The Persistence and Fate of Phosphamidon in a Forest Environment

by I. W. VARTY
Maritimes Forest Research Centre
Department of the Environment
Canadian Forestry Service
Fredericton, New Brunswick, Canada
and W. N. YULE
Chemical Control Research Institute
Department of the Environment
Ottawa, Ontario, Canada

Phosphamidon (2-chloro-N,N-diethyl-3-hydroxycrotonamide, dimethylphosphate) is a relatively long-established organophosphate insecticide. It has been used increasingly since 1963 in aerial sprays, mostly at 210-280 g/ha to control spruce budworm (Choristoneura fumiferana Clemens) in Canadian forests, accumulating to 3 million ha treated. Although a large fund of scientific and practical information is available (GUNTHER, 1971), the distribution, persistence, and fate of phosphamidon have never been studied adequately in the forest environment (cf. DDT and fenitrothion, YULE, 1973; YULE and DUFFY, 1972). This paper describes the first such study made in the summer of 1974, measuring residues in foliage, soil, and water components of a forest stand operationally sprayed with phosphamidon in New Brunswick, Canada.

MATERIALS AND METHODS

Insecticide spraying

The aqueous solution of phosphamidon (Dimecron^{R}) was sprayed by a team of three Grumman Avenger TBM aircraft in formation on a normal operational run. The application rate was 210 g phosphamidon/1.4 ℓ water/ha through Diaphragm Teejet nozzles, producing a fine spray cloud with droplets mostly in the 50-100 μ range. Spraying took place about 0730 h on 31 May 1974 in York County, New Brunswick; the wind was southeasterly at 5-8 kph, and the spray settled well. The weather was sunny, dry, and mild (min. 2°C, max. 20°C) on spray day, and remained mostly sunny during the following week excepting light showers on 1 and 5 June.

Spray block 318 was selected as the study site because of typical fir-spruce forest cover (balsam fir Abies balsamea (L.) Mill., red spruce Picea rubens Sarg., white spruce P. glauca (Moench) Voss, red maple Acer rubrum L., trembling aspen Populus tremuloides Michx and white birch Betula papyrifera Marsh). The conifers were severely infested by spruce budworm, and had been defoliated in preceding years.

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Field sampling

Samples were collected on day 0 (pre-spray, 28 May) and thereafter in a geometric progression beginning day 1 (6 h postspray, 31 May), then on days 2, 4, 8, 15, 33, 64 and 130 (7 Oct.). The sampled materials were (1) balsam fir buds or shoots of the current year (flushing in 1974), (2) 1-year-old balsam fir foliage (flushed in 1973), (3) spruce buds or shoots of the current year, (4) 1-year-old spruce foliage, (5) red maple foliage, (6) soil (with litter) from the fir-spruce stand, (7) water from a small, shallow, fast-flowing stream.

The conifer foliage and soil samples were collected along a 400 m transect across the spray swath. Ten fir trees and ten spruce trees (five red spruce + five white spruce) were chosen as sample trees and used throughout the season; one branch was cut from the midcrown of each tree, and approximately 10 g foliage of each age class (1974, 1973) were clipped from each branch. 10 g red maple foliage were clipped from each of ten sample trees in a scattered stand 400 m distant from the conifer transect. The soil and overlying litter were collected by sampling to a depth of 15 cm with a Wisconsin auger (core diam. 2 cm); 20 samples were collected in open sites near each fir and spruce tree, and mixed in a plastic bag for transport to the laboratory. It was a shallow, acidic, organic top soil typical of fir-spruce forest. The water was collected from the stream at a single point 1500 m outside the sprayed area of the block; however, the tributaries which supplied the stream were inside the sprayed area. On each collection date, a sample in excess of 1 ℓ was collected in a dark glass bottle, and transported cool and dark to the laboratory.

Processing of samples

Each 100 g (fresh weight) sample of each foliage category was placed immediately in a quart Mason jar with 100 ml pesticide-grade acetonitrile (Caledon Laboratories, Georgetown, Ont.); the jar was sealed with an aluminum-foil-lined screw cap and stored in the dark at 4°C for 3 months. Each soil sample was prepared by screening stones and twigs (#10 sieve, 2 mm mesh), calculating the fraction so removed. 100 g of sieved material was stored with 100 ml acetonitrile in a quart Mason jar at 4°C. In foliage and soil samples, the percentage dry matter was determined from a 10 g aliquot.

After the pH was recorded, 1 ℓ samples of water were extracted twice with pesticide-grade chloroform within 3 h of collection; then the extracts were dried with anhydrous Na_2SO_4 and stored as 100 ml samples in bottles shielded by aluminum foil, at 4°C.

Analysis

Several standard methods of organophosphorous analysis were tried with forest soils and foliage fortified with phosphamidon, to measure recoveries and assess GC backgrounds (VOSS et al. 1971; WESTLAKE et al. 1973; YULE and DUFFY, 1972). None of these was satisfactory as described, and a modification of the CIBA method which was reasonably convenient, and gave recoveries of at least 80 percent α and β phosphamidon and an acceptable background for GC and analysis with all the types of forest samples, was finally adopted for this work.

