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Pesticide Residues in Spray Aircraft Tank Rinses and Aircraft Exterior Washes

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There has been much concern in recent years over the amount of pesticide waste generated as a result of pest control in agriculture. These concerns were expressed and discussed at two national workshops that dealt with the disposal of pesticide waste (EPA 1985 and 1987). Regulated wastes may include excess pesticide concentrate, unapplied diluted material, and discarded containers remaining after application (Ehart 1985). Unapplied diluted material could include spray tank rinses and exterior washes of spray equipment. However, residue levels in exterior washes are low enough to exempt them from regulation (*unpublished report*). Furthermore if tank rinsates are applied to the treated crop, they may also be exempt from regulation.

At neither workshop was the nature of rinsewater contents dealt with directly (Seiber 1987); only in one report prior to the workshops was it addressed in any detail (*unpublished report*). The purpose of this study was to determine the concentrations of pesticides and of some breakdown products and impurities in tank rinsates and exterior washes derived from spray aircraft operated under typical conditions in California agriculture. In particular, the efficiency of tank rinsing was assessed and the tank residue levels were compared to those found in the exterior washes. While we recognized that the washwater might also contain adjuvants, such as solvents, emulsifiers, activators, and spreaders, these "inert" ingredients were not included within the scope of this study.

MATERIALS AND METHODS

Spray aircraft tank rinses and aircraft exterior washes were collected from two separate applicators. The pesticides sampled included Pydrin, Lorsban, Comite, Orthene, Kelthane, and Phosdrin (Table 1). In addition to tank rinses, tank mix samples were also taken to establish initial concentrations. Usually one tank mix sample was taken for each compound, along with two-three samples from each tank rinse and four samples from each exterior wash (Table 2). Rinse water was delivered to the spray tanks using the same mixing/loading system used to create the tank mixes; in both cases, tank contents were agitated. For the exterior washes, the drain of the wash pad beneath the aircraft was plugged by a

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Table I. Pesticide application data[a].

Pesticides	Appl'n Date	Formulation	Dilution Rate	Other Ingredients[b]	Crop Treated
Pydrin	6/24/86	Shell: 0.29 kg/L	4.44 g/L water	1.25 mL/L Butacide	sunflowers
"	6/25/86	"	14.5 mL/L water	1.25 mL/L Adhere	sunflowers
Lorsban	"	Dow: 0.48 kg/L	35.7 mL/L water	Nu-Film-P	sugar beets
Pydrin	7/9/86	Shell: 0.29 kg/L	10.0 mL/L water	2.5 mL/L Buffercide	sunflowers
Comite	"	Uniroyal: 0.79 kg/L	25.0 mL/L water	1.25 mL/L Nu-Film-P	corn
Kelthane	7/23/86	MFEC: 0.48 kg/L	23.4 mL/L water	none	beans
Orthene	"	Ortho: 75 S	10.0 g/L water	none	beans
Pydrin	8/5/86	Shell: 0.29 kg/L	13.5 mL/L water	none	sweet corn
Phosdrin	"	Wilbur Ellis: 0.48 kg/L	15.4 mL/L water	none	sweet corn

a Two types of equipment were used: Cessna Ag Truck, 800 L capacity; Grumman Gulf Stream Ag Cat, 1,100 L capacity.

b Butacide and Adhere are activators, Nu-Film-P is a sticker/spreader, and Buffercide is a buffering agent.

Table 2. Tank rinse and exterior wash water volumes.

		Volume of Tank Rinse, L			Approximate Volume
Pesticides	Appl'n Date	First	Second	Third	Ext. Wash Water, L
Pydrin	6/24/86	378	378	227	76
Pydrin	6/25/86	227	227	227	76
Lorsban	6/25/86	378	378	378	76
Pydrin	7/09/86	227	227	227	151
Comite	7/09/86	227	227	227	151
Kelthane	7/23/86	378	–	–	–
Orthene	7/23/86	378	–	–	–
Pydrin	8/05/86	227	227	–	–
Phosdrin	8/05/86	227	227	–	–

plastic tarp covering the wash pad. After sampling, the tarp was slit allowing the water to drain. The tanks were sampled with a 1L stainless steel beaker whose contents were then divided into approximately 50 mL aliquots and stored in 100 mL screw-cap amber glass jars. The exterior washes were sampled in a similar manner and also stored in amber jars. All samples were transported to the laboratory under ambient conditions and stored at -10°C until analyzed.

For Pydrin, Comite, and Kelthane,1-10 mL tank mix aliquots and whole (~50 mL) tank rinse and exterior wash samples were mixed with 50 mL 2% aqueous sodium sulfate and extracted for two minutes with 40 mL ethyl acetate using vigorous shaking. In the case of Lorsban, extraction was done with 3x20 mL ethyl acetate, two minutes each. On the other hand, µL aliquots of Orthene and Phosdrin tank mix and first tank rinse samples were simply diluted with solvent (acetone or ethyl acetate) and analyzed. However, 2 mL of the Phosdrin second tank rinse was saturated with about 2 g ammonium sulfate and filtered through a cyclohexyl Bond-Elut® column (Analytichem, Harbor City, CA). Phosdrin was eluted from the column using 5 mL ethyl acetate.

The Pydrin, Lorsban, Comite, and Kelthane samples in ethyl acetate or methanol were analyzed by high pressure liquid chromatography (HPLC) using a Waters (Milford, MA) system (Model 6000A solvent delivery system, Model 450 variable wavelength detector, Model U6K manual injector, Model 720 system controller, and Model 730 data module) with a C_{18} reverse-phase column, 90/10 methanol/water mobile phase at 0.5 mL/min, and ultra-violet detection at 280 nm. For gas chromatographic analysis and confirmation by electron-capture detection (p,p' and o,p isomers of Kelthane, as well as p,p'-DDT and p,p'-DDE in Kelthane formulation; Pydrin; Lorsban), the samples were dissolved in hexane and analyzed using a Varian Model 2100 gas chromatograph (Varian Associates, Palo Alto, CA) equipped with a 1.8m x 0.32cm (ID) glass column packed with 1.5% SP 2250/1.95% SP 2401 on 100/120 mesh Supelcoport (Supelco, Inc., Bellefonte, PA) at 170°C (Lorsban), 200°C (Kelthane, p,p'-DDE), or 230°C (Pydrin, p,p'-DDT). Orthene was analyzed by N/P thermionic detection using a Hewlett-Packard Model 5710A gas chromatograph (Hewlett-Packard, Palo Alto, CA) equipped with a 30m x 0.25mm (ID) DB-1701 fused silica open tubular (FSOT) column (J&W Scientific, Rancho Cordova, CA) at 200°C. Orthene's major hydrolysis product, O,S-dimethyl phosphorothioate (DMPT), was analyzed by alkali-flame ionization detection using a Varian Model 1700 equipped with a 30m x 0.53mm (ID) DB-1701 FSOT column coupled to a 3m x 0.53mm (ID) DB-225 FSOT column at 130°C. DMPT was methylated during injection with trimethyl anilinium hydroxide (Churchill et al. 1978; Moody et al. 1985). All samples were quantitated by comparing peak areas and/or heights with those of standard injections. Extraction efficiency by liquid-liquid and Bond-Elut® partition was determined by spiking tap water with standards of the test chemicals.

RESULTS AND DISCUSSION

Pesticide residue levels in tank rinsates and exterior washes are reported as concentration in Table 3 and, for the tank rinses, percent of initial tank mix concentration in Table 4. Since aqueous solubilities are low for many of the compounds, the reported concentrations actually represent emulsified suspensions. Liquid-liquid extraction efficiencies were greater than 80%. Phosdrin, which is completely miscible with water, was recovered from its second tank rinse at >70% efficiency using the cyclohexyl Bond-Elut® cartridge.

The Kelthane tank mix and tank rinse contained about 0.25% and 0.5% (w/w total Kelthane) p,p'-DDT and p,p'-DDE, respectively (Table 3). These results indicate that over about 19 g and 40g of p,p'-DDT and p,p'-DDE, respectively, were released to the environment for each tank load of Kelthane mix. Orthene, in the same tank mix with Kelthane, contained about 6% (w/w) DMPT, which increased to about 8% in the tank rinse (Table 3). DMPT is a hydrolysis product of Orthene and its formation is pH-dependent (Chukwudebe et al. 1984). The hydrolysis half-life of Orthene in the alkaline ground water used to make up the tank mix was greater than a day. Based on these results, about 0.5 kg of DMPT would be applied for each tank load of Orthene mix.

