Fate of Glyphosate in a Canadian Forest Watershed. 1. Aquatic Residues and Off-Target Deposit Assessment

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Glyphosate and AMPA residues in oversprayed and buffered streams were monitored following application of ROUNDUP (2.0 kg/ha) to 45 ha of a coastal British Columbia watershed. Maximum glyphosate residues (stream water, 162 μg/L; sediments, 6.80 μg/g dry mass; suspended sediments, <0.03 μg/L) were observed in two intentionally oversprayed tributaries, dissipating to <1 μg/L within 96 h postapplication. Buffered streams were characterized by very low glyphosate residue levels (2.4–3.2 μg/L in streamwater). Results of the off-target deposit assessment indicated <0.1% of applied glyphosate at 8 m from the spray boundary. Increases in residue levels were observed in relation to the first storm event postapplication. Ratios of maximum stream water concentrations of glyphosate observed in buffered and oversprayed tributaries relative to literature toxicity values indicated a substantial margin of safety under either operational or worst case scenarios.

Glyphosate [*N*-(phosphonomethyl)glycine], marketed under the trade names ROUNDUP or VISION (Monsanto Corp., St. Louis, MO), has been registered for use in site preparation and conifer release programs in Canada since 1984 (Malik and Vanden Born, 1986). The behavior of glyphosate in aquatic systems has been investigated in the United States and elsewhere (Comes et al., 1976; Rueppel et al., 1977; Edwards et al., 1980; Ghassemi et al., 1981; Norris et al., 1983; Newton et al., 1984; Wan, 1988). However, only the latter two reports are pertinent to the environmental fate of glyphosate in a coastal watershed ecosystem. In the province of British Columbia, Canada, coastal watersheds are used extensively for timber production. In such areas, the steep-sloped terrain, high annual rainfall (>2000 mm), and proximity of treatment areas to salmon spawning streams combine to approximate a worst case scenario with respect to potential for aquatic impacts following silvicultural chemical applications. As a result, current regulatory guidelines in British Columbia require the establishment of a 10-m pesticide-free zone with appropriate buffers, usually 100 m, to protect aquatic ecosystems. These guidelines restrict silvicultural treatment of the highly productive forest lands that border rivers and streams in coastal regions. In 1984, as a component of the continuing investigations on the effects of forestry practices on native fish populations in the Carnation Creek watershed (Hartman, 1982), a study was initiated to investigate the environmental fate of glyphosate in major aquatic and terrestrial compartments of the ecosystem, following a silvicultural application of ROUNDUP herbicide. Components of the environmental fate research program relating to aquatic residues and off-target deposit assessment are described in this, the first of a two-part series. The specific objectives of this portion of the environmental fate research were (1) to monitor residue levels and dissipation rates of glyphosate and AMPA in water, stream-bottom sediment, and suspended sediment of both buffered and oversprayed streams and (2) to assess the off-target deposit of glyphosate following an aerial spray application and evaluate the effectiveness of a 10-m vegetation zone in protecting forest streams from contamination resulting from off-target deposit.

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MATERIALS AND METHODS

Site Description. The study site was located in the Carnation Creek watershed on the west coast of Vancouver Island, British Columbia (45°50′ N, 125°2′ W), approximately 200 km northwest of Victoria (Figure 1). The 10-km^2 watershed is within a coastal hemlock and cedar ecozone (Krajina, 1969) and is characterized by annual precipitation ranging from 2500 to 3800 mm, occurring mainly from October through March (Hetherington, 1982).

Following clear-cutting in 1975, the study area was site-prepared and planted in 1976 (Dryburg, 1982). Seedlings were soon dominated by salmonberry (*Rubus spectabilis* Pursh) and red alder (*Alnus rubra* Bong.) (King and Oswald, 1982). In September 1984, salmonberry and alder ranged in height from 1.5 to 2.5 m and 7 to 10 m, respectively.

The main stream of Carnation Creek meanders through an alluvial floodplain and is fed by a number of permanent and ephemeral tributaries. The main stream and side channels support populations of coho (*Oncorhynchus kisutch* Walbum) and chum (*Oncorhynchus keta* Walbum) salmon. The four tributaries involved in this study have confluences with the main stream channel at 750, 1450, 1600 and 2200 m (C-Creek) upstream from the Carnation Creek estuary. The locations of spray blocks relative to the streams and main creek channel are shown in Figure 1. Tributaries 750, 1450, and C are ephemeral and in 1984 started flowing with the first seasonal rainfall (35 mm), which occurred on September 4.

