Bull. Environ. Contam. Toxicol. (1994) 53:337–343

Environmental
Contamination
and Toxicology

Mass Losses and Changes in Concentration of Chlorpyrifos and *Cis*- and *Trans*-Permethrin Applied to the Surface of a Stream

R. J. Wilcock, G. L. Northcott, J. W. Nagels

NIWA Ecosystems, National Institute of Water & Atmospheric Research, P.O. Box 11-115, Hamilton, New Zealand

Received: 7 July 1993/Accepted: 30 January 1994

Pesticide residues in agricultural runoff can sometimes yield inputs to streams and rivers that are harmful to aquatic organisms. A number of reviews have addressed this issue from a consideration of the physico–chemical properties of pesticides, the ways in which they are used, and climatic factors, to predict "edge–of field" pesticide concentrations in runoff (Wauchope 1978; Wauchope and Leonard 1980; Willis and McDowell 1982; Wilcock 1993). An understanding of the in–stream processes governing the dissipation and concentrations of these residues is necessary to relate the pesticide inputs to changes in quality of receiving waters and to predict ecological impacts. The rate at which pesticides are assimilated, broken down or in other ways dispersed so that they no longer affect stream biota is of crucial importance in understanding the connections between pesticide runoff and stream effects. Also, the effect of several similtaneous inputs of a given pesticide to different tributaries of a stream network may be negligible if the substance is short–lived, or may have an additive effect on downstream concentration if it is more persistent.

In this study, two insecticides were added to an upland stream draining an area of grazed pasture upstream of a region of more intensive agriculture and water use. The purpose of the study was to quantify mass losses and concentration changes occurring in the first 2–3 hr of travel time in a reasonably simple stream channel, in which sediment uptake was not likely to be a major mechanism for pesticide loss from the system. The stream is similar to many in the region.

The organophosphate, chlorpyrifos [*O,O*–diethyl *O*–(3,5,6–trichloro–2–pyridyl) phosphorothioate], and the synthetic pyrethroid, permethrin [3–phenoxybenzyl (1R,S)–*cis,trans*–3–(2,2–dichlorovinyl)–2,2 dimethylcyclopropanecarboxylate], are insecticides used widely in New Zealand in horticulture. Chlorpyrifos and permethrin are both highly toxic to fish and aquatic invertebrates and typically have 96–hr LC50 values of 0.1–10 mg/m^3 (Anderson 1989; Bradbury and Coats 1989; Coats et al. 1989; Haya 1989; Mokry and Hoagland 1989; Worthing and Hance 1991). The pure forms of both pesticides have low–moderate solubility in water (2 ppm for chlorpyifos and 0.2 ppm for permethrin), have low vapor pressures (2.5 mPa (25°C) for chlorpyrifos; 0.0025 and 0.0015 (20°C) for *cis*

Correspondence to: R. J. Wilcock

and *trans*–permethrin, respectively), and have octanol–water partition coefficients of 10^5–10^6 (Schimmel et al. 1983; Worthing and Hance 1991). These data suggest that both pesticides have a tendency to accumulate in the non–aqueous compartments (biota, sediments) and that chlorpyrifos may be more susceptible to volatility losses from the stream surface than permethrin.

MATERIALS AND METHODS

The Te Tahi Stream, located in the western Waikato region of the North Island of New Zealand (Christian and Walter 1984), was chosen for the study. The stream channel was characterized by a hard rocky base of volcanic origin covered with a thin layer of sediment. No rooted aquatic plants were apparent and stream vegetation was limited to filamentous algae covering rock surfaces. The banks were stable, steeply sloping with an overhanging mixture of pasture grasses and shrubs. Significant populations of a variety of caddisflies and freshwater crayfish, *Paranephrops planifrons*, were observed.

A study reach was established with water sampling sites at distances of 35, 67, 139, 271, 458, and 545 m downstream from the point at which pesticides were added to the water surface. These are referred to as sites 1, 2, 3, 4, 5 and 6. The upstream end of the study reach was narrow and moderately fast flowing (0.2 m/sec) while the lower reach was characterised by riffles and pools. Average stream width and depth were about 2 m and 30 cm, respectively. Stream flow during the study was monitored continuously at the furthest site downstream and was 55 L/sec throughout.

