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PHOSPHAMIDON RESIDUES IN FOREST ENVIRONMENTAL SAMPLES

by

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INTRODUCTION

Phosphamidon [(C_{10} H_{19} Cl NO_5 P) (2-Chloro-N,N-diethyl-3-hydroxycrotonamide dimethyl phosphate)] is a broad-spectrum systemic insecticide comprising of a mixture of *cis* - (or β) and *trans* - (or α) isomers in the proportion 73:27 (Gunther 1971). For the past few years, the chemical has been used extensively to control spruce budworm *Choristoneura fumiferana* (Clemens) infestation in Canadian forests. During the 1976 spray grogram, *ca* 215,000 hectares of New Brunswick and *ca* 60,000 hectares of Quebec forests have been sprayed with the insecticide as an aqueous formulation, at the operational level of 0.14 to 0.28 kg AI/ha. At the beginning of the spray program, a collaborative arrangement has been worked out among the Pesticide Chemistry Section at the Chemical Control Research Institute (CCRI), the Environmental Impact Section of CCRI and Ciba-Geigy Canada Ltd., the manufacturer and distributor of the insecticide, to monitor the spray program and study the phosphamidon residue levels present in various forest environmental samples collected after the spray application in the provinces of Quebec and New Brunswick. The present report embodies the residue data obtained by the Pesticide Chemistry Section at CCRI on 47 samples received from Ciba-Geigy through the Environmental Impact Section at CCRI.

MATERIALS AND METHODS

All the 47 samples analysed and recorded in this report were supplied by Dr. C.H. Buckner and Mr. B. McLeod of the Environmental Impact Section at CCRI. The foliage and avion samples were stored in glass jars containing ethyl acetate. The fish samples received were in the frozen state and the formulations supplied were in brown bottles kept at room temperature. The breakdown of the 47 samples analysed according to various types are as follows:

Foliage (spruce and fir)	=	36
Birds (sparrows)	=	2
Fish	=	4
Formulations (Tech. material)	=	5
Total	=	47

The analytical method used for the substrates involved solvent extraction, partitioning, charcoal-Celite column cleanup and final quantitation of phosphamidon isomers by a flame photometric (P mode) gas-liquid chromatography (GLC). Full details of the analytical methods used in the quantitation of phosphamidon isomers present in the forest environmental samples have been published elsewhere (Sundaram 1974, 1976). The technical concentrates of the insecticide were analysed by a GLC method similar to that used for methoxychlor (tech.) analysis (Sundaram 1975).

All organic solvents used in the analytical studies were either pesticide grade or freshly distilled in glass. The chemicals and glassware used were free from any detectable insecticide contamination.

Table 1

Analysis of Spruce Foliage for Phosphamidon From Acadia Forest, New Brunswick - 1976 Spray Program

Sample No.	Supplied ID No.	CCRI No.	Sample Description			Time Post-spray (hrs)	Number of Application	Phosphamidon ppm		
			Block	Plot	Date			Trans	Cis	Total
1	108	25/76/377/435	1	1	JN 28	PRE	-	N.D.	N.D.	N.D.
2	107	25/76/378/436	1	2	JN 28	PRE	-	N.D.	N.D.	N.D.
3	116	25/76/379/437	2	3	JN 28	PRE	-	N.D.	N.D.	N.D.
4	106	25/76/380/438	2	4	JN 28	PRE	-	N.D.	N.D.	N.D.
5	115	25/76/381/439	1	1	JL 5	18	1	0.14	0.23	0.37
6	113	25/76/382/440	1	2	JL 5	18	1	0.14	0.54	0.68
7	111	25/76/383/441	2	3	JL 5	18	1	0.28	1.08	1.36
8	119	25/76/384/442	2	4	JL 5	18	1	0.11	0.30	0.41
9	109	25/76/385/449	Control		JL 6	36	1	N.D.	N.D.	N.D.
10	110	25/76/386/448	Control		JL 6	5	2	N.D.	N.D.	N.D.
11	105	25/76/387/443	1	1	JL 6	6	2	0.11	0.51	0.62
12	118	25/76/388/444	1	2	JL 6	6	2	N.D.	N.D.	N.D.
13	104	25/76/389/445	1	2	JL 6	8	2	0.07	0.59	0.66
14	112	25/76/390/446	1	3	JL 6	4	2	N.D.	0.19	0.19
15	114	25/76/391/447	2	4	JL 6	4	4	N.D.	0.27	0.27
16	101	25/76/392/450	1	1	JL 10	18	3	0.25	0.51	0.76
17	102	25/76/393/451	1	2	JL 10	18	3	0.03	0.27	0.30
18	120	25/76/394/452	2	3	JL 10	18	3	0.10	0.51	0.61
19	130	25/76/395/453	2	4	JL 10	18	3	0.10	0.51	0.61

