Bull. Environ. Contam. Toxicol. (1991) 46:815–821

Bulletin of Environmental Contamination and Toxicology

Contamination of Ponds by Fenitrothion during Forest Spraying

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Fenitrothion (0,0-dimethyl 0-4-nitro-m-tolyl phosphorothioate) has been the chemical of choice in spray programs directed at forest defoliators in New Brunswick, Canada for over twenty years. Contamination of watercourses by pesticide is an unavoidable aspect of large block spraying. A recent review of the environmental effects of forestry fenitrothion use, indicated that although most watercourse contamination does not cause major biological impact, certain water bodies may be of higher risk (Fairchild et al. 1989). Those are small, still water bodies which are shallow and have reduced forest canopy. Such water bodies are of the type that are most difficult to detect from the air and therefore to protect with buffer zones. There is also evidence which indicates that in ponds with low pH, biological impact may be serious. Studies have indicated that at simulated operational dosage rates, aquatic invertebrate impacts in bog ponds are of such magnitude as to substantially alter energy flows through those ecosystems (Fairchild 1990). It was necessary to determine the contamination of small ponds by forestry insecticides during operational spray programs in order to assess the exposure to lentic biological systems.

MATERIALS AND METHODS

Six ponds were selected within operational spray blocks of the 1989 spruce budworm spray program in New Brunswick. The pond selection criteria were: small size (less than 0.5 ha); easy accessibility; and central location within the spray block. All blocks were scheduled to be treated twice, approximately 5 to 10 days apart. The intent was to monitor surface deposit and initial surface water contamination after each spray; all ponds were not sampled after each spray but ten discrete deposit events were sampled. All blocks were sprayed with a water solution containing 11.0% fenitrothion, 1.5% Dowanol TPM, 1.5% Atlox 3409F and 86.0% water. The total volume of spray solution emitted was 1.46 L/ha, for a nominal application rate of 210 g active ingredient/ha. Spray was applied by Gruman TBM Avenger aircraft equipped with Tee Jet 11010 nozzles. Aircraft height was

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approximately 25 m above the tree canopy and speed was about 280 km/h.

Deposit was collected on 20 cm diameter cellulose filter papers which were clipped to stainless steel plates supported 30 cm above the pond surface by rods attached to styrofoam floats. Six such samplers were distributed over the surface of each pond. Within 15 min of the treatment, filters were retrieved and immersed in 100 mL of hexane until analysis.

One-litre surface water samples (0-1 cm) were also obtained prior to and at 15 min post-spray at the same locations as deposit collectors by immersing a 1-L narrow necked bottle so that one half of the mouth was submerged. In addition, replicate water samples were obtained from each pond outflow at various times, ranging from 15 min to 2 h post spray. The initial extraction (100 mL hexane with vigorous shaking for 5 min) was initiated within one hour of spray. Final extractions were subsequently performed within two weeks of collection and immediately prior to gas chromatographic analysis using flame photometric detection (Department of Environment 1979).

Where possible, foliage samples from balsam fir trees adjacent to the ponds were also collected before and immediately after spray at approximately three-quarters crown height. Sufficient foliage was removed from collected branches to make up a 50-g sample which was immersed in 100 mL of hexane and maintained in a frozen state until analysis.

Measurements were also made of: windspeed and direction at 10 m height (Gill Anemometer Bivane); air and water temperature; and water pH. Pond size, depth and outflow rate were estimated and surrounding vegetation and topography recorded.

RESULTS AND DISCUSSION

Observations from the ground at the time of spraying indicated that the spray aircraft did not stop spraying when approaching any of the ponds and all ponds appeared to receive a direct application. That is normal spray procedure in the province of New Brunswick where spray buffer zones are not required for small water bodies (i.e. non-designated rivers and lentic bodies less than 40 ha in size). Ground observation and review of spray team flight reports indicated that there were perceived problems in flight line alignment or other delivery aspects in 30% of the observed sprays in the immediate location of the pond. Such events may contribute to variable deposit.

