diluted as necessary and analyzed by the GLC method shown without further cleanup. Chlordane, disulfoton, and phorate were extracted from the aqueous wash solutions with ether, evaporated to dryness, and taken up in hexane. The carbaryl wedges and water were extracted with dichloromethane and analyzed by a colorimetric method (KARINEN et al., 1967).

Table I Extraction and GLC Conditions Used

Pesticide	Extraction Solvent	Instrument and GC Column	°C
Chlordane	ethyl ether	EC[a]: 5' x 1/4" glass 10% OV-1	245
Disulfoton	ethyl ether	EC: 8' x 1/8" glass 7% OV-1	200
Phorate	ethyl ether	EC: 6' x 1/8" glass 7% OV-1	185
2,4-D and 2,4,5-T	5% NaOH	EC: 6' x 1/8" glass 7% OV-1	170
2,4,5-T LV ester	hexane	Microcoulometric: 4' x 1/4"	160
Malathion (EC and flowable)	hexane	EC: 4' x 1/8" glass 7% QF-1/DC-11 (2/1)	180

[a] Electron capture, ^{3}H

RESULTS AND DISCUSSION

As can be seen from Table II, each process significantly removed additional pesticide from the barrels. Most of the pesticide was removed when both triple rinsing and plant processing was employed. Using both processes sequentially, more than 95% of the phorate was removed from the barrels tested. Either one of the processes used singly removed more than 60% of the residual phorate, and had much greater variability than when both processes were used. The mean was lower for plant processing, and a t-test showed that the difference in the means for plant processing and triple rinsing was significant. Analysis of variance shows significant difference between all means at the 0.01 level. The average amount of phorate remaining in the dual processed barrels was 1.27 g/drum. If all of the phorate remaining in the drum were dissolved in 55 gallons of a liquid contained in the drum, a concentration of 6.1 ppm would result. On the basis of an LD_{50} value of 3.7 mg/kg, this is significant and could be considered a major health hazard, were such drums to be used for drinking water purposes. Smaller animals, including pets, would be exposed to sub-lethal levels of phorate compound under these conditions.

The results from barrels analyzed before and after washing are also shown in Table II. When the amount of phorate before and after washing is compared for each barrel separately, greater variability and apparently less cleanup occurred. One of the analyzed barrels showed only 37% decrease in residue with the remaining 9 barrels showing 77-95% decrease, which suggested that occasionally a barrel was not washed properly or there was considerably more residue within the chime or otherwise inaccessible which was not removed by the cleaning methods. The average residue removed was 89% leaving 2.63 g phorate in each drum. This represents 12.6 ppm phorate in 55 gallons of liquid. Another possible explanation for the overall higher amount of phorate present may be due to the fact that these barrels were washed after the other two sets of barrels had been processed; thus the higher concentration of phorate in the wash water may have caused some cross-contamination.

Table II. Pesticide Residues in Washed Containers

Pesticide	Mean g/drum	Range g/drum	Percent Removed	Barrels n
Phorate, U[a]	39.0	15.9 -64.9	--	10
Phorate, TR[a]	8.63	3.98 -15.20	77.9	10
Phorate, P[a]	4.69	0.80 - 8.37	88.0	10
Phorate, TRP[a]	1.27	0.33 - 2.12	96.7	10
Phorate, U[b]	31.43	12.66 -58.56	--	9[b]
Phorate, TRP[b]	2.63	2.10 - 3.56	91.2	9[b]
Disulfoton, U	18.80	17.80 -19.70	--	4
Disulfoton, TR	0.74	0.11 - 1.73	96.0	6
Disulfoton, TRP	0.25	0.05 - 0.44	98.7	6
Carbaryl, TRP	0.105	0.055- 0.158	--	6
Chlordane, TR	3.10	1.25 - 8.34	--	6
Chlordane, TRP	2.44	0.29 -10.78	--	17
2,4-D, TR	4.76	0.86 -10.90	--	4
2,4-D, P	0.56	0.30 - 0.90	--	6
2,4-D, TRP	0.14	0.08 - 0.25	--	16
2,4,5-T, TR	7.22	1.67 -21.71	--	4
2,4,5-T, P	1.24	0.03 - 0.97	--	6
2,4,5-T, TRP	0.19	0.06 - 0.28	--	16

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[a] U = unprocessed; TR = triple rinsed; P = processed; TRP = triple rinsed and processed.

[b] Same drums sampled before and after.

Table III. Residual Pesticides Remaining After Rinsing in 5 Gallon Containers

Pesticide[a]	Unprocessed Normal Drain (g)/5 gal	Triple Rinse (g)/5 gal	Pesticide Removed (%)
2,4,5-T LV ester	94.25	0.22	99.8
Malathion (flowable)	110.00	2.60	97.7
Malathion (EC)	52.00	4.10	92.1
Malathion (EC)	52.00	3.00[b]	94.2

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[a] One sample of each.

