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Disappearance Constants of Carbaryl from Streams Contaminated by Forest Spraying

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Acute toxicity of chemicals to aquatic organisms is traditionally expressed as a concentration that kills a certain percentage of the organisms after a stated exposure. For persistent pesticides this procedure probably inadequately reflects the potential impact in nature, where the total exposure time may be much longer than the duration of the tests. Because many organophosphate and carbamate pesticides break down rapidly, toxicity tests carried out at a constant level of exposure overestimate the effects in the field. After a week, jars filled with a solution of carbaryl in river water contained only 5% of the carbaryl initially present (EICHELBERGER & LICHTENBERG 1971). Carbaryl is broken down largely by alkaline hydrolyses (ALY & EL-DIB 1971) and bacterial decomposition (MENZIE 1978). In addition to being chemically degraded, pesticides also disperse in water currents. Toxicity tests would be more realistic if progressive declines in concentrations were taken into account. Fenitrothion disappeared over a several day period from water contaminated with spray applied to forests (EIDT 1975; FLANNAGAN 1975; HALL et al. 1975; McLEESE 1976) and rice fields (KANAZAWA 1975). McLEESE (1976) attempted to simulate stream conditions for toxicity tests on crayfish by adjusting levels of fenitrothion in static test containers. Accurate simulation of field concentrations requires knowledge of the disappearance rates of the chemical from the environment. EIDT & SUNADARAM (1975) and LYONS et al. (1976) mentioned a negative exponential decay for fenitrothion, and RABENI & STANLEY (1979) cited a disappearance rate for acephate; in general however, "decay" constants have not been published for non-persistent pesticides in natural waters.

The objective of this study was to determine disappearance constants of carbaryl from streams that received drift from spraying of nearby forests.

MATERIALS AND METHODS

Carbaryl (Sevin-4-oil) was applied from aircraft to 0.46 million ha of forests in 1978 and 1.1 million ha in 1979 in the State of

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Maine, USA. Of 18 streams in which residue levels in water were measured, the occurrence of carbaryl in progressively lesser amounts enabled us to calculate disappearance constants in 9: Clayton, Carry, Squirrel, Mud, and Wyman brooks; Burntland and Presque Isle streams; and Machias and Penobscot rivers. Measurements were not suitable in some streams because rainfall washed additional pesticide into the water, and in others because residues were detected in only a single sample. All applications were at 0.84 kg/ha active ingredient. For the forest near Squirrel Brook one third of the dose was applied 12 days before the application reported here. For Wyman Brook, different parts of the spray area were treated on two dates 5 days apart. Buffer zones that were to remain unsprayed were 150 m wide on each side of the streams except that Squirrel Brook had no buffer and the Penobscot River had a 300 m buffer.

Water samples were frozen and stored 3 to 5 months. The Pesticide Laboratory of the Maine Department of Human Services, Augusta, Maine, analyzed the carbaryl according to the method of BLAGG & RAWLS (1972), using electron capture gas chromatography to detect derivitized 1-naphthol. In this method, carbaryl is converted to 1-naphthol, derivitized, and then analyzed on a gas chromatograph. Also detected is any 1-naphthol produced naturally by hydrolysis of carbaryl. The minimum level detectable was 0.05 µg/L, and the precision was ±5%.

The disappearance constant corresponds to a decay constant. We use the word disappearance instead of decay to avoid the impression that degradation is being measured. The disappearance constant (λ) was calculated by the equation:

$$\ln\frac{c}{c_o} = -\lambda t$$

where c_0 was the highest measured pesticide level after spraying and c the concentration after t hours. For most streams sufficient data were available to determine λ by regression of $\ln(c/c_0)$ against t, in which λ was the slope. A standard deviation was also calculated for the constant for each of seven streams for which sufficient samples were available. We compared constants for brooks (less than 8 m wide) with those for rivers (over 15 m wide) using a Student's t test.

RESULTS

Spraying of forests with carbaryl to control spruce budworm in Maine resulted in contamination of the streams. Peak concentrations occurred shortly after spraying; the maximum measured level ranged from 0.93 to 7.8 µg/L in brooks and from 0.44 to 2.0 µg/L in rivers. In one stream (Squirrel Brook) sprayed in 1978, the maximum level was 16 µg/L. These peak concentrations rapidly decreased after spraying and followed an exponential decay curve.

Disappearance constants of carbaryl ranged from 0.005 to 0.068 h^{-1} (Table 1). The average constant of 0.03 ± 0.008 h^{-1} for brooks did not differ significantly from the constant of 0.025 ± 0.008 h^{-1} ($\alpha = 0.05$) for rivers; thus the size of the stream was unimportant. The constant did not depend on the initial concentration of carbaryl in the water: in streams with initial carbaryl concentrations of less than 2 µg/L, the constants ranged from 0.005 to 0.068 h^{-1}; in Mud Brook (initial concentration, 7.8 µm/L) the constant was 0.024 h^{-1}; and in Squirrel Brook (16 µg/L) the constant was 0.013 h^{-1}.

Table 1. Peak concentrations of carbaryl and mean disappearance constants (λ) in Maine streams contaminated from spraying of nearby forests. (Standard deviations are shown in parentheses).

Stream	Width (m)	Peak conc. (µg/L)	constant (h^{-1}) ± S.D.
Brooks			
Clayton	3	0.9	0.068
Carry	5	1.1	0.052
Squirrel	5	16.1	0.013 (0.009)
Burntland	7	1.0	0.009 (0.002)
Mud	8	7.8	0.024 (0.001)
Wyman - 1st Spray	8	2.1	0.030 (0.006)
2nd Spray		1.8	0.012 (0.003)
$\bar{x}$ ± SE		4.4 ± 2.2	0.030 ± 0.008
Rivers			
Presque Isle			
Upstream site	15	1.3	0.017 (0.001)
Downstream site	15	2.0	0.005 (0.004)
Machias			
Upstream site	30	0.6	0.014 (0.001)
Downstream site	30	0.4	0.047 (0.008)
Penobscot	100	1.6	0.042 (0.005)
$\bar{x}$ ± SE		1.2 ± 0.3	0.025 ± 0.008
Grand mean ± SE, all streams		3.0 ± 1.3	0.028 ± 0.006

Contrary to our expectation, the disappearance curve of the log plot did not significantly change in slope, when samples taken shortly after spraying were compared with those taken later. We anticipated that the rate of disappearance would seem lower immediately after spraying because residues would continue to enter the stream.

The half-life of carbaryl was 23 h in brooks, 28 h in rivers, and 25 h for all streams combined. Thus about half of the residue remaining disappeared each day.

DISCUSSION

The rate of disappearance of carbaryl from streams was not greatly different from that reported for pond or river water in the laboratory. We calculated a constant of 0.017 h^{-1} for decay of the pesticide from jars of river water (EICHELBERGER & LICHTENBERG 1971) and 0.028 h^{-1} for its disappearance from aerated aquaria containing pond water (KANAZAWA 1975). The mechanisms for loss of carbaryl in laboratory containers may be different from those in the field. We were less interested in the pathways than in determining how long the pesticide was in contact with organisms that maintained their position in a stream. Obviously, instream exposure is not equivalent to a static solution of pesticide. Rather, solutions moved downstream and were replaced by other solutions. Our disappearance constant of 0.028 h^{-1} represents the average at which levels of exposure declined.

We believe that the disappearance of carbaryl from a particular section of stream was related to the balance between downstream flushing and the addition of residues from upstream. The similarity of ratios of flushing and input in large and small streams probably accounts for the similar disappearance constants. The more rapid currents in the larger streams dissipated the pesticide more quickly, but the greater additions from the larger watersheds compensated for this faster loss, consequently the dissappearance rate was about the same as in a brook with a smaller watershed and slower current. Also possible was a difference between large and small streams in the rate of volatilization of pesticide, which was mentioned as a possible route of loss by KUHR & DOROUGH (1976). Since brooks are usually more turbulent than rivers, a greater loss of pesticide to the atmosphere would be expected.

The disappearance rate of carbaryl was apparently lower than that for fenitrothion, judging by our inspection of graphs published by EIDT (1975), FLANNAGAN (1975), and HALL et al. (1975). Either fenitrothion breaks down more rapidly than carbaryl or the flushing rate in Canadian streams was greater. Constants would have to be established for each pesticide before realistic toxicity testing could be designed.

The disappearance constants determined for carbaryl in Maine streams should be useful for toxicologists designing toxicity tests. Our average value of 0.028 h^{-1} may apply to any running water. It would be relatively simple to calculate and control the inflow of water through a test container to duplicate the dissipation of carbaryl in streams. Simulated field concentrations could be maintained with an inflow of uncontaminated water into a tank at the rate of 2.8% of the volume of the test container per hour.

We recommend that toxicity testing be initiated for representative organisms held under simulated field conditions. Carbaryl was shown to be toxic to the stonefly (*Pteronarcys californica*) and scud (*Gammarus pseudolimnaeus*) at doses encountered during operational spraying (SCHOETTGER & MAUCK 1976). Such organisms should be retested. Levels of contamination were considerably below toxicity levels for fish (HAYNES 1971; CHAIYARACH et al. 1975; SCHOETTGER & MAUCK 1976). Consequently toxicity tests need not be redesigned for fish.

The disappearance constants we calculated would be useful in assessing performance standards by applicators. The label for carbaryl specifies that it is not to be applied to water, and in Maine a concentration of 30 µg/L has been arbitrarily assigned as indicating direct application. The use of our disappearance constant would make it possible to back calculate the approximate concentration in the stream shortly after a particular block had been sprayed. Criteria needed would be the confidence intervals on the samples taken and the back-calculated concentration.

The chemical breakdown of carbaryl was not taken into account. This carbamate hydrolyzes to 1-naphthol but the rate at the pH of Maine rivers (roughly pH 5.5-7.0) would be rather slow. Because the analytical method measured both the parent compound and its chief product, the levels of carbaryl were overestimated. The constants we calculated underestimated the rate of disappearance of carbaryl by about 3%, as judged by the effects of pH on hydrolysis (ALY & EL-DIB 1971). However, the hydrolysis could have been faster because of sunlight (ALY & EL-DIB 1972) and agitation (HUGHES 1971) in the streams.

Ecologically, it might be more important to know the disappearance rate for carbaryl and 1-naphthol together because both are toxic. In sea water, carbaryl was more toxic than 1-naphthol to crustaceans, but less toxic than 1-naphthol to mollusks and fish (STEWART et al. 1967). In fresh water, however, carbaryl was more toxic than 1-naphthol to brown trout, *Salmo trutta* (BURDICK et al. 1965).

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