A summary of the method for foliage and soil is given here. Reference should be made to VOSS et al. (1971) for details of the original standard method for plant materials.

A further 100 ml acetonitrile was added to the Mason jar containing the original 100 g sample and this was attached to a Sorvall Omni-Mixer using an adaptor, and extracted for 5 minutes at high speed. A volumetric aliquot equivalent to 20 g sample was filtered using Sharkskin paper and a Buchner funnel, the residue was rinsed with acetonitrile and the filtrate transferred to an evaporating flask. The acetonitrile extract (containing 20-30 percent water) was evaporated slowly under light vacuum to a volume of less than 10 ml, 40 ml distilled water was added, and the aqueous extract was partitioned 3 times with 50 ml chloroform in a separating funnel.

The chloroform extract was dried with Na_2SO_4, and evaporated to a volume of 3 ml and made up to 10 ml with hexane, the process being repeated 3 times. The hexane concentrate was then added to a chromatographic column pre-wetted with hexane containing 2 g Woelm silica gel Activity Grade I (ICN Pharmaceuticals Inc., Cleveland, Ohio), sandwiched between two layers of 5 g Na_2SO_4. The sample was first eluted with 30 ml 50 percent hexane ethyl acetate (discarded), then 50 ml ethyl acetate (collected). The eluant was evaporated to 3 ml and made up to 10 ml with hexane before analysis by gas chromatography, as follows:

Instrument: Hewlett Packard 7610A.
Detector: Tracor flame photometric; 526 mμ filter.
Temperatures °C: Injector 235, oven 185, detector 195.
Gas flow rates ml/min: Nitrogen 80, Air 50, Oxygen 18, Hydrogen 150.
Column: 4' x 1/4" U-shaped, glass packing, Chromosorb W. HP 80-100 mesh; loading, 5 percent OVI.
Electrometer settings: Range 103, attenuator 32.
Recorder: Tracor model 17503A, span 1mV, chart rate 0.5 in/min.
Retention times: Trans phosphamidon (α) 2.68 min (0.81), cis phosphamidon (β) 3.31 min (1.00).

TABLE 1 Phosphamidon deposits and residues in spruce buds/new shoots (1974 foliage)

Days Relative to Application	Phosphamidon (ppm fresh weight)			Total (ppm oven-dry weight)
	α	β	Total	
Pre-Spray	0.0	0.0	0.0	0.0
Spray (1)	1.716	1.642	3.358	4.640
2	0.396	0.375	0.771	1.010
4	0.331	0.375	0.706	0.954
8	ND	ND	—	—
15	ND	ND	—	—
33	ND	ND	—	—
64	0.056	0.063	0.119	0.173
130	ND	ND	—	—

TABLE 2 Phosphamidon deposits and residues in 1-yr-old spruce shoots (1973 foliage)

Days Relative to Application	Phosphamidon (ppm fresh weight)			Total (ppm oven-dry weight)
	α	β	Total	
Pre-Spray	0.147	0.147	0.294	0.470
Spray (1)	1.175	1.113	2.288	3.642
2	0.433	0.475	0.908	1.407
4	0.216	0.306	0.522	0.831
8	0.163	0.175	0.338	0.538
15	0.078	0.138	0.216	0.339
33	ND	0.090	0.090	0.135
64	ND	0.029	0.029	0.044
130	ND	ND	—	—

ND = not detectable < 0.038 α, < 0.012 β ppm fresh weight.

TABLE 3 Phosphamidon deposits and residues in fir buds/new shoots (1974 foliage)

Days Relative to Application	Phosphamidon (ppm fresh weight)			Total (ppm oven-dry weight)
	α	β	Total	
Pre-Spray	0.0	0.0	0.0	0.0
Spray (1)	1.300	1.075	2.375	3.527
2	0.750	0.538	1.288	1.803
4	0.663	0.538	1.201	1.698
8	0.206	0.150	0.356	0.441
15	ND	ND	—	—
33	ND	ND	—	—
64	ND	ND	—	—
130	ND	ND	—	—

TABLE 4 Phosphamidon deposits and residues in 1-yr-old fir shoots (1973 foliage)

Days Relative to Application	Phosphamidon (ppm fresh weight)			Total (ppm oven-dry weight)
	α	β	Total	
Pre-Spray	0.0	0.114	0.114	0.180
Spray (1)	5.875	5.250	11.125	17.590
2	0.200	0.313	0.513	0.802
4	0.888	0.413	1.301	2.052
8	0.450	0.138	0.588	0.936
15	0.114	0.046	0.160	0.251
33	ND	ND	--	--
64	ND	ND	--	--
130	ND	ND	--	--

ND = not detectable < 0.038 α, < 0.012 β ppm fresh weight.