[b] Combined triple rinsed and detergent.

Also shown in Table II are the results when barrels containing disulfoton, an organophosphate similar to phorate, were washed. Although the triple rinse appears to have been more effective with disulfoton than phorate, the percent removed for the combined processes is nearly the same.

The effectiveness of triple rinsing for removal of 2,4,5-T LV ester and malathion shown in Table III shows three water washings removed nearly all of the measurable residual pesticides from five gallon drums. These results agree with those of WOLFE (1961) who showed that 98% of the parathion residue was removed with only two water rinses. Although it would appear that the water rinses were less effective at removing malathion (EC) than 2,4,5-T, this could be explained on the basis that only two quarts total rinsing was used for the malathion (EC) drums while the 2,4,5-T were containers rinsed with a total of three gallons of water.

Limited cleaning efficiency studies were carried out on containers using the triple rinsing and detergent washing procedures with carbaryl, chlordane, 2,4-D, and 2,4,5-T. Since initial determinations of residue levels were not made, only the final residue levels are shown in Table II. The levels of carbaryl, 2,4-D, and 2,4,5-T remaining in the containers are comparable to phorate, disulfoton, and malathion. The residue left for chlordane is higher, as is expected due to the water insolubility of chlorinated hydrocarbons; in fact, the residue level is an order of magnitude higher.

The wash solutions contained high chlordane and 2,4-D residues (Table IV) which reflects their stability in basic solutions when compared to the other pesticides tested. Carbaryl had been completely hydrolyzed to 1-naphthol and most of the phorate ($\sim$ 80%) had been oxidized to the phorate sulfoxide. Phorate sulfoxide is four times more toxic than the parent compound (BOWMAN and CASIDA, 1958). Thus, disposal of solutions of phorate and compounds forming oxons presents a more serious problem.

Just washing empty pesticide drums should not be a means for justifying immediate recycling. To "destroy all empty containers immediately," (STOJANOVIC et al., 1972) is still the final step to insure human safety and environmental protection. However, an important step in the proper disposal of these containers is the maximum reduction of pesticide residue remaining. In the cases of phorate, disulfoton, the phenoxy herbicides, and malathion, the evidence shows good removal of pesticide by either triple rinsing or detergent cleaning. In most cases, triple rinsing when used by applicators in the field, is sufficient to reduce the hazards of residual pesticides to a low level. From the indirect evidence presented concerning chlordane; i.e., the amount of residue in the wash solution, it can be seen that this formulated pesticide likewise can be largely removed by either triple rinsing or detergent processing. If we assume that an average of 192 g/container residue was present and 2.44 g remained in the drum for a triple rinsed

Table IV Pesticide Remaining in Wash Solution

Pesticide	Grams Pesticide	Number Containers
Phorate	84.01	30
Disulfoton	0.183	48
Chlordane	4222.4	22
Carbaryl (1-naphthol)	28.73	11
2,4-D	621.5	38

and washed container, then at least 98% of the chlordane was removed by these procedures. If we further assume that a similar quantity of chlordane was present in drums which were only triple rinsed, then only 10% or 3.1 g on the average remained. Triple rinsing, therefore, removed better than 90% of the chlordane. In either case the procedure effectively reduced the residues present in the containers. Similar reasoning might be applied to carbaryl. Although no data on the triple rinsing is available, one would expect that if chlordane can be removed by either procedure, carbaryl should be removed as well.

Despite the success of removing most of the residues from pesticide containers by triple rinsing and/or washing and the resultant large decrease in the environmental hazard, these containers should, nevertheless, be handled with discretion. As was noted with phorate, a sufficiently high residual of this highly toxic chemical remained in the drum to remain a potential health hazard, however reduced, if not used properly. These containers cannot be recommended for food stuffs because the pesticide residue cannot be completely removed. Their use for materials other than those that humans might ultimately contact should also be discouraged since the history of containers become lost and the hazards to the public associated with the presence of unknown toxicants increase. The reuse of these containers for pesticides or other chemicals increases the probability of cross-contamination.

Triple rinsing of pesticide containers should be considered a mandatory first step in their proper disposal even when incineration is the ultimate processing method. Implementation of this procedure would minimize the risks to human health and the environment. If the applicator adds the washings to his spray apparatus for maximum utilization of the pesticide, economic benefits would result as well. Washings from pesticide containers, if not added to the sprayer apparatus, pose still another environmental problem: the question of what to do with the wash solution. As shown with chlordane and 2,4-D in these studies, high quantities of some pesticides still remain in the wash solutions. The disposal of container washings from central washing facilities will require concentration and incineration in an efficient furnace with scrubbers or some other means of preventing the escape of toxic substances into the atmosphere. These disposal methods will entail costly technology. This is another important reason for the recommendation that triple rinsing be used and the rinse solutions added to the spray tank. Triple rinsing used in this manner will decrease the amount of waste pesticide requiring disposal.

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