Recovery of Trichlorfon (Dylox®) and Carbaryl (Sevin®) in Songbirds Following Spraying of Forest For Gypsy Moth

by
DAVID A. KURTZ
Pesticide Research Laboratory
Pennsylvania State University
University Park, Pa. 16802
and
CLINTON R. STUDHOLME
Division of Wildlife Services
U. S. Dept. of Interior
University Park, Pa. 16802

Gypsy moth (*Porthetria dispar*) infestations have been moving west from northeast coast infestations in the last few years. While numerous studies are being conducted for biological control, short-lived chemical pesticides are being considered and used. In fact, the current strategy for gypsy moth control is an integrated method involving biological, chemical and other methods. Trichlorfon [O,O-dimethyl(1-hydroxy-2,2,2-trichloroethyl)phosphonate (Dylox/Dipterex)] and carbaryl [1-naphthyl N-methylcarbamate (Sevin)] are two biodegradable chemical pesticides. This study was concerned with the quantity of trichlorfon and carbaryl that was picked up by songbirds either by contact or ingestion of food materials in a sprayed area. Baltimore orioles, crested flycatchers, and blue jay were used in the trichlorfon study. These birds are referred to as canopy-feeders (as opposed to ground feeders). The carbaryl study used towhees which are considered ground feeders.

The analysis for trichlorfon is the sum of both the parent compound and its metabolite. Trichlorfon in alkaline soil degrades to DDVP (dimethyl-2,2-dichlorovinyl phosphate). The sum of both these was determined in the gas chromatographic analysis. Carbaryl degrades *in vivo* to 1-naphthyl N-hydroxymethylcarbamate, 4- and 5-hydroxy 1-naphthyl N-methylcarbamate, and 1-naphthol. All these metabolites are analyzed with the parent in the colorimetric procedure used herein. However, a large portion of the metabolites formed from carbaryl is water soluble and is excreted by the birds. Most (75-80%) of the carbaryl administered to chickens is excreted in the urine (PAULSON 1970). Thus it is unlikely that our analysis includes much more than carbaryl itself.

EXPERIMENTAL

Spraying and Sample Collection. The trichlorfon study was done in southern Monroe County in eastern Pennsylvania. Birds were collected in a 150 acre area in about the center of the 2200 acre spray area. Trichlorfon was sprayed on May 24, 1972 at a rate of 1 lb/A. Pre-spray collection was done one day in advance and post-spray collection three days later. The potential exposure time was 76 hours.

The carbaryl study was done in southeastern Pike County, also in eastern Pennsylvania. Post-spray birds were collected in the center of the 2200 acre spray area. Carbaryl was sprayed on June 8, 1972 at a rate of 1 lb/A. Control birds were collected in a

Bulletin of Environmental Contamination & Toxicology,
Vol 11, No. 1 © 1974 by Springer-Verlag New York Inc.

non-sprayed area 5 to 6 miles distant 1 and 2 days after spraying in a presumably non-sprayed area. Sprayed birds were collected 3 days after spraying. The birds were collected by being shot with fine shot, field-stored in dry ice, and subsequently stored in a laboratory freezer. The maximum holding time was 23 days.

Sample Handling. Samples were kept frozen until extracted. For trichlorfon, the time amounted to 17 and 21 days for control birds and 19 and 23 days for sprayed birds. For carbaryl storage time was 4 days for "pre-spray" birds and 10 days for post-spray birds. While frozen, the feathers, skin, wings, legs, tail, neck, and head from each bird were removed by hand. The remaining torso was ground twice in a hand meat grinder while covered with granular dry ice. The samples were preserved at freezer temperatures in covered plastic-coated cups. A 500-800 mg sample was taken by quartering to that size; the operation was performed in the freezer.

Extraction: Trichlorfon. Extraction procedures for trichlorfon followed those of OLSON (1969) except that they were modified to micro size using procedures developed by THOMPSON (1971). This method used a tissue grinder to homogenize a 500 mg sample in the presence of a solvent. Other operations were performed in a 25 ml test tube with transfer of liquids by disposable bulb pipets. Methylene chloride was used in place of chloroform.

The extracted samples were stored in acetone solution because trichlorfon volatilizes when in pure form. Immediately prior to gas liquid chromatographic (GLC) analysis, the samples were gently evaporated with nitrogen flow to dryness. The residue was dissolved in 40 ul of acetone (pesticide quality) and GLC analysis was conducted with a 5 ul aliquot.

Extraction: Carbaryl. Extraction of carbaryl followed AOAC (1970) procedures except that the color developing reagent used was one-fourth concentration requiring an 8 min developing time. For other extractions the micro procedures of THOMPSON were used.

Gas Chromatographic Quantitation of Trichlorfon. Quantitation of trichlorfon samples was accomplished in a 160 cm, 0.35 cm I.D. glass U-column containing 15% XF-1150 on 60/80 mesh Chromasorb WHP. The Microtek MT-220 chromatograph was equipped with a flame photometric detector in the phosphorus mode. Operating temperatures for the column were 270°C inlet, 155°C oven (isothermal), and 191°C detector. The column flow rate of nitrogen gas was 82 ml/min. The flame flow rates were 200 ml/min for hydrogen, 55 for air, and 12 for oxygen.

Under these conditions the retention times for dimethyl phosphite and DDVP were 125 and 420 seconds, respectively.

The high inlet temperature, 270°C, assured thermal degradation to both dimethyl phosphite and DDVP. The sum of these two moieties was used for analysis since the ratio between them was not constant.

Peak quantitation was done by a combination of electronic integration (Infotronics Model CRS-100) and polar planimetric methods.

The sensitivity of the GLC system was found to vary greatly even during the course of injecting only a few samples. Two procedures were followed to get reasonably accurate analyses: (1) The column was conditioned by 6 injections of standard and sample extract material. Two injections were 125 ng trichlorfon alternated by 2 each of extract and 20 ng trichlorfon standard. This seemed to sensitize the column to a usable point. (2) During the course of the GLC analysis the trichlorfon sensitivity was monitored by 5 injections of 5 ng trichlorfon and 3 injections of 20 ng trichlorfon. Figure 1 shows the trend of these 5 ng injections. Figure 2 shows both the linearity and the response range. The linearity is shown by response values for 1.0, 2.0, 3.0 and 5.0 ng trichlorfon injected. The shaded areas shows the response range during the course of the gas chromatographic analysis. The range was determined by 5 ng injections.

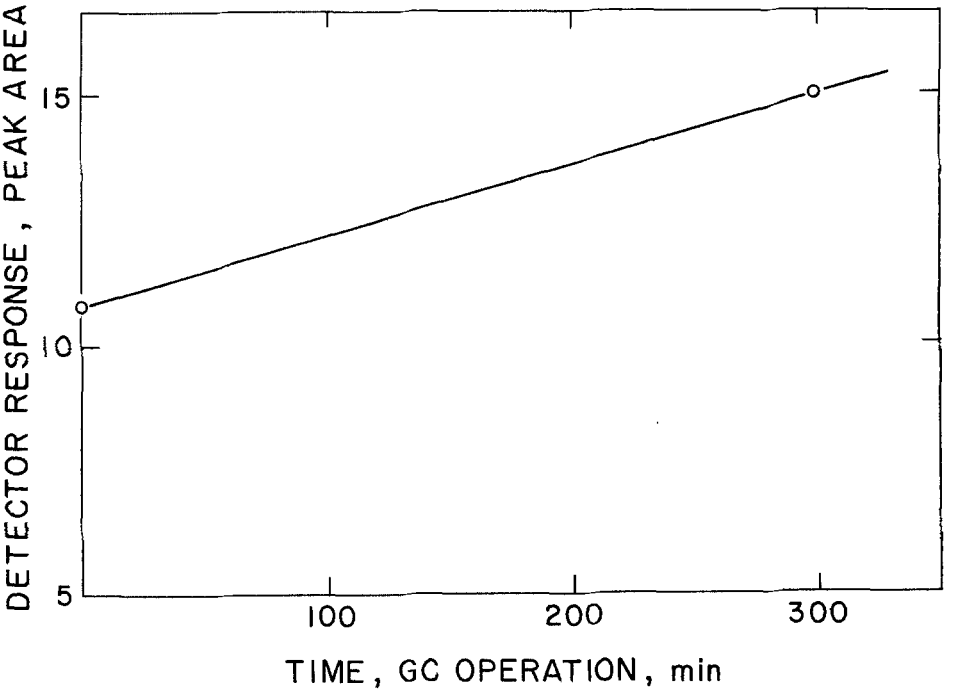

Figure 1. The sensitivity of the GLC detector for 5 ng trichlorfon during injection of standards and samples.