A preliminary dye study was carried out on 10 May 1993 to establish the behavior of a "conservative" tracer (compared to the pesticides), and to determine the travel times necessary for sampling the pesticide peak concentrations the following day. Flow–proportional QS samplers (Quality Environment Ltd, Cheltenham, England) were installed at the six sampling sites and weighted down to counter the initial bouancy of the empty sample compartments. These samplers operate on the principal that the rate of sampling is proportional to the depth of water above the inlet port of each sampler. A sampling rate (L/hr) is set for a given water depth by adjusting a calibrated air release valve. A quantity of dye (210 mL of 20% rhodamine WT) was added to the stream at the upstream end of the study reach and, in addition to the flow–averaged samples, discrete samples were collected at appropriate intervals at each of the downstream sampling sites. Each of the QS samplers collected stream water over a period of about 160 min. When the dye cloud had completely passed the last site (about 3 hr from the start of the study) the QS samplers were emptied into clean borosilicate glass bottles and, together with the discrete samples, analyzed using a Turner model 112 digital fluorometer calibrated with rhodamine WT standards (Rantz 1982). Times of travel for peak concentrations were obtained from the respective concentration–time curves at each site (using the discrete sample data), and dye masses were calculated either by multiplying the area under each curve by the flow, or from the product at each site: QS sampler (average) concentration x sampling time x flow.

The addition of pesticides to the stream was carried out on 11 May 1993, at the same point and with the same sampling sites as in the dye study. Aqueous solutions (500 mL) of commercial aqueous emulsions of chlorpyrifos (1.5 g) and permethrin (1.3 g each of the *cis*– and *trans*– isomers) were added to the stream and three samples taken (based on the dye data) at, or close to, the estimated peak concentration for each site. These were collected in clean borosilicate glass bottles.

In addition, the QS samplers were installed to obtain flow–averaged samples at each of the six sites. The QS sampler contents were transferred to clean borosilicate glass bottles at the completion of the study (i.e., about 3 hr after the addition of pesticides) and refrigerated overnight with the other water samples, prior to analysis.

Water samples were extracted and analyzed for chlorpyrifos based on Dow Chemical USA method ACR 79.8 (J. Cowles, DowElanco (NZ) Ltd, pers. comm.), and for the *cis*– and *trans*–permethrin isomers (Anon 1992). Sample aliquots (20 mL) were transferred to a 40–mL teflon sealed vial, and hexane (10 mL) added. The vials were shaken on a mechanical shaker for 15 min, allowed to settle, and the hexane phase passed through a Na_2SO_4 (anhyd) column. The process was repeated, an additional 10 mL of hexane added to the column, and the combined hexane extracts collected. Bromophos ethyl (50–100μL of 1000 pg/mL) was added as an internal standard, and 2 mL heptane added as keeper solvent. The extracts were reduced in volume to 0.25–0.5 mL prior to analysis by GC–ECD.

Analysis of the water samples was carried out with a Hewlett Packard 5890 Series II GC equipped with an HP 7636A automatic cool on–column injector, and a fused silica capillary column (Alltech SE54, 15 m x 0.2 mm i.d.), using the following temperature program: 90°C for 0.1 min, then 25 °C/min to 100°C, then 10°C/min to a final temperature of 280°C. The injector was maintained (oven trap) at 3°C above the oven temperature. Carrier gas (H_2) pressure was kept at 10 psi with electronic pressure control, and N_2 makeup gas was used to maintain a flow of 30 ml/min through the ECD (300°C). Detection limits for water samples were 0.01 mg/m^3 for chorpyrifos and 0.05 mg/m^3 for the permethrins. Blanks made with nanopure water showed no traces of any of the analytes. Water samples spiked with 1–10 mg/m^3 chlorpyrifos and *cis*/*trans*–permethrin gave recoveries of 98 ± 2 % and 95–98 %, respectively.

RESULTS AND DISCUSSION

Complete dye concentration profiles were obtained from the discrete samples collected at sites 1, 3, 5 and 6. When integrated and multiplied by the stream flow (55 L/sec) dye masses of 41.2, 44.3, 42.8 and 41.1 g (± 7%) were obtained, compared with 40.6 g added to the stream. Dye masses calculated from the QS sampler concentrations (each multiplied by the flow and the sampling period) gave more variable results for sites 1–6, being 50, 41, 36, 37, 35 and 37 g (± 20%). These results confirmed that rhodamine WT behaved as a conservative tracer in the study reach of the Te Tahi Stream.