The canopy around all ponds was open with no overtopping vegetation that would intercept sprays, preventing direct deposit. Riparian vegetation consisted of short (1-2 m) willow and alder that had no foliage at the time of application. The width of that vegetation zone varied from 2-30 m and was adjoined by mature conifers which were 20-25 m in height. Topography surrounding the ponds was generally flat, except for Ponds 4 and 5 which were situated at the bottom of a steep valley.

Characteristics of the sampled ponds and the conditions at time of spray are contained in Table 1.

Measured deposit of fenitrothion on filter paper after spray ranged from 24.3 to 0.7 mg/m^2. Mean deposits (Table 2) ranged from 17.6 $\pm$ 4.6 mg/m^2 on Pond 1 after the first spray event to 1.2 $\pm$ 0.2 mg/m^2 on Pond 1 after the second spray event. The highest mean deposit represents 84% of the emitted application rate, however, total mean deposit was approximately 32% of the emitted application rate.

Table 2. Fenitrothion deposit on flat collectors and immediate pond surface water concentrations after forest spraying

Pond	Spray event	Mean deposit - mg/m^2 (X ± S.D.)	Mean surface water concentration - mg/L (X + S.D.)
1	1	17.6 $\pm$ 4.6	0.8 $\pm$ 0.7
2	1	12.8 $\pm$ 3.0	1.5 $\pm$ 0.5
3	1	3.3 $\pm$ 0.5	0.04 $\pm$ 0.02
4	1	4.2 $\pm$ 0.8	0.2 $\pm$ 0.09
5	1	6.6 $\pm$ 0.4	0.09 $\pm$ 0.1
6	1	4.2 $\pm$ 2.9	0.2 $\pm$ 0.1
1	2	1.2 $\pm$ 0.2	0.02 $\pm$ 0.01
2	2	5.8 $\pm$ 1.2	0.3 $\pm$ 0.1
4	2	5.9 $\pm$ 0.8	0.3 $\pm$ 0.3
5	2	4.8 $\pm$ 0.7	0.04 $\pm$ 0.04

The pre-spray surface water concentration of fenitrothion ranged from 0.0011 mg/L to <0.00005 mg/L (the detection limit for the analysis). Surface water concentrations of fenitrothion after spraying, ranged from 2.5 mg/L to 0.006 mg/L. Mean surface water concentrations ranged from 1.5 $\pm$ 0.5 mg/L on Pond 2 after the first spray event to 0.04 $\pm$ 0.04 mg/L on Pond 5 after the second spray event.

There were no obvious influences of meteorological conditions at the time of spray, topography, or perceived application anomalies on deposit. Concentrations of fenitrothion in outflow water were much smaller than those in pond surface water (Table 3). Mean outflow concentrations ranged from 26.0 µg/L to 0.2 µg/L. No consistent pattern in outflow concentration changes with time was evident, however, in five of the seven spray events monitored, concentrations increased or remained relatively stable with time up to 2 h after spray.

Residues of fenitrothion in conifer foliage after the first spray event had a mean value of 3.0 ± 1.7 µg/g (N = 9). Residues in foliage after the second spray event were similar with a mean of 2.3 $\pm$ 1.5 µg/g (N = 9). Two samples obtained prior to the first spray event contained 0.57 and 0.51 µg/g fenitrothion while those

TABLE 1. **Characteristics of sampled ponds and conditions at time of spray**

Pond #	Spray event	Pond dimensions (m)	Depth (m)	Outflow (L/S)	Water temp. (°C)	Air temp. (°C)	pH	Wind speed (m/s)	Wind direction (°)	Spray time	Spray deviation
1	1	25 x 25	1.0	.63-.95	4.5	-	6.6	.300	200	06.31	None
2	1	40 x 20	1.0	.63-.95	4.5	-	6.6	.300	200	06.31	None
3	1	50 x 30	0.5	<.63	-	-	6.0	.511	-	18.10	None
4	1	20 x 30	0.75	6.3	-	-	6.0	.511	10	19.27	Booms off on one plane
5	1	30 x 50	0.57	6.3	-	-	6.0	.511	10	19.27	Booms off on one plane
6	2	80 x 15	1.0	.63-.95	-	7.0	6.6	1.256	90	07.36	None
2	1	40 x 20	1.5	.63	14.0	19.0	6.6	no wind	-	08.19	Plane off flight line
4	2	20 x 30	0.75	6.3	-	-	6.0	3.81	-	06.02	None
5	2	30 x 50	0.5	6.3	-	-	6.0	3.81	-	06.02	Plane off flight line

obtained prior to second spray (N = 6) contained a mean of 0.4 ± 0.2μg/g.