Tributary 750, a small, ephemeral stream, occluded by riparian vegetation for most of its length was intentionally oversprayed in this study. At the time of application, it was slow flowing (0.001 m^3/s); however, owing to its steep drainage pattern, flow rates increased markedly during storm events. Tributary 1600 received direct chemical application for about 600 m of its 800-m length. At the time of application the stream was fast flowing (0.02 m^3/s) and contained pools ranging from 0.5 to 1 m in depth. Stream banks were covered with salmonberry and alder vegetation, but occlusion of the stream channel was less than that for tributary 750.

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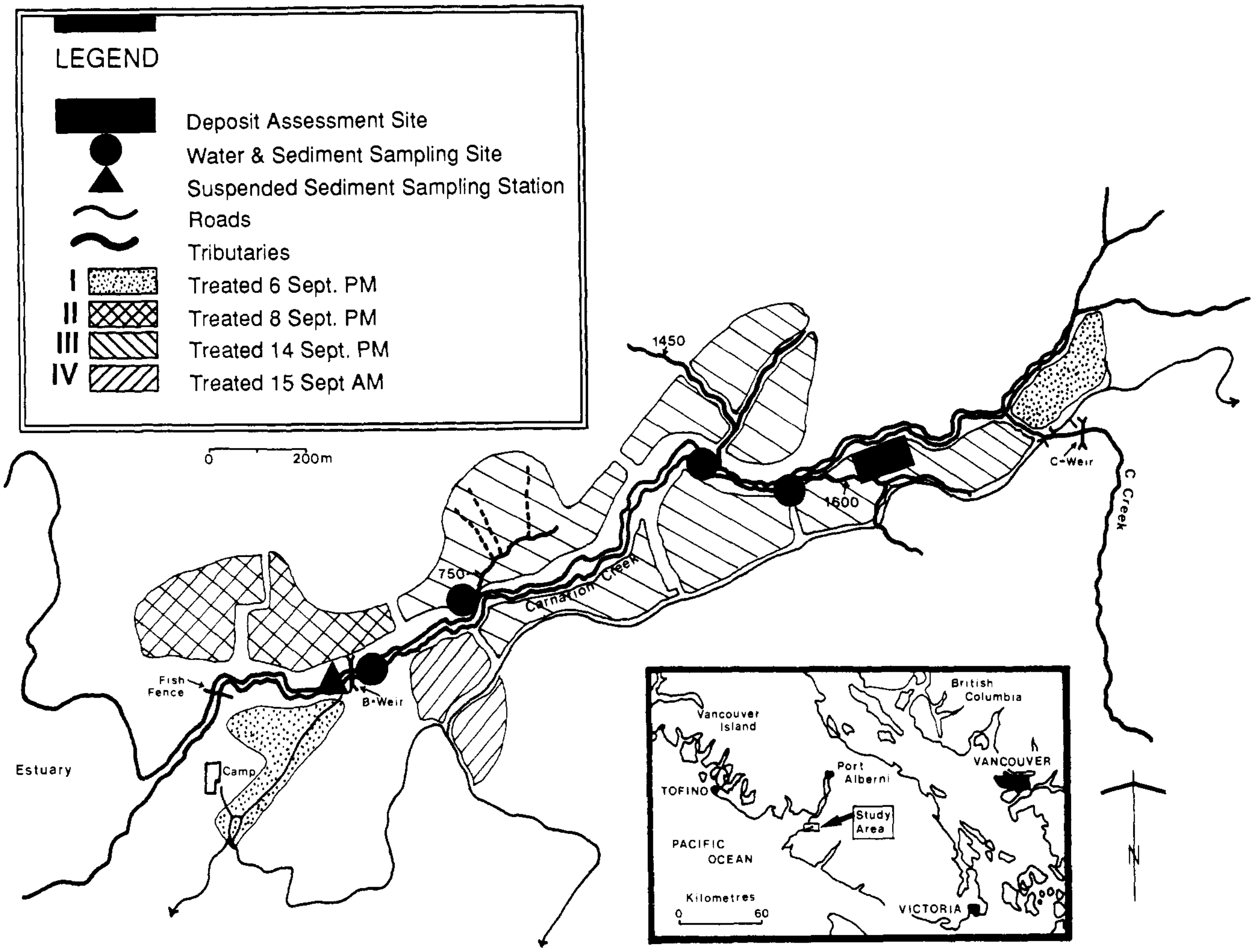

Figure 1. Location of the Carnation Creek watershed study area, aquatic and off-target deposit sampling sites.