Near peak concentrations for the dye and the pesticides were averaged (n = 3) at each site and are listed with 95% confidence limits (2 x standard error) in Table 1. Average peak concentrations for the pesticides and the dye declined with distance (and travel time) downstream in the order dye < chlorpyrifos ≈ *cis*–permethrin < *trans*–permethrin. Relative concentrations, expressed as fractions of the respective site 1 values, declined with distance downstream (Fig.1) to values of 0.5 for chlorpyrifos, *cis*–permethrin and *trans*–permethrin before site 3 (139 m), corresponding to travel times of 27, 23 and 23 min, respectively. The dye concentration declined to 0.5 the site 1 value after 43 min (about 270 m downstream). The temperature of the Te Tahi stream was 12.6–13.3°C during the study, so that the vapor pressures of chlorpyrifos and the permethrins would be

Table 1. Mean peak concentrations of rhodamine WT, chlorpyrifos, *cis*- and *trans*-permethrin (± 2 x standard error, n = 3)

Compound	time (min)	Site	Concentration (mg/m^3)
rhodamine WT	8	1	1088 ± 30
	14	2	885 ± 30
	30	3	650 ± 10
	62	4	496 ± 10
	105	5	366 ± 20
	114	6	293 ± 10
chlorpyrifos	8	1	31.4 ± 2.3
	14	2	17.9 ± 1.5
	30	3	14.5 ± 0.9
	62	4	8.86 ± 0.87
	105	5	5.39 ± 0.26
	114	6	4.52 ± 0.29
cis-permethrin	8	1	32.2 ± 3.5
	14	2	19.4 ± 1.5
	30	3	14.7 ± 0.7
	62	4	8.69 ± 0.99
	105	5	4.75 ± 0.54
	114	6	4.52 ± 0.10
trans-permethrin	8	1	32.1 ± 3.9
	14	2	17.6 ± 1.3
	30	3	13.5 ± 0.6
	62	4	7.26 ± 0.83
	105	5	3.67 ± 0.39
	114	6	2.85 ± 0.07

very low (Walker and Hance 1991). Volatilization rates for organic compounds from streams are strongly related to their vapor pressures (Rathbun and Tai 1988) and losses of the pesticides in this study might, therefore, be expected to be low. Studies of permethrin losses from Canadian forest streams (Kreutzweiser and Wood 1991; Sundaram 1991) have measured concentration changes at downstream sites and shown that they have an exponential form (first order with respect to concentration). In the present study pesticide peak concentrations (Table 1) also declined in a roughly exponential way with elapsed time. The conservative tracer (i.e., the rhodamine WT dye) may be used to compensate for changes in the pesticide peak concentrations due to dispersion and dilution, analagous to the way dissolved gas tracer concentrations are modelled in streams (Kilpatrick et al. 1989). Thus,

$$\ln\left[\frac{(C_p/C_d)_u}{(C_p/C_d)_d}\right] = K(t_d - t_u) \qquad (1)$$

where C_p and C_d are peak concentrations (mg/m^3) of pesticide and dye, respectively, t is time (min), and the subscripts u and d refer to upstream and downstream sites. The upstream site was defined to be the point where the dye and pesticides were added to the stream, with the initial (t=0) ratio C_p/C_d being equal to the ratio of the masses of dye and pesticide added. A plot of $-\ln(C_p/C_d)_t$ against time yielded straight lines for each pesticide with r^2 values of 0.81, 0.85 and 0.94