Table 3. Fenitrothion concentrations in pond outflow at various times after spray

Pond	Spray event	Mean surface concentration (μg/L)	Outflow concentration* (μg/L) post-spray 15 Min.	30 Min.	1 h	2 h
3	1	40	1.7	0.8	2.2	3.4
5	1	100	24.0	15.0	26.0	23.0
6	1	200	2.6	2.8	2.8	3.0
1	2	20	0.2	0.2	0.2	0.3
2	2	300	2.9	5.0	18.0	19.0
4	2	300	12.0	N/A	N/A	N/A
5	2	40	13.0	12.0	8.3	8.0

* Means of two samples.

Although the deposit on filter papers was highly variable, which may be related to observed delivery anomalies, mean deposit (31.6% of emitted active ingredient) was comparable to that reported by Armstrong (1977) to be typical of operational forestry sprays (25-30% of emitted dosage rate). Also deposit on sampled foliage was similar to that previously recorded for forest spraying (Pierce and Ernst 1988).

Surface water concentrations of fenitrothion reported here are greater than those which have been previously observed in lentic water after operational spraying. There have been several reports of peak lentic water concentrations which range between 0.2 mg/L and 1.1 mg/L (Mamarbachi et al. 1985, Moody et al. 1978, and Morin et al. 1986), however, most studies have reported peak concentrations of less than 0.06 mg/L (Ernst et al. 1980, Kingsbury 1977, Holmes et al. 1984). Those studies however, have measured concentrations in large bodies of water such as lakes, many of which may have been protected by buffer zones or at least not directly oversprayed. Concentrations of forestry insecticides are greater in lentic than in lotic systems immediately after spraying (Fairchild et. al. 1989), and in one study, residue concentrations measured in a pond were five times those measured in a stream immediately after forestry spraying with fenitrothion (Hiramatsu et al. 1990).

The maximum mean surface water concentrations observed are within the range of fenitrothion 96-h LC 50's (0.7 - 1.9 mg/L)for salmonid fish (Doe et al. 1988, Sanders et al. 1983, Wells et al. 1979) and that observed to cause decreased survivability and embryo deformity of medaka (Oryzias latipes) (Hiraoka et al. 1990). It must be recognized, however, that the maximum surface water concentrations are rapidly attenuated due to dilution and degradation (Kingsbury 1977,Maguire and Hale 1980) and are not directly comparable to concentrations of fenitrothion used to develop laboratory toxicity values.

A dilution factor can be estimated by assuming that the total deposit (on plates) is mixed evenly throughout the water column. Those calculations indicate the initial concentrations which may be expected range from 11.7 µg/L to 0.8 µg/L. The time to reduce such concentration to 50% of their initial value, based on pond water replacement times (Sprague, 1973), would range from approximately 0.5 d to 16 d.

Residue concentrations in outflow water are representative of well-mixed water column concentrations and were much lower than the surface concentrations of the ponds they drained. In some cases however, they exceeded the 20 µg/L threshold for lotic benthic invertebrate impact calculated by Ahern and Leclerc (1981). Furthermore, the pattern of residue concentration changes with time in outflow water reflect the lower mass replacement rates of ponds compared with streams and indicate that the duration of elevated residue concentrations in streams draining sprayed ponds may be somewhat longer than that normally encountered in lotic systems.

Total arthropod benthos density depletions of approximately 50% (primarily Chironomidae and Ceratopogonidae) have been reported in bog ponds which had immediate surface post-spray concentrations of 42 - 81 µg/L fenitrothion in an experimental ground application (Fairchild 1990). While the effect that low water pH has on modifying the magnitude of those impacts has not been determined, the residue concentrations in this study of 10 to 20 times those of Fairchild (1990), indicate that the impact of forestry use of fenitrothion on benthic invertebrates in small ponds may be substantial and should be determined.

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Received July 7, 1990; accepted December 30, 1990.