N.D. Not detected.

Table 2

Analysis of Environmental Samples for Phosphamidon from Chipman, New Brunswick - 1976 Spray Program

Sample No.	Supplied ID No.	CCRI No.	Sample Description					Phosphamidon ppm		
			Type	Plot	Date	Time Post-Spray (hrs)	Ounces per acre	Trans	Cis	Total
20	206	25/76/396/458	Spruce	1	May 29	PRE	-	N.D.	N.D.	N.D.
21	204	25/76/397/460	Spruce	5	May 30	2	2	N.D.	0.02	0.02
22	203	25/76/398/461	Fir	6	May 30	2	2	0.02	0.05	0.07
23	205	25/76/399/462	Spruce	1	May 30	3	3	N.D.	0.02	0.02
24	202	25/76/400/463	Spruce	2	May 30	3	3	N.D.	N.D.	N.D.
25	207	25/76/401/464	Spruce	6	May 14	16	4	0.11	0.43	0.54
26	201	25/76/402/459	Fir	CTL	May 31	24	-	N.D.	N.D.	N.D
27	-	25/76/403/475	Sparrow	6	May 15	24	4	0.08	0.25	0.33*
28	-	25/76/404/476	Sparrow	CTL	May 12	-	-	N.D.	N.D.	N.D.

N.D. Not Detected

* Sparrow weight unknown; ppm calculated from estimated wet weight (in ethyl acetate) as 25 g. per bird.

Table 3

Analysis of Phosphamidon Formulations used in Spray Programs

Sample No.	CCRI No.	Sample Description	% Active Ingredient
29	25/76/405/495	Larose Spray, 1975	84 ± 2
30	27/76/406/496	1976 Spray Program	88 ± 2

Table 4

Analysis of Foliage Sample for Phosphamidon from Quebec 1976 Spray Program

Sample No.	CCRI No.	Sample Description	Phosphamidon ppm		
			Trans	Cis	Total
31	25/76/407/477	Balsam Fir, Prespray, Control Plot 211, La Tuque, Quebec, April 28, 1976.	N.D.	N.D.	N.D.

Table 5

Analysis of Phosphamidon Samples from 1976 Quebec Spray Program

Sample No.	CCRI ID No.	Sample Description	Phosphamidon Conc. Wt. Percent
	25/76/408/226	Box # 6, St. Honoré, Barrel 530298M - 248	
32		Sample 1	85 ± 2
	25/76/409/227	Box # 7, St. Honoré, Barrel 530298M - 903	
33		Sample 1	89 ± 2
	25/76/410/228	Box # 7, St. Honoré, Barrel 530298M - 831	
34		Sample 1	88 ± 2

Table 6

Analysis of Spruce Foliage for Phosphamidon and Fenitrothion* from Chipman, New Brunswick - 1976 Spray Program

Sample No.	CCRI No.	Sample Description: Plot	Date	Time Post-Spray (hrs.)	Ounces per Acre	Phosphamidon Concn. (ppm) Trans	Cis	Total	Fenitrothion* (ppm)
35	25/76/411/557	-	May 10	PRE+	4 in 12	N.D.	T	T	0.03
36	25/76/412/558	5	May 13	0.33	4 in 12	1.32	2.97	4.29	N.D.
37	25/76/413/559	6	May 13	0.66	4 in 12	1.78	3.39	5.17	N.D.
38	25/76/414/560	7	May 13	1.0	4 in 12	N.D.	N.D.	N.D.	0.05
39	25/76/415/561	8	May 13	1.2	?	N.D.	N.D.	N.D.	0.09
40	25/76/416/562	3	May 13	2.0	3 in 9	1.28	3.84	5.12	N.D.
41	25/76/417/563	4	May 13	2.0	3 in 9	2.11	4.79	6.90	0.06
42	25/76/418/564	1	May 13	2.5	3 in 9	N.D.	N.D.	N.D.	0.04
43	25/76/419/565	2	May 13	2.5	3 in 9	0.11	0.20	0.31	0.03

+ Pre - Prespray sample
N.D. - Not detected
* - Fenitrothion was not sprayed in 1976. Results indicate the persistence of the material from an earlier spray operation.

Table 7

Analysis of Fish Samples for Phosphamidon from Bonaventure River - 1976 Spray Program

Sample No.	CCRI No.	Sample Description			Phosphamidon Concn. (ppm)		
		Type	Total Weight (gm)	Sample Weight (gm)	Trans	Cis	Total
44	25/76/420/545	Smelt	34.3	20.0	N.D.	N.D.	N.D.
45	25/76/421/546	Smelt	77.9	20.0	N.D.	N.D.	N.D.
46	25/76/422/547	Smelt	15.1	15.1	N.D.	N.D.	N.D.
47	25/76/423/548	Smelt	31.6	20.0	N.D.	N.D.	N.D.

N.D. Not detected.

RESULTS AND DISCUSSION

Phosphamidon residues found in the conifer (spruce and fir) foliage samples collected during the pre- and post-spray periods are given in Tables 1, 2, 4 and 6. Residue levels of the insecticide found in bird and fish samples are recorded in Tables 2 (Sample Nos. 27 and 28) and 7 respectively. The weight percent of the active ingredient present in the technical materials analysed are given in Tables 3 and 5. All residue concentrations present in the substrates are expressed in units of ppm (µg/g) on the basis of wet weight of the material analysed. The recovery studies for the insecticide isomers conducted on spiked samples of foliage, fish and bird tissues, using the analytical method published, showed consistently above 80% for 20 g level of the substrate with the minimum detection limit of 0.02 ppm. The deviation from the mean in the weight percent for the formulations studied were *ca* 2%.

None of the foliage samples collected during the prespray period as well as the samples from the control plots contained any detectable levels of phosphamidon. The concentration of the phosphamidon in the post-spray samples varied widely but generally decreased with time probably due to common factors such as weathering, breakdown and growth dilution. Usually the amount of the *cis* (or β) isomer compared to the *trans* (or α) form found in the foliage was lower in relation to their occurrence in the technical material (ratio *cis* : *trans* 2.7 : 1.0). Some of the foliage samples analysed (Table 6) contained detectable levels of fenitrothion (0.09 to 0.03 ppm) although the area has not been sprayed with the chemical during the 1976 spray season.

One of the bird (sparrow) samples analysed contained 0.33 ppm of phosphamidon (see the footnote in Table 2) indicating that it had been exposed to the spray cloud. The weight percent concentration of the five phosphamidon technical materials analysed (Tables 3 and 5) ranged from 84 to 89 giving an average value of 87 ± 2.

The monitoring program undertaken by the Environmental Impact Section at CCRI and the Ciba-Geigy Canada Ltd. for the 1976 phosphamidon spray program in the provinces of New Brunswick and Quebec is a very useful venture and it is hoped that this program would be continued as long as this long-established organophosphate insecticide is used in insect control programs in Canada.

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