TABLE 5 Phosphamidon deposits and residues in red maple foliage

Days Relative to Application	Phosphamidon (ppm fresh weight)			Total (ppm oven-dry weight)
	α	β	Total	
Pre-Spray	0.0	0.0	0.0	0.0
Spray (1)	4.675	4.675	9.350	12.139
2	1.063	0.813	1.876	2.234
4	0.813	0.613	1.426	1.856
8	0.294	0.163	0.457	0.598
15	0.091	0.066	0.157	0.208
33	ND	ND	--	--
64	ND	ND	--	--
130	ND	ND	--	--

TABLE 6 Phosphamidon deposits and residues in forest soil (fir-spruce stand)

Days Relative to Application	Phosphamidon (ppm fresh weight)			Total (ppm oven-dry weight)
	α	β	Total	
Pre-Spray	0.0	0.0	0.0	0.0
Spray (1)	0.083	0.042	0.125	0.216
2	0.180	0.131	0.311	0.529
4	0.145	0.047	0.192	0.322
8	ND	ND	--	--
15	ND	ND	--	--
33	ND	ND	--	--
64	ND	ND	--	--
130	ND	ND	--	--

ND = not detectable < 0.038 α, < 0.012β ppm fresh weight.

Separate calibrations were made for trans (α) and cis (β) phosphamidon, using a single analytical standard of 98% purity (25/73) supplied by CIBA-Geigy Co., Switzerland.

RESULTS AND DISCUSSION

The results of this investigation (Tables 1-7) demonstrate that phosphamidon sprays produce deposits and residues which penetrate various superficial aspects of the biome but are short-lived in the forest environment; the half-lives in several types of foliage, soil, and water are only a few days. A few erratic results are apparent, for example in pre-spray measurements (Tables 2 and 7), which may have been due to spray drift and contamination from other spray operations in the vicinity.

The residues were apparently less persistent on flushing buds of spruce and fir (Tables 1 and 3) than on 1-year-old foliage (Table 2) and 4). The difference may be an artifact derived from the "dilution" of the deposit on new shoots due to their rapid growth in the weeks following spray date.

The presence of residues on current spruce shoots on Day 64 (Table 1) is an anomaly for which no explanation can be proffered, unless it is the result of an error in sample labelling.

Some of the curves of persistence are not as smooth as might be expected (e.g. Table 4). Exceptionally high or low deposits may reflect the high variability of within-tree deposit known to occur from aerial spraying. Branches from 10 trees across the swath may not have been enough to discount such variability.

The briefest persistence occurred in stream water; no phosphamidon was detected after Day 2 (Table 7). These values incorporate the effects of dilution and transport out of the sample plot, as well as the effects of breakdown of resident insecticide. The peak value on Day 1, 19.25 ppb, and persistence thereafter, is roughly in agreement with peaks and persistences of the organophosphate insecticide fenitrothion found in forest streams following aerial sprays (Eidt and Sundaram 1975).

Indeed, the deposits and persistences of phosphamidon in these tree, soil, and stream sites are quite similar to the values for fenitrothion in similar sites reported by YULE and DUFFY (1972).

Compared to DDT and fenitrothion, the other two insecticides that have been used on a large scale for spruce budworm control in Canadian forests, phosphamidon appears to be of greater concern to ecologists as an acute poison (ref. FOWLE etc.), but of less concern as a persistent and cumulative residue (YULE, 1973; YULE, 1974). It is also apparent from these results

TABLE 7 Phosphamidon content of fast-running stream water

Days Relative to Application	Phosphamidon (Ug/ℓ) ppb α	β	Total	Water pH
Pre-spray	0.0	0.425	0.425	6.2
Spray (1)	10.375	8.875	19.250	6.2
2	6.55	5.373	11.925	5.9
4	ND	ND	--	6.2
8	ND	ND	--	6.5
15	ND	ND	--	6.9
33	ND	ND	--	6.1
64	ND	ND	--	6.9
130	ND	ND	--	6.3

ND = not detectable, < 0.035 ppb α, < 0.016 ppb β

(Tables 1-7), in comparing isomer ratios of residues with the technical formulation (β/α : 73/27%) that the cis (β) isomer of phosphamidon generally has a more rapid rate of dissipation in the forest environment than trans-phosphamidon (see also BULL et al. 1967; WESTLAKE et al. 1973), and the differential in toxicity and stability between isomers may be of some significance in determining the ecological impact of phosphamidon in the forest.

This investigation and the analytical methods that were developed for it, have been concerned only with the parent insecticide phosphamidon. Breakdown products have not yet been studied in the forest environment, but common plant metabolites such as desethylphosphamidon and γ-chlorophosphamidon have shown stability characteristics very similar to the parent material in various green plants (VOSS et al. 1971).

Two further observations on the fate of phosphamidon in the forest environment may be related to its greater polarity compared with DDT and fenitrothion. That is, the initial spray deposits of phosphamidon on tree foliage declined rapidly not only due to common factors such as weathering, breakdown, and growth dilution, but probably also by absorption and translocation (and dilution) within the trees (VOSS et al. 1971). Also, in water, phosphamidon spray contamination would decline rapidly due to adsorption and dilution in streams as well as by breakdown and transport.

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