

ARTICLES

RECYCLING SUITABILITY OF WASH WATERS FROM MOSQUITO ABATEMENT VEHICLES AND EQUIPMENT INTO SPRAY DILUENT

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ABSTRACT. In response to changing laws as well as increased concern over environmental pollution, there is a current need to examine the best means of disposal of wash water generated by mosquito abatement operations. A study of wash waters from 6 central California mosquito abatement districts shows that herbicide levels were low enough so as not to preclude the use of these waters for recycling back into insecticide spray diluent. In one case, oil levels were high and an oil/water separation is probably necessary to prevent gum formation and clogging of spray equipment. Recycling of wash waters appears to be a feasible solution to the disposal problem once water contaminant levels are defined.

INTRODUCTION

Mosquito abatement agencies routinely utilize a variety of insecticides and herbicides in carrying-out their programs. Spraying necessarily results in the contamination of spray equipment and vehicles; the contamination are eliminated by washing but this results in the generation of wash waters. The latter are presently discharged into open pits or drained into sewage, septic systems or storage tanks. As this contributes to environmental pollution, there is a need to consider alternative means of wash water disposal. Also, open disposal pits must be eliminated in California by 1988 (Katz Act).

During the fall of 1986 and the spring of 1987, wash water samples were collected from the sumps of vehicle wash areas (MAD nos. 1, 2, 5 and 6), open disposal pits (MAD no. 4) and wash water storage tanks (MAD no. 3) from 6 mosquito abatement districts in central California. These samples were extracted and analyzed for oil and grease, carbamates, ureas and triazines in order to determine the suitability of such wash waters for recycling back into insecticide diluent. Insecticide residues were not considered as detriments for recycling and therefore were not determined. Details of the analytical methods are provided since these are not defined in the official EPA methods cited (note: the EPA methods can be obtained from US, EPA, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268).

MATERIALS AND METHODS

Oils and greases (EPA Method 413.1). Multiple 1-liter samples of water from each site were collected in glass graduate cylinders. Each sample was acidified with hydrochloric acid immediately after collection and then transported to the laboratory where they were extracted on the same day. Oils and greases were extracted 3 times with 30 ml aliquots of 1,1,2-trichloro-1,2,2-trifluoroethane. The solvent was removed under reduced pressure in a rotating evaporator and the amounts of total oil and grease were determined gravimetrically.

Carbamates and ureas (EPA Method 632). One-liter water samples were extracted 3 times each with 30 ml aliquots of methylene chloride. The combined methylene chloride was evaporated to dryness and the sample dissolved in 10 ml hexane and subjected to column chromatography on a 20 mg Florisil column to separate the oil from the carbamate-urea fractions. The oil components were eluted with 200 ml hexane followed by 100 ml 20% ethyl ether in hexane, then 100 ml 20% ethyl ether in hexane followed by 200 ml 40% acetone in hexane. The ether/acetone eluates were combined, evaporated to dryness and then dissolved in acetonitrile or methanol for high-performance liquid chromatographic (HPLC) analysis. High performance liquid chromatography analyses were conducted using a Perkin-Elmer Model 400 unit with an ultra-violet detector (254 nm). Two sep-

arate analysis were conducted on each sample: (1) Using a C-18 column (octadecylsilane bonded to 3 μm silica spheres) 4.6×150 mm and eluted with 1% acetic acid and methanol programmed as follows:

Step	Time (min)	Flow rate (ml/min)	1% acetic acid (%)	MeOH (%)
0	0.5	2.0	95	5
1	20.0	2.0	5	95
2	0.5	2.0	—	100
3	3.0	2.0	—	100
4	1.0	2.0	95	5
5	10.0	2.0	95	5

(2) Using a C-8 column (octyldimethylsilane bonded to 5 μm silica spheres), $4.5 \text{ mm} \times 83$ mm and eluted with acetonitrile and water as follows:

Step	Time (min)	Flow rate (ml/min)	H ₂ O (%)	CH ₃ CN (%)
0	0.5	2.0	82	18
1	9.0	2.0	35	65
2	3.0	2.0	35	65
3	0.5	2.0	82	18
4	6.0	2.0	82	18

Both columns were held in a water jacket which was connected to a circulating, temperature-controlled water bath held at 34°C. (Note: temperature control is critical for consistent retention times.)