Tributary 1450 was selected to represent a worst case situation for operational spraying. This tributary consisted of a network of branching stream channels, midportions of which either flowed underground or were covered with dense 2-m-high salmonberry. The stream boundary of these sections could not be clearly identified from the air. About two-thirds of its length (600–800 m) was adjacent to treatment area III (Figure 1). Stream flow at the time of application was 0.01 m^3/s.

A weather station and a broadcast weir (B-weir) were established near the mouth of Carnation Creek to monitor precipitation and stream discharge throughout the study period.

Herbicide Application. ROUNDUP (isopropylamine salt of glyphosate) was applied in September 1984 at 2 kg of acid equivalent (ae)/ha utilizing a Bell-47 helicopter equipped with a MICROFOIL (Union Carbide Inc., Ambler, PA) boom and 1.5-mm hayrake nozzles, calibrated to deliver 258 L/ha at an airspeed of 40 km/h and flying at a height of 6–18 m above the canopy (Reynolds et al., 1989). The main channel of Carnation Creek, as well as tributaries 1450 and C, were buffered with a 10-m untreated vegetation zone. Tributaries 750 and 1600 were intentionally oversprayed. A total of 45 ha was sprayed on four different days (Figure 1); the specific times, dates, and conditions associated with each application are presented in Table I.

Aquatic Residue Sampling. Sampling stations for the three tributaries were located about 5 m from the confluence with the main channel of Carnation Creek. The sampling station for Carnation Creek was located at B-Weir, 500 m upstream from the estuary and immediately below the major treatment area (Figure 1). At each station, intensive sampling of the stream water was conducted for the first 96 h postapplication. Intensive sampling was achieved by taking integrated stream water samples (IS) (six samples of 150 mL at 10-min intervals to yield a final sample (900 mL) integrating streamwater residues over the 1-h period of collection) during the initial period and single grab samples of 900 mL thereafter; the frequency of intensive streamwater sample collection is provided in Table II.

Storm event sampling was initiated when the instantaneous discharge of Carnation Creek at B-weir reached a threshold level of 7 m^3/s. Poststorm sampling commenced when the discharge decreased to below the same threshold. The frequency of sample collection and correlation with storm events is indicated in Table II. In conjunction with major storm events, water samples were collected at B-weir and at tributaries 750, 1450, and 1600. Suspended sediment samples (20 L of water filtered through Whatman No. 114 filters contained in a 15-cm Buchner funnel) collected during each storm event were taken at B-weir only.

Long-term water and bottom sediment point samples were collected on a biweekly schedule at B-weir and from tributaries 750, 1600, and C; frequency of long-term sampling is indicated in Table II. Long-term water samples were obtained as

Table I. Meteorological Conditions for Chemical Applications at Carnation Creek Watershed (Modified from Reynolds et al. (1989))

block[a]	date[b]	time[c]	area[d]	temp[e]	WS[f]	skies[g]	rain[h]
I	6	1900–2005	5.6	15	<7	OC, I	nil
II	8	1416–1940	8.5		7–10	OC	nil
III	14	1430–1931	24.2	21	5–11	OC, I	nil
IV	15	1041–1101	3.4	14	<5	S	1345

[a] Treatment block numbers (refer to Figure 1). [b] Date of application for Sept 1984. [c] Time of application, 2400-h clock (begin–end). [d] Total area (ha) of spray block treated. [e] Air temperature (°C). [f] Wind speed (km/h). Wind direction was east to west for all applications. [g] General cloud cover during chemical application: OC = overcast; I = intermittent sun; S = sunny. [h] Time of initiation of rainfall subsequent to application.

Table II. Sampling Schedules for the Carnation Creek Watershed Study

sampling site	schedule[a]	time postapplication
Intensive Stream Water Sampling (Time, h)		
Carnation Creek	IS	0 1 2 3 4 5 6 7 8
	PS	11 14 20 29 30 31 32 33 48 72 96
tributary 750	IS	0 1 2 3
	PS	6 9 15 27 36 48 72 96
tributary 1450	IS	0 1 2 3 4
	PS	7 10 16 22 48 72 96
tributary 1600	IS	0 1 2 3 4 5 6 7
	PS	10 166 28 30 32 34 48 72 96
Storm Event Sampling for All Substrates (Time, Days)		
major storm events[b]		23 25 49 59 66 84 91 150
all sites		23 24 25 27 30 33 40 47 49 51 53 57 59 60 62 66 67 69 73 80 84 85 87 150 151 153 157 164 171
Long-Term Stream Water and Bottom Sediment Sampling (Time, Days)		
all sites		196 210 224 238 252 263 280 297 311 326 750 339 355 364

[a] Key: IS = integrated sample, 6 × 150 mL taken at 10-min intervals; PS = point sample (1 × 900 mL). See Figure 1 for exact location of sampling sites. [b] Major storm events designated as those resulting in a stream discharge of 7.0 m^3/s or greater at B-weir of Carnation Creek.

indicated for PS samples in the intensive monitoring period. Bottom sediments were collected using a wide-mouth plastic bottle (250 mL) to scoop samples from areas containing fine sediments within the sample area. Large organic debris were excluded from the sample, and excess water was decanted from the sample prior to closure. Samples of all matrices were cooled immediately following collection and frozen within several hours of collection. Samples were maintained in a frozen state during transport and subsequent storage until extracted and analyzed.

Assessment of Off-Target Deposit. The off-target deposit study area (100 × 20 m) bordered the southern bank of Carnation Creek and was located approximately 2000 m upstream of the estuary (Figure 1). The area included a vegetation buffer strip 10 m wide by 100 m long, divided roughly in half relative to the two dominant vegetation types (salmonberry and red alder). Within each vegetation zone, three transects 20 m long and oriented at right angles to the stream bank were established at 20-m intervals. Off-target deposit (the amount of chemical impinging on surfaces outside the intended zone of application) was assessed with deposit collection plates placed at 5-m intervals along each transect (Figure 2). In open areas, deposit collection plates (400 cm^2) constructed of aluminum foil sheets on corrugated cardboard were placed 20 cm above either ground or water level. In areas with vegetation, collectors were set at levels roughly corresponding to the height of salmonberry canopy (170 cm). The actual swath edge (Figure 2), defined as the line demarcating the zone of 100% injury to salmonberry, was determined by assessing phytotoxicity 10 months postapplication. The distances of the deposit collectors to the actual swath edge were remeasured and used for subsequent interpolation of glyphosate deposit at various distances from the target area.

Residue Analysis. Samples of ROUNDUP formulation (nominally 356 g of AI/L) were collected prior to mixing for application and kept at ambient temperature. Quadruplicate 1-mL aliquots were serially diluted (105×) with KH_2PO_4 buffer solution (mobile phase). The diluents were filtered with Millipore filter units (Millex HV, 0.45 μm) and subjected to HPLC analysis for glyphosate and AMPA. Tank-mix samples (400 mL) collected immediately prior to application on each day of treatment were stored frozen until analysis. Duplicate 1-mL aliquots were diluted (103×) in buffer solution, filtered, and quantified by an HPLC–vis technique as described by Thompson et al. (1989).

Residues of glyphosate and AMPA were extracted from the deposit collector sheets with use of an intensive rinsing/shaking and sonicating procedure with 0.1 N HCl as the extraction solvent. The extracts were then subjected to cation- and anion-exchange column cleanup (Monsanto, 1985a) prior to quantification by HPLC analysis. The limits of detection (LOD) observed for deposit collectors equated to 2.5×10^{-5} kg/ha AI. Limits of quantification (LOQ) were established as 1.25×10^{-4} kg/ha AI.

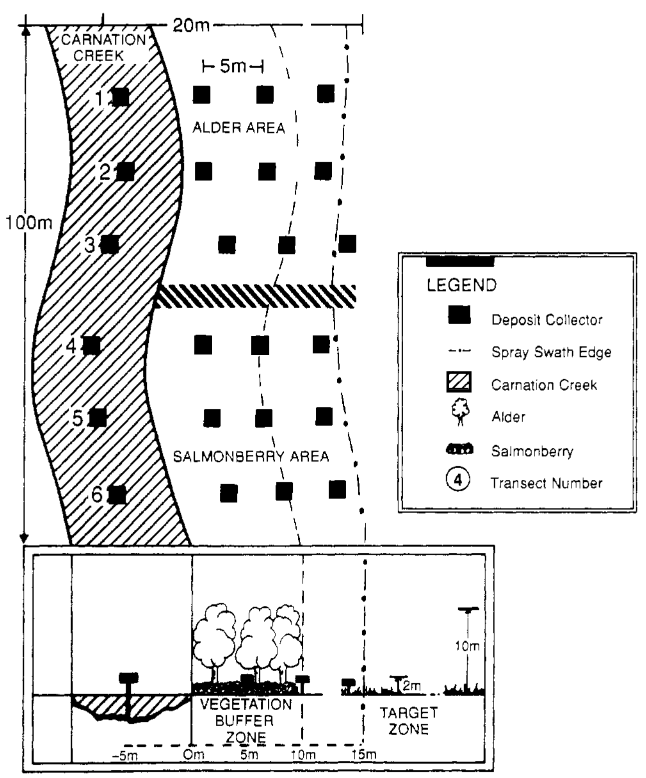

Figure 2. Experimental layout for the off-target deposit assessment.

Frozen water samples were thawed, acidified with HCl to pH 2, and filtered through a Millipore filtering apparatus (0.45-μm HA disk filters), prior to cation- and anion-exchange column cleanup. For water samples, the extraction and cleanup procedures of Cowell et al. (1986) were used with slight modification to provide samples for HPLC analysis. The procedure was altered by elution of the cation-exchange column with 6.5 N HCl and recovery of the final sample in mobile-phase solution. A preliminary validation for determination of glyphosate and AMPA from water indicated quantitative recovery with good precision (Table III). On the basis of these results, residues in water samples were not corrected for losses in the analytical method.

Samples of bottom sediments were air-dried, and aliquots (20-g air-dry mass) were extracted, cleaned up, and analyzed, with residue levels reported as micrograms per gram of dry mass. Suspended sediment samples including filter papers were weighed, homogenized, and extracted, with residue results calculated as micrograms per liter, based on 20 L of filtered water. For both bottom and suspended sediment samples, extraction, cleanup, and analyses were conducted following the method of Thompson et al. (1989).

Throughout the course of analytical determinations for bottom and suspended sediment samples, a quality control (QC) program was conducted. Blank field samples fortified with varying levels of glyphosate and AMPA were processed and analyzed daily in conjunction with field samples. Results of the QC program are presented as an indication of the accuracy and precision of the method (Table III). The QC data were used to correct the field sample data for recovery efficiency of the analytical method. For the purposes of this study, limits of detection were defined as concentrations yielding a signal at the retention time of interest equivalent to twice the value of the noise generated by a field blank (2 × S:N). Limits of quantification were established based upon the lowest concentrations in fortified quality control samples with coefficients of variation <15% (Table III).

Statistical Analysis. Residue data from stream water, bot-

Table III. Quality Control Data for Analytical Methods

substrate type (amt)	spike level,[a] μg	N^b	analyte	mean ± SE (CV, %)	LOD, ppb	LOQ, ppb
water (900 mL)	1.0–40.0	25	GLYPH	98.4 ± 7.6 (7.8)	0.1	1.0
	0.25–10.0		AMPA	86.4 ± 6.3 (7.3)	0.025	0.25
bottom sediment (20 g)	1.0–16.0	36	GLYPH	79.7 ± 6.3 (7.9)	30	50
	0.25–4.0		AMPA	64.0 ± 10.1 (15.4)	10	12.5
suspended sediment (20 L of water)	0.50–4.0	16	GLYPH	65.5 ± 9.1 (13.9)	0.003	0.03
	0.13–1.0		AMPA	54.3 ± 8.5 (15.7)	0.001	0.01

[a] Spike level = mass of glyphosate added per quantity of substrate. [b] N = total number of samples analyzed.

tom sediment, and suspended sediment analyses were plotted on arithmetic scales, and the time required for residues to dissipate below limits of detection was interpolated directly from the graphs.

Total residues (glyphosate plus AMPA as glyphosate equivalent) on the off-target deposit plates were converted to kilograms of AI per hectare rates. Log-transformed off-target deposit residue data were subjected to linear regression analysis with the equation $\log Y = a + b(\log X)$, where X = distance off-target (m) and Y = rate (kg/ha) of glyphosate deposited. Statistical differences between regression lines were determined by means of t-tests, comparing slopes (b) and elevations (a) of the lines as described by Zar (1984). Regression equations were used to interpolate distances at which deposit estimates were equal to 10, 1, and 0.1% of full deposit in the target area.

RESULTS AND DISCUSSION

Formulation and Tank-Mix Analyses. Analyses of the ROUNDUP formulation used in this study indicated an active ingredient (glyphosate) content of 363 g/L ± 2% CV. This value is approximately 2% in excess of label concentration (356 g of ae/L). No AMPA was detected in the formulation, which had been stored at ambient temperature (20 °C) for 3 months.

Analyses of tank mix samples showed concentrations of 7889 and 58 μg/L of glyphosate and AMPA, respectively, in the tank mix used for application to part of treatment area III. AMPA was found in only one of four tank-mix samples and not in the formulation samples. Detection of AMPA in this tank mix was attributed to a 6% (v/v) contamination of the tank mix with a mixture used 6 days earlier to spray areas adjacent to the Carnation Creek watershed.

Initial Stream Water Residues in Oversprayed Tributaries. Initial residues of glyphosate in the two directly oversprayed tributaries (750 and 1600) are presented in Figure 3. The maximum stream water residue (162 μg/L) was observed in tributary 1600, 2 h postapplication. In contrast, initial residues in tