DDT in Forest Streams

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Summary

Water was sampled from a tributary of the Miramichi River of New Brunswick before, during, and up to two years after the final operational application of DDT to this area of forest. Gas chromatographic analysis of petroleum ether extracts of the water showed that only during and for a few hours after actual spray application did the DDT concentration in the stream exceed a steady background level of 0.5 ppb. pp'DDT ($<$ 17 ppb.), and this DDT flush occurred mainly as a surface film associated with the formulating oil. Bottom sediments, extracted with hexane-acetone (2/1) for chromatographic analysis, showed a downstream dilution gradient of DDT residue from tributary to estuary, and these averaged only 12.5 per cent of the DDT concentration found in the soils of surrounding forests. Much of the pp' DDT applied in the original technical spray was decomposed to DDE and DDD in the bottom sediments of forest streams.

Introduction

Many millions of acres of New Brunswick (N.B.) forest were sprayed between 1952 and 1967 with DDT to conserve this major resource from economic depletion by Spruce budworm (Choristoneura fumiferana Clemens) attack (1). Much of the treated area lies in the watersheds of the St. John, Restigouche and Miramichi Rivers, world-famous for Atlantic salmon fishing (Fig. 1), and controversy has arisen over the possibility that forest protection with toxic chemicals might be damaging to related resources of water, fishing and recreation. Fishery scientists have demonstrated large declines in fish populations (and other aquatic fauna) in rivers after the surrounding forest was sprayed with DDT (2), yet circumstantial evidence such as commercial fishery returns, reflect no serious long-term deleterious effects due to large-scale use of DDT in the forest (3). Little direct quantitative

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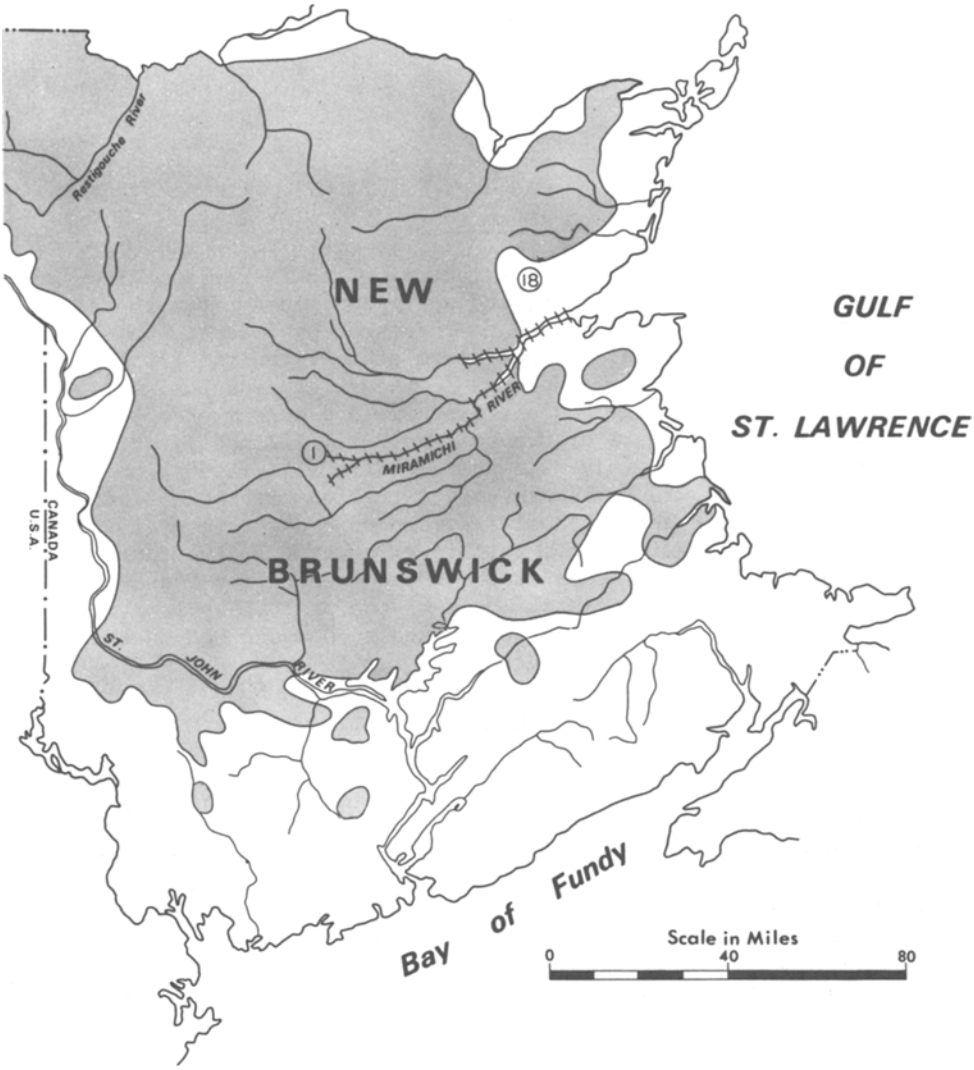

Figure 1. Approximate area (shaded) of New Brunswick forest sprayed with DDT between 1952 and 1967 (after (1) and (2). Main river systems draining the sprayed area also shown together with sampled stretch of Miramichi (hatched) of Tables 1 and 2.

chemical and toxicological data have been produced on amounts of DDT occurring in river water and aquatic flora and fauna (4) to help resolve the situation.

While direct DDT-spraying of main rivers was superseded in 1963 by buffer-spraying of river courses with phosphamidon, and more selective and less persistent chemicals (e.g. fenitrothion) have been used for Spruce budworm control since 1967 (5), the persistent nature of DDT residues in the environment and possible biological effects are still cause for concern to ecologists. This paper gives levels of DDT occurring on the surface and in the deep running water of a forest stream before, during, and up to 2 years after the final operational use of DDT in 1967, and also traces the amounts and forms of DDT residues occurring in river sediments of parts of the Miramichi watershed. It is hoped that the quantitative measurements of DDT in stream water will help to resolve the toxicological controversy on fish kill, and that the sediment-DDT data will provide some ecological perspective on DDT residues in the forest and river environments.

Experiments and Results

Stream Water

Sampling. Water samples were taken from Crooked Bridge Brook, a tributary of Big Hole Brook and the S.W. Miramichi River, below its exit from the Priceville Pesticides Study Area (Fig. 1). This is a 1000-acre area of forest draining into Crooked Bridge Brook which was set aside in 1967 for research on the effects of pest control operations on the forest ecosystem. The area represents a large sector of forest which has had a total of 70 oz./acre of DDT applied to it by aircraft between 1956 and 1967. Water samples were taken at the same site before, during, and up to 2 years after the final application of DDT in 1967.

Grab samples of running water were collected in pre-washed and acetone-rinsed brown glass bottles (250 ml.) fitted with an Al foil-lined screwcap. Surface waters were sampled by breaking the Al seal, holding the bottle horizontally with the neck facing up-current and half-submerged in the running water, and resealing when filled. Deep water samples were taken at the same place and times by submerging the sealed bottle to a depth of 12-18 inches in the running water then opening and replacing the Al top under water. Sample bottles were stored in the dark in a refrigerator (4^{o}C) until analysed.

Analysis. The volume of each sample (200-250 ml.) was measured and the water poured into the steel container of a Sorvall Omni-Mixer (500 ml.), and extracted at high speed for

TABLE 1

Concentrations of pp'DDT* found on and in stream water from Crooked Bridge Brook at its exit from the Priceville Pesticides Study Area**, in relation to time of DDT spraying.

Time of sampling	pp'DDT content, ppb. (ng./ml) Surface water	 12-18 in. deep water	Remarks
Average laboratory background with distilled water and solvents	0.31	0.31	
Pre-spray, May 1967	0.66	0.76	
During spraying, June 16, 1967	17.57*	1.69	1/4 lb. DDT/acre applied to forest
Post-spray + 2 hours	17.11*	0.71	
Post-spray + 4 hours	8.62*	0.74	
Post-spray +12 hours	0.90	0.78	
Post-spray + 1 day	0.98	0.58	
Post-spray + 3 days	0.71	0.74	
June 20, 1967	----	----	respray, 1/4 lb. DDT/acre
Post-spray + 3 months	0.92	0.94	
Post-spray + 1 year	----	0.75	
Post-spray + 2 years	----	0.72	

* X 1.3 for total DDT's

** site 1 of Table 2 and Fig. 1.

15 minutes with 100 ml. petroleum ether (Burdick and Jackson, distilled-in-glass grade, B.P. 30-60°C), which had first been used to rinse the sample bottle. The mixture was transferred to a separatory funnel to stand overnight, then the water phase was re-extracted as before using fresh petroleum ether. The total volume of petroleum ether (300-400 ml. including rinsings) was dried by passing through 2 columns of anhydrous Na_2SO_4. The dried extract was reduced to a volume of 10 ml. by flash evaporation, and transferred to 2 ml. n-hexane by warm air evaporation. Two microliter aliquots were analysed directly using an F & M 810 gas chromatograph fitted with a single electron capture (H3) detector and operated under the following standard conditions. Column: 120 x 0.635 cm. glass, containing 3.8% SE 30 on Chromosorb W. AWDMCS, 60-80 mesh: temperatures; column 185°C; detector 210°C; injector 200°C: argon-methane (20/1) carrier gas flow rate 60 ml./min. Minimum recoveries of 90% pp'DDT were obtained with this method of analysis on fortified distilled water.