Triazines (EPA Method 619). The samples of wash waters were extracted and subjected to column chromatography on Florisil as described for carbamates and ureas. The residues from the ether/acetone eluates were dissolved in ethyl acetate for analysis by gas-liquid chromatography using a Hewlett-Packard 5890 gas chromatograph with a nitrogen/phosphorus detector. A DX-3 capillary column (50% polyethylene glycol, 50% polysiloxane) $30 \text{ m} \times 0.25$ mm id $\times 0.25 \mu\text{m}$ film was used and the carrier gas was helium, maintained at 22 cm/sec. The oven was held at 150°C for 4 min and then programmed at 3°/min to 225°C. The injection port was held at 160°C and the detector at 250°C. The detector output was linked to a Hewlett-Packard 5895 gas chromatography work station for data handling.

Samples which were positive for given triazines were then subjected to gas-chromatography-mass-spectroscopy. For the latter, a Hewlett-Packard 5890 gas chromatograph attached to a Hewlett-Packard 5970 quadrupole mass spectrometer was utilized. The column and gas chromatography conditions were as above. Spectra were recorded on a Hewlett-Packard 200 work station.

RESULTS AND DISCUSSION

Oil and Grease. Table 1 shows the concentration of oil and grease. These values represent the total amounts of oil and grease substances from vehicles plus any residues of larvicidal oils. In the sumps the concentrations do not reach high values as they float-off with water in the discharge; the sumps in vehicle wash pads averaged 30.2 mg/liter. If overflow from these sumps were not discharged, considerably higher values would be expected. The storage tank sample had the lowest level of oil and grease and the pit the highest. The pit represents a dead-end condition where oils concentrate on the surface of a much larger water volume; only 2 of the 6 samples had very high values and they were in an area where an oil slick had concentrated, apparently due to wind.

If these waters were to be recycled into spray diluent, it appears likely that an oil/water separation would first be necessary.

Carbamates and Ureas. The following standards were run using the HPLC methods described: Fenuron, Tebuthiuron, Monuron, Bromacil, Baygon, Propham, Linuron and Chloroprotham. All of these separated on the C8 column but Monuron and Bromacil eluted together from the C18 column and so did Protham and Tebuthiuron. Copies of the chromatograms will be provided to interested persons, following request. Linuron, which was not present in any of the wash waters collected at the various mosquito abatement districts, was used as an internal standard and assigned a relative retention time of 1.00; relative retention times for all other compounds were then calculated by dividing their actual retention times by that of Linuron, which was added to each sample analyzed.

Diuron was found in 3 of the 6 wash water samples (Table 2), and since it is used for controlling weeds, this result is not surprising. Protham was found in one of the 6 locations. There

Table 1. Total oil and grease in the wash water samples of 6 central California mosquito abatement districts (in ppm).

MAD no.	No. 1-liter samples	Average concentrations	Range
1	4	21.9	19.3-27.2
2	6	58.9	32.5-83.6
3	4	10.8	9.3-11.9
4	6	2338.6	12.7-2338.6*
5	4	23.3	20.6-27.7
6	4	16.6	11.9-20.2

* An oil slick was present in two areas of the pit which had values of 2,063.3 and 11,883.2.

Table 2. Carbamate, urea and triazine herbicides found in the wash waters of 4 central California mosquito abatement districts (in ppm).^a

MAD no.	Diuron	Propham	Simazine	Atrazine
1		0.12		
2	0.02		0.003 ^b	0.004 ^b
3	0.24		0.14 ^c	
4	0.11		0.015 ^c	

^a Herbicides were not detected from MADs nos. 5 and 6.

^b Identity not confirmed following gas-chromatography-mass spectroscopy analysis.

^c Identity confirmed following gas-chromatography-mass spectroscopy analysis.

were no carbamates or ureas identified in 2 of the locations.

Triazines. The tentative identifications of triazines using the nitrogen/phosphorus detector revealed Simazine in 3 of the 6 sampling locations and Atrazine in another (Table 2). The presence of Simazine was not surprising as some mosquito abatement districts utilize it for weed control within their yards. The identities of Simazine in MADs nos. 3 and 4 were confirmed by mass spectroscopy but neither Simazine or

Atrazine could be confirmed in MAD no. 2, even by selective ion monitoring of characteristic ions (m/z 203, 201, 186 and 173 for Simazine and 217, 215, 202, 200 for Atrazine).

CONCLUSIONS

In situations where herbicide residues are considered high enough to pose a phytotoxicity problem in sprays, sufficient dilution of the wash water would be essential. Also, where oil levels are sufficiently high, e.g., MAD no. 4, an oil/water separator would be needed to prevent gum from forming and then clogging the spray system. It is essential that residues be determined prior to any consideration of wash water recycling. Based on these studies the recycling concept appears to be a reasonable means of disposal for some mosquito abatement programs without a high risk of phytotoxicity problems.

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