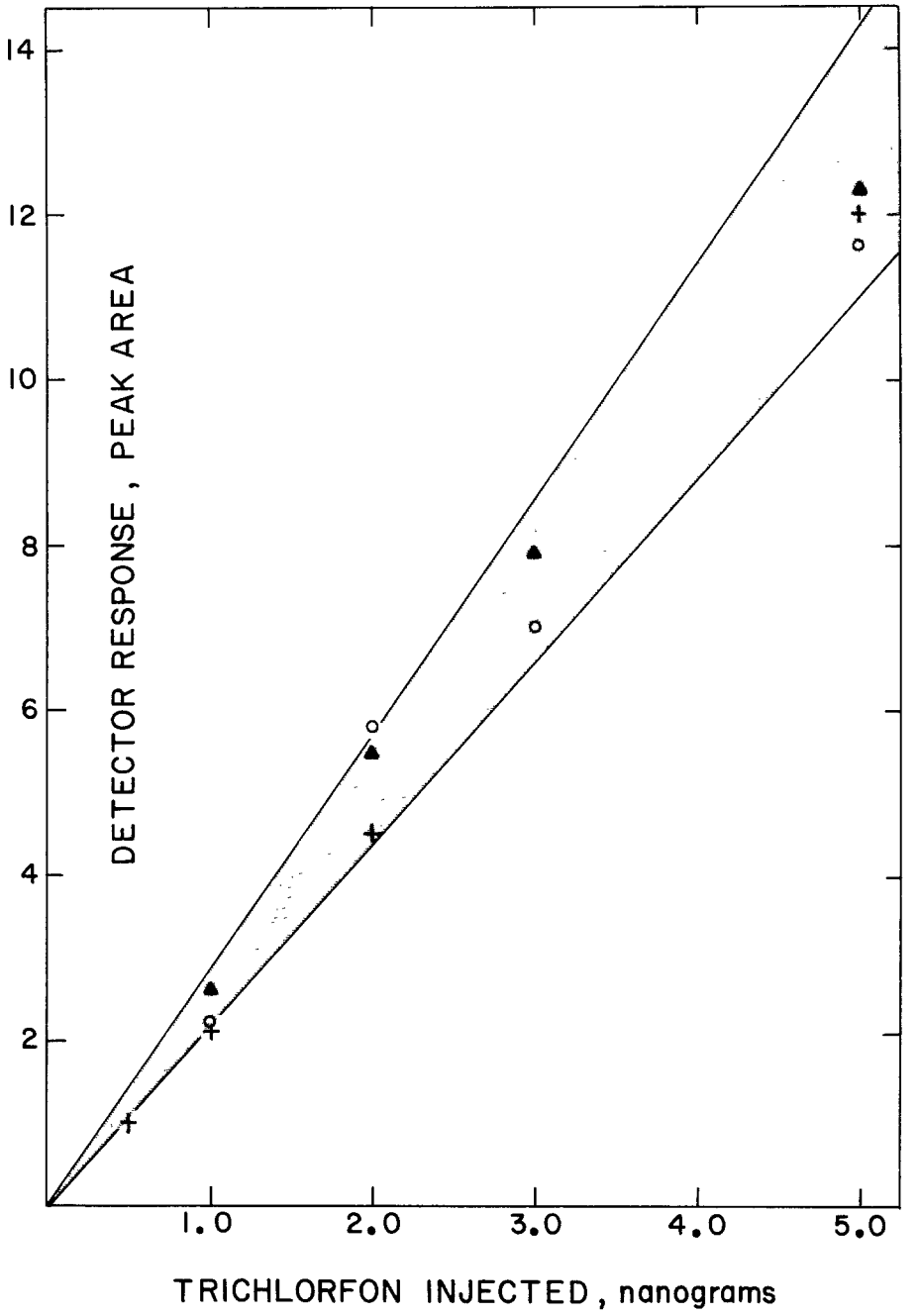

Figure 2. Range of detector response versus trichlorfon injected. Peak area is sum of both phosphorus peaks.

RESULTS AND CONCLUSIONS

Analytically detectable amounts of trichlorfon were found in all songbirds collected after spraying while no pesticide was found in the control birds. The minimum detectably amount analyzed was 0.001 ppm (ug/g). The amounts found (Table 1) were 0.001 ppm for the blue jay, 0.003 to 0.01 ppm for the crested flycatchers, and 0.005 to 0.04 ppm for the Baltimore orioles. These amounts were for the sum of the trichlorfon parent compound and its metabolite DDVP.

TABLE 1

Trichlorfon in Songbirds Sprayed and Control Areas

	Control			Sprayed		
Sample	#	Torso wt.g.	Trichlorfon ug/g	#	Torso wt.g.	Trichlorfon ug/g
Baltimore oriole	1	20	0[1]	1	18	0.005
				1	18	0.013[2]
	2	∿20	0	2	22	0.03
	3	∿20	0	3	17	0.04
	4	∿20	0	4	15	0.03
	5	∿20	0			
Crested flycatcher	1	20	0	1	20	0.01
	2	∿20	0	2	23	0.01
Blue jay				1	52	0.01

[1]Sensitivity of analytical method was 0.001 ug/g. These values could be recorded as 0.001 ug/g. [2]Repeat analysis.

By species, it was evident that the orioles contained more than the flycatchers which in turn contained more than the jay.

The amount of trichlorfon these birds contained can be considered to be small even though the samples were taken near to the time of maximum concentration of the spray. The USDA (1970) has no registered uses for trichlorfon on poultry, but it allows 0.1 ppm in beef (and 0.01 ppm in milk). In addition, a period of 14 days is required before slaughter. For vegetables, the Department indicated for applications of from 1.0 to 1.5 lb/A. the usual tolerance is 0.1 ppm. This is true for beets, cabbage, corn, lettuce and peppers. Usually a minimum of 14 days is required after spraying for harvest. The residues found are clearly within these values showing that the environmental impact on wildlife for this spraying should be small.

For carbaryl this case is similar but even more convincing. In these analyses no carbaryl was detected in the post-spray birds (Table 2). The minimum amount of detectability was 0.1 ppm (ug/g). The analysis showed three samples that contained trace amounts,

but at the same time two control birds contained trace amounts. These amounts were mainly for unmetabolized carbaryl.

TABLE 2

Carbaryl in Songbirds Sprayed and Control Areas; All Towhees

	Control		Sprayed	
Sample #	Torso wt. g.	Carbaryl	Torso wt.	Carbaryl
1	26	0	24	tr
2	24	tr[1]	24	tr
3	25	0	24	0
4	23	tr	22	0
5	21	0	24	tr

[1]tr was 0.1 to 1.0 ug/g of sample.

The amounts of carbaryl that the towhees contained were small even though the samples were taken near to the time of spraying. The half-life of carbaryl in soil has been measured to be one week (UNION CARBIDE CO., 1970). Compare with the USDA (1970) tolerance data: the tolerance of carbaryl in game birds and chickens is 5 ppm. Dosages allowed are 0.05 lbs/100 birds. Waiting period after application is 7 days. The tolerance for vegetables varies between 5 and 10 ppm with dosages of 1-2 lbs/A. Hence from all standpoints discussed the spraying of carbaryl should have at most a small impact on birds at the sprayed area. It must be remembered that towhees are ground feeders and that only a small amount of carbaryl may have passed through the trees to the ground.

Pesticide recoveries for trichlorfon were found to be very good (89%) and for carbaryl to be adequate (62%) (Table 3).

TABLE 3

Pesticide Recoveries

Trichlorfon from Beef Muscle*		Carbaryl from Bird Tissue	
Added ng	Recovery %	Added ug	Recovery %
150	91.5	25	69
150	87.2	25	63
		25	55
Averages	89		62

*Porterhouse steak from Penn State Meats Laboratory

ACKNOWLEDGMENT

The author gratefully acknowledges the technical aid in the analysis given by Ida. M. Harris and Susan K. Gage. This work was supported in part by the Pennsylvania Agricultural Experiment Station (Journal Series No. 4323), authorized for publication October 31, 1972.

REFERENCES

AOAC: OFFICIAL METHODS OF ANALYSIS, 11th Ed., Washington, D. C.: Section 29.066, p. 493 (1970).

OLSON, T. J.: Determination of Residues of Trichlorfon in Bovine Animal Tissues by Thermionic Emission Gas Chromatography, Chemagro Corp., Kansas City, Mo.: Report No. 24808 (1969).

PAULSON, G. D. *et al.*: J. Agr. Food Chem. 18(No. 1), 110 (1970).

THOMPSON, J. F., Ed.: Analysis of Pesticide Residues in Human and Environmental Studies, Perrine Primate Res. Labs., Environmental Protection Agency, Perrine, Fla.: Jan. 4, 1971.

UNION CARBIDE CORP.: Technical Information of Sevin, New York (1968).

UNITED STATES DEPARTMENT OF AGRICULTURE, Summary of Registered Uses, May 22, 1970.