Both applicators followed the practice of returning tank rinses to the treated fields. One applicator routinely sprayed the rinses to the treated field by making several passes, just as would be done for the original tank mix. The other applicator who applied the Kelthane/Orthene mix made only one tank rinse after the residual tank mix had been applied to the treated field by releasing it directly from the tank into the air stream. The residual rinse was handled in the same manner. This applicator also followed the practice of dedicating spray aircraft to either insecticides only or herbicides only. Both applicators occasionally dispensed with tank rinses for efficiency and cost reasons if the next chemical to be sprayed was compatible with the residues of the previous chemical and if this residual chemical was also registered on the crop to be treated with the next chemical.

Table 5 lists regression equations relating pesticide residue levels in the tank rinsates with the number of rinses. With the exception of the samples obtained on 8/5/86, all regressions were based on four points (tank mix plus three rinses). Average slope for the four-point curves was 2.75±0.09 (±3.27%) indicating that rinsing efficiency was essentially unrelated to the nature of the compound and the initial tank mix concentration. Average correlation (r^2) for all curves was 0.98±0.03 (±3.06%). After three rinses, Pydrin and Lorsban, for example, had residue levels of 0.32-1.80 mg/L and 2.89 mg/L, respectively. By comparison, residue levels in the exterior washes were 0.008-0.05 mg/L

Table 3. Concentrations of pesticides in spray plane tank rinses and exterior washes.

		Concentration, mg/L[a]					
Sample Designation	Date Taken	Pydrin	Lorsban	Comite	Phosdrin	Kelthane[b]	Orthene[c]
Tank Mix	6/24/86	3,514	-	-	-	-	-
First Tank Rinse	"	112±2	-	-	-	-	-
Second Tank Rinse	"	3.15±0.15	-	-	-	-	-
Third Tank Rinse	"	1.53±0.53	-	-	-	-	-
Exterior Wash	"	0.020	-	-	-	-	-
Tank Mix	6/25/86	4,511	15,969	-	-	-	-
First Tank Rinse	"	528	151.3±52.7	-	-	-	-
Second Tank Rinse	"	25.2	9.53±0.19	-	-	-	-
Third Tank Rinse	"	1.80	2.89±0.66	-	-	-	-
Exterior Wash	"	0.008	0.014	-	-	-	-
Tank Mix	7/9/86	2,018	-	15,385	-	-	-
First Tank Rinse	"	53.0	-	1,195±99	-	-	-
Second Tank Rinse	"	7.18	-	89.0±7.6	-	-	-
Third Tank Rinse	"	0.32	-	4.13±0.19	-	-	-
Exterior Wash	"	0.05	-	0.70±0.24	-	-	-
Soap Solution	"	0.004	-	-	-	-	-
Tank Mix	7/23/86	-	-	-	-	10,542	9,288
First Tank Rinse	"	-	-	-	-	109.9±4.0	134±13
Tank Mix	8/5/86	2,140	-	-	8,790	-	-
First Tank Rinse	"	130.4±10.4	-	-	200±22	-	-
Second Tank Rinse	"	14.2±1.1	-	-	9.8±1.3	-	-

[a] Calculated tank mix concentrations (mg/L): Pydrin--4,504 (6/24), 4,180 (6/25), 2,882 (7/9), 3,880 (8/5); Lorsban--17,158; Comite--19,667; Phosdrin--7,391; Kelthane (p,p'+o,p)--11,260; Orthene--10,009.

[b] Tank mix and tank rinse contained 54.0 mg/L and 0.521±0.047 mg/L p,p'-DDE, respectively. Tank mix and tank rinse contained 25.5 mg/L and 0.272±0.024 mg/L p,p'-DDT, respectively.

[c] Tank mix and tank rinse contained 579 mg/L and 10.9±2.0 mg/L dimethyl phosphorothioate (DMPT), respectively. DMPT is a hydrolysis product of Orthene (579 mg/L DMPT=746.5 mg/L Orthene).

Table 4. Pesticide residues in spray plane tank rinses, expressed as percent of the tank mix.

		Relative Residue Levels, Percent					
Sample Designation	Date Taken	Pydrin	Lorsban	Comite	Phosdrin	Kelthane	Orthene
Tank Mix	6/24/86	100	-	-	-	-	-
First Tank Rinse	"	3.19	-	-	-	-	-
Second Tank Rinse	"	0.090	-	-	-	-	-
Third Tank Rinse	"	0.0435	-	-	-	-	-
Tank Mix	6/25/86	100	100	-	-	-	-
First Tank Rinse	"	11.70	0.947	-	-	-	-
Second Tank Rinse	"	0.559	0.060	-	-	-	-
Third Tank Rinse	"	0.040	0.018	-	-	-	-
Tank Mix	7/9/86	100	-	100	-	-	-
First Tank Rinse	"	2.63	-	7.77	-	-	-
Second Tank Rinse	"	0.356	-	0.578	-	-	-
Third Tank Rinse	"	0.016	-	0.027	-	-	-
Tank Mix	7/23/86	-	-	-	-	100	100
First Tank Rinse	"	-	-	-	-	1.04	1.44
Tank Mix	8/5/86	100	-	-	100	-	-
First Tank Rinse	"	6.09	-	-	2.28	-	-
Second Tank Rinse	"	0.66	-	-	0.111	-	-

and 0.014 mg/L for Pydrin and Lorsban, respectively. To achieve similar residue levels in the tank rinsates, about five rinses would be needed.

Table 5. Regression equations for pesticide residues in spray aircraft tank rinsates.

Date Taken	Pesticide	Regression Equation[a]
6/24/86	Pydrin	Ln(mg/L)=7.63-2.68(#rinses)
6/25/86	Pydrin	Ln(mg/L)=8.60-2.65(#rinses)
6/25/86	Lorsban	Ln(mg/L)=8.80-2.86(#rinses)
7/9/86	Pydrin	Ln(mg/L)=7.34-2.82(#rinses)
7/9/86	Comite	Ln(mg/L)=9.75-2.73(#rinses)
8/5/86	Phosdrin	Ln(mg/L)=8.95-3.40(#rinses)
8/5/86	Pydrin	Ln(mg/L)=7.57-2.51(#rinses)

[a] Each equation for 6/24/86-7/9/86 is based on one tank mix and three tank rinse samples. The 8/5/86 equations are based on one tank mix and two tank rinse samples each.

The applicator who provided the exterior aircraft wash samples allowed the wash water to drain into an open ditch bordering the facility. It is noteworthy that concentrations of Pydrin and Lorsban in the exterior washes exceeded the LC_{50} (96-h) for rainbow trout (~0.004 mg/L Pydrin; 0.003 mg/L Lorsban). Of course this may become a problem only if the exterior washes allowed to drain into the open ditch are carried to a canal or major waterway, such as a river, which our data show should be avoided for exterior washes and, certainly, for tank rinses. Photodecomposition half-life for Pydrin in river water is about four days under Summer sunlight and 2-18 days on soil, depending on soil type (Mikami et al. 1980). Hydrolysis half-life for Lorsban in pH 8 water is about 1.5 days under laboratory conditions. Hydrolysis rate increases with pH, temperature, and the presence of chelating metals (e.g., copper) (BCPC 1987). Thus, residues in exterior washes and tank rinses may persist long enough to present localized toxic residues if they are released directly to waterways.

These results indicate that the practice of rinsing equipment tanks several times with water, and then spraying the rinsewater to the treated field, represents a viable method of disposing of residual tank mix remaining after application is completed. The number of rinses needed to reduce rinsewater to sub-toxic levels may be calculated for a given pesticide from the regression equations reported herein. A minimum of three rinses will reduce rinsewater residues to less than 1% of the tank mix concentration for aircraft of the type described in this study. Tests of the type we have described could be applied to a variety of spray equipment to generate regression equations of predictive utility for determining the number of rinses needed to reduce rinsewater residues to low enough levels to safeguard water quality. Exterior washwaters contained residue concentrations much lower than those encountered in the first three tank rinses. Whether such washwaters can be discharged directly to natural waterways will depend on the toxicity and environmental persistence of the pesticide in question.

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