Results. The results of analyses (Table 1) show that the stream water contained a small (above-background) amount of pp'DDT before the 1967 forest treatment. The amount increased greatly, particularly in the surface water, during the aerial application of 4 oz. technical DDT in 1/2 U.S. gal. light oil per acre of forest, and declined within a few hours to a level similar to pre-spray amounts, where it has remained relatively steady for the following 2 years. Because of the very small amounts contained in most samples, only during the actual spraying could other DDT isomers in the stream waters be measured quantitatively, and as might be expected, they reflected the formulation analysis (see Table 3).

River Sediments

Sampling. Sediment samples were taken from Crooked Bridge Brook, Big Hole Brook, and at several points down-stream in the main Miramichi River in June 1968 (Fig. 1, Table 2). The bottom sediments of these cold, clear salmon and trout streams which run over rocky beds for most of their course, consist largely of sand and gravel, but pockets of vegetation and deep mud do occur in slacker stretches of the main rivers. Sample sites were selected where loose bottom sediments could be seen from the surface. Where the water was shallow, samples of upper layers of sediments were collected by hand while wading. Where the river was too deep for wading, sediments were collected using a metal spring scoop on a line from a boat. All sediments were collected sufficiently far out from the bank of a stream to be sure they were normally covered with water. Free water was allowed to run off the sample which was then placed in a double-wall 10 lb. plastic bag at the

TABLE 2

Survey of DDT residue amounts and forms in bottom sediments of parts of the Miramichi River system (see Fig. 1)

Ref.	River System	Sample Site (nearest place name)	Total DDT's (ppm. oven dry)	pp'DDT %*
	S. W. Miramichi R.			
1S	Tributary of 2	Crooked Bridge Bk.	0.16	25
2M	" " 3	Big Hole Bk.	0.23	33
3S	Main River	Mc Namee	0.29	57
4M	" "	Carrols Crossing	0.26	47
5M	" "	Storeytown	0.29	30
6M	" "	Doaktown	0.28	20
7S	" "	Blissfield	0.06	43
8M	" "	Weaver	0.42	19
9M	" "	Moore's Bk.	0.14	24
10M	" "	Upper Blackville	0.24	21
11S	" "	Howard	0.09	38
12S	" "	Blackville	0.04	47
13S	" "	Renous	0.04	55
14S	Tidal Water	Millerton	0.16	54
15S	begins	Derby Junction	0.03	68
	N. W. Miramichi R.			
16M	"	Red Bank	0.09	26
17S	"	N. Esk Boom	0.05	28
18S	Miramichi Estuary	Newcastle	0.02	60

S Sandy bottom

M Muddy bottom

* see also Table 3

sampling site, to approximately quarter-full level, and stored at -20°C until analysed.

Analysis. Whole samples were thawed overnight, placed in a large filter funnel to drain off free water, then broken down and thoroughly mixed by hand in a clean enamel tray. A total composite sample of 50g. sediment was selected by hand from the mass sample, and mixed and ground with 50g. anhydrous Na_2SO_4 by mortar and pestle. The sample was extracted twice with 100 ml. hexane-acetone (2/1 mixture), (6), washed thoroughly with distilled water and cleaned-up by means of a florisil column, as for forest soils (7). Recoveries of 80-100% DDT were obtained using this method, compared with exhaustive soxhlet extraction of sediments. The cleaned-up extract of each sample was analysed using a Hewlett Packard 5755B gas chromatograph fitted with dual electron capture (Ni 63) detectors and 120 x 0.635 cm. glass columns. Each column was packed with Chromosorb W, AWDMCS, 60-80 mesh, and liquid phases of (a) 3.8% SE 30 (b) 4% SE 30 + 6% QF_1. Operating temperatures were: injector 220°C; columns 185-190°C; detectors 250°C. Argon/methane (20/1) carrier gas flow rates were (a) 50, and (b) 70 ml. per min.

Results. DDT residues were quite variable throughout the river system (Table 2). However, although the sampling scheme used was not systematic and was of low intensity, a definite dilution effect from headwater to estuary is apparent from these results. A similar but less consistent trend in degree of decomposition of pp'DDT in river sediments is also apparent from tributary to estuary (Tables 2 and 3). When average residue compositions are compared (Table 3), it is apparent that much of the pp'DDT originally present in the technical formulations that were applied to the forest, and which has persisted in adjacent forest soil residues (7), has been broken down in the fresh water environment to DDE and DDD. The degree of decomposition does not appear to be related to sediment type (Table 2). Isomer identification was confirmed by dual-column gas chromatography (above), and by thin-layer chromatography (8).

Discussion

A relatively large amount of DDT occurred on the surface of stream water, associated with the oil used for airspray formulation, during and for only a few hours after spraying (Table 1). This confirms Hopewell's (4) findings for other N.B. streams in previous years, using different analytical methods. Macdonald's review (2) of field determinations of fish populations in streams before and after DDT spraying of surrounding lands, demonstrates that a large population decrease and an increase in numbers of dead fish occurred within a few days after DDT spray application. If the

TABLE 3

Comparison of average amounts and compositions of DDT residues found in N.B. forest soil and river sediment in 1968, and in the original technical formulation.

Material	Average DDT concentration (total DDT's ppm.oven-dry)	Average % composition of DDT's			
		pp'DDT	op'DDT	pp'DDE	pp'DDD
Forest soil at Priceville (at site 1 of Table 2)	0.88	85	8	7	trace
Miramichi sediments (Table 2)	0.11	38	12	22	28
DDT formulation applied to forest in 1967	----	77	21	2	trace

lethal level of DDT in water for "young salmon" is averaged at 50 ppb. from the bioassay work reviewed by Macdonald (2), the DDT concentrations in water at different times relative to spraying (Table 1), and the delayed occurrence of fish kills in sprayed streams, all suggest that a lethal dose of DDT must be accumulated by stream fish over the first few days after spraying (9). However, the DDT concentration in water dropped to a very low level (0.5 ppb.) within a few hours of spraying (Table 1), and a much more likely route for fish poisoning is offered from Hopewell's work (4). This shows that although water levels of DDT were consistently much below 50 ppb. soon after spraying (except where surface oil-slicks were intentionally sampled), the DDT content of suspended coarse solid material in the stream rose as high as 606 ppm. within the first few days after spraying, then declined. The screened-out solid material was not classified (4), but might well be organic matter since it floated, and if this was used for food by fish, the delayed mortality occurring in streams after spraying is more readily understood.

Study of the available measurements (Tables 1 and 2) (4), suggests that most of the comparatively large flush of DDT that occurred on stream water at the time of spraying was probably carried out to sea, in the case of the comparatively fast-running rivers of N.B., still in solution in the formulating oil. Some DDT was absorbed on organic materials in the streams (4), the suspended components of which may have been deposited as bottom sediments in slack river water (but see Table 2), or else carried out to sea (10). It is postulated that a major route of entry into biological food chains could have occurred by this means. The DDT content of stream water was thereafter steady and very small (e.g. 0.5 ppb., Table 1) without further applications of DDT to the forest. This amount may have comprised dissolved DDT derived, e.g. by continuous desorption from bottom sediments and vegetation, but it was more likely to be adsorbed on suspended material being carried along in the stream. It has been found that DDT is very tightly bound in forest topsoils (7), and is not leached directly into ground water systems, so that adsorbed particulate material may reach streams by surface run-off from land, and by aerial transport of dust and organic debris (11). The ecological effect of these persistent amounts of DDT in water is considered more likely to be resistance induction or selection in aquatic fauna rather than catastrophic mortality (12, 13, 14), although concentration in food chains may produce chronic biocidal effects at higher trophic levels. (15).

DDT persists in aquatic sediments of the forest environment, although in much smaller total amounts, and in less toxic forms (Tables 1 and 3), than in land strata such as foliage and soil (16, 7). The chemical breakdown and detoxification of DDT in river sediments, compared to the relatively stable state of affairs on land (Table 3), is of particular interest (17). In lake water, pp'DDT has been found to break down to DDD (18), and several workers have shown both aerobic and anaerobic microbial production of DDD from DDT under various conditions.(19). Microbial decomposition of DDT may occur readily in river sediments, and this should be investigated. The production of DDE from pp'DDT is commonly due to enzymatic breakdown and alkaline dehydrochlorination (20). Chemical attack in these cold, clean, near-neutral streams (water pH average 7.5; sediments all weakly acid, pH 5.2 - 6.0) appears an unlikely mechanism, whereas enzymatic breakdown by plants, animals and micro-organisms is quite tenable.

Further measurements of DDT residues in water and sediments in N.B. streams will be made for several more years, to follow the route and rate of decontamination of the forest environment.

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