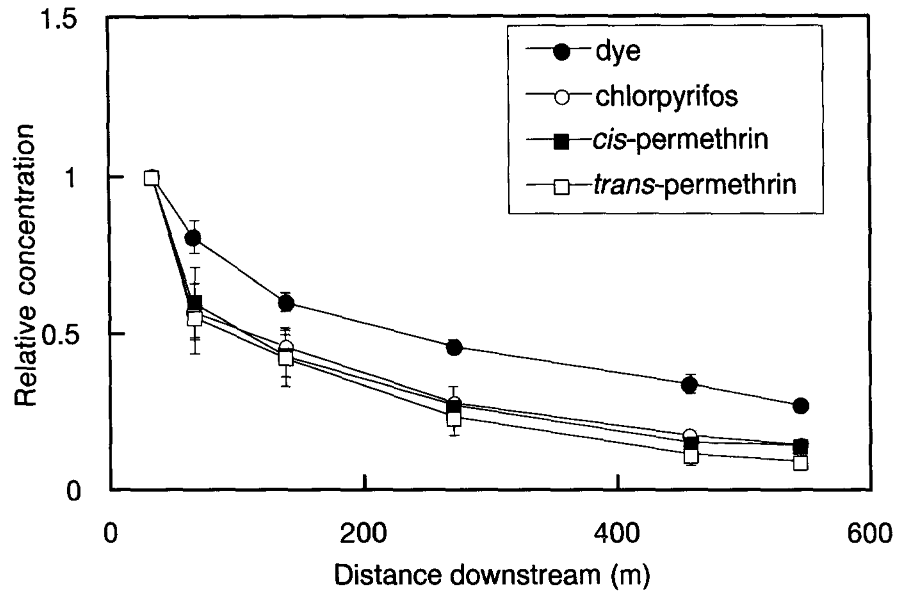

Figure 1. Average values of peak concentrations relative to site 1 for dye and pesticides with distance downstream (n = 3)

(n=6), and slopes (K values) of 4.73×10^{-3}, 6.26×10^{-3} and 9.25×10^{-3} min^{-1} for chlorpyrifos, *cis*– and *trans*–permethrin, respectively. Corresponding half–lives calculated from 0.693/K were 146, 116, and 75 min and are smaller than values reported for losses from specific sites in Canadian streams treated by aerial spraying with permethrin (Kreutzweiser and Wood 1991). This may be partly due to differences in the methods of application (e.g., slow release from riparian vegetation compared to direct application to the water in this study). A half–life of 3.9 hr was reported for losses from sites 1–1.4 km downstream from the aerial spray site and is closer to the values observed in the present study than values measured upstream (10.3 hr). The half–lives calculated here using C_p/C_d data are about 2.5 x those obtained from Fig.1 and show that dispersion (but not dilution, since there was little tributary inflow in the study reach) was a major reason for the observed declines in concentration.

Three (of the six) QS samplers failed to collect an adequate volume of water for pesticide analysis and therefore, could not provide flow–averaged concentrations. The experimental uncertainty (both in volume sampled and water chemistry) of the other three samplers led to the QS samplers being rejected for calculating pesticide stream masses at each site. Estimates of mass losses from the stream were made by assuming that the mass of pesticide passing each site declined over time at a rate proportionate to that for C_p/C_d (again, analagous to the first order loss of a volatile substance (Kilpatrick et al. 1989). Thus,

$$K(t_d - t_u) = \ln(m_u/m_d) \qquad (2)$$

where m_u and m_d refer to upstream and downstream masses, respectively. Calculated masses for each of the three pesticide compounds as a function of distance downstream, with the initially added masses as the upstream reference

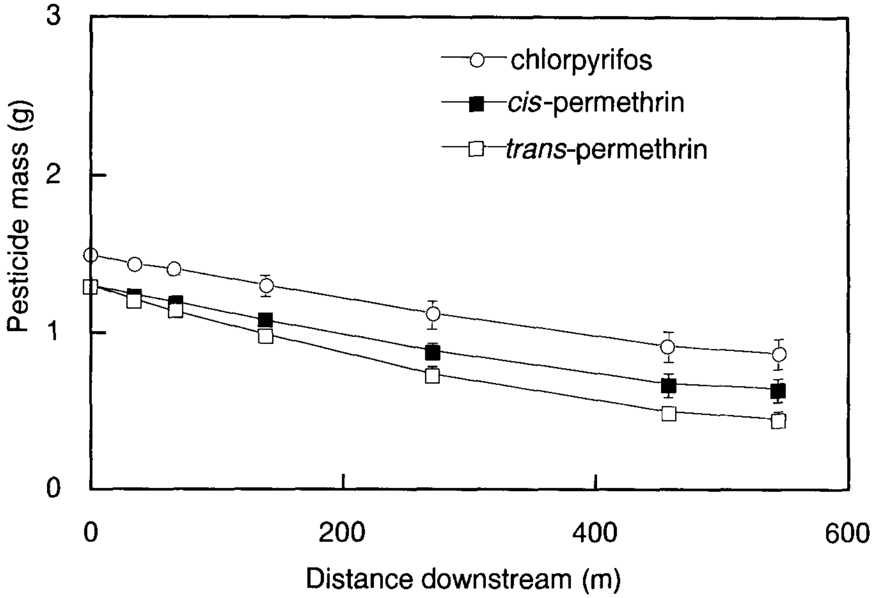

Figure 2. Change in mass of pesticides with distance downstream

values, are shown in Fig.2. Mass losses showed the same order as the concentration change (Fig.1), with chlorpyrifos ≈ *cis*–permethrin < *trans*–permethrin. Some pesticide losses from sediment adsorption and uptake by biota would be expected, given the magnitude of the octanol–water partition coefficients (Connolly and Pedersen 1988) and the observation by Kreutzweiser and Wood (1991) of measurable bioconcentrations of permethrin in fish up to 28 d after overspraying of forest streams.

The study has shown that pulsed inputs of chlorpyrifos and permethrin undergo marked reductions in concentration through dispersion and that further adsorption and bioaccumulation may cause additional mass losses from the water. About 50 % of the applied chlorpyrifos and *cis*–permethrin, and 60 % of the *trans*–permethrin, masses were lost from the water within the 545 m study reach. A slower moving stream with more organically enriched sediments, such as is typically found in horticultural areas of intensive pesticide use, would exhibit even greater adsorptive losses of such insecticides from the water column.

REFERENCES

Anderson R (1989) Toxicity of synthetic pyrethroids to freshwater invertebrates. Environ Toxicol Chem 8: 403–410

Anon (1992) Determination of synthetic pyrethroid insecticides in waters by gas liquid chromatography 1992 (tentative method). The Standing Committee of Analysts, Department of the Environment, London, UK

Bradbury SP; Coats JR (1989) Toxicokinetics and toxicodynamics of pyrethroid insecticides in fish. Environ Toxicol Chem 8: 373–380

Christian R, Walter KM (1984) Index to hydrological recording sites in New Zealand. Water & soil Miscellaneous Publication No 67, Ministry of Works and Development, Wellington, New Zealand

Coats JR, Symonik DM, Bradbury SP, Dyer SD, Timson LK, Atchison GJ (1989) Toxicology of synthetic pyrethroids in aquatic organisms: an overview. Environ Toxicol Chem 8: 671–679

Connolly JP, Pederson CJ (1988) A thermodynamic–based evaluation of organic chemical accumulation in aquatic organisms. Environ Sci Technol 22: 99–103

Haya K (1989) Toxicity of pyrethroid insecticides to fish. Environ Toxicol Chem 8: 331–391

Kilpatrick FA, Rathbun RE, Yotsukura N, Parker GW, Delong LL (1989) Determination of stream reaeration coefficients by use of tracers. Techniques of Water–Resources Investigations of the US Geological Survey, Book 3, Ch A18, Denver

Kreutzweiser DP, Wood GA (1991) Permethrin treatments in Canadian forests. Part 3: Environmental fate and distribution in streams. Pestic Sci 33: 35–46

Mokry LE, Hoagland KD (1990) Acute toxicities of five synthetic pyrethroid insecticides to *Daphnia magna* and *Ceriodaphnia dubia.* Environ Toxicol Chem 9: 1045–1051

Rantz SE (1982) Measurement and computation of streamflow: volume 1. Measurement of stage and discharge. Geological Survey Water–Supply Paper 2175, US Department of the Interior, Washington DC

Rathbun RE, Tai DY (1988) Application of the two–film model to the volatilization of acetone and t–butyl alcohol from water as a function of temperature. Geological Survey Water–Supply Paper 2342, US Department of the Interior, Washington DC

Schimmel SC, Garnas RL, Patrick JM, Moore JC (1983) Acute toxicity, bioconcentration and persistence of AC222, fenvalerate, methyl parathion and permethrin in the estuarine environment. J Agric Food Chem 31: 104–113

Sundaram KMS (1991) Fate and short–term persistence of permethrin insecticide injected in a northern Ontario (Canada) headwater stream. Pestic Sci 31: 281–294

Wauchope RD (1978) The pesticide content of surface water draining from agricultural fields. J Environ Qual 7: 459–472

Wauchope RD, Leonard RA (1980) Maximum pesticide concentrations in agricultural runoff: a semiempirical prediction formula. J Environ Qual 9: 665–672

Worthing CR, Hance RJ (1991) The Pesticide Manual, 9th ed. Unwin Brothers, Surrey, UK

Wilcock RJ (1993) Application of land–use data and screening tests for evaluating pesticide runoff toxicity in surface waters. Environ Manage 17: 365–371

Willis GH, McDowell LL (1982) Review: pesticides in agricultural runoff and their effects on downstream water quality. Environ Toxicol Chem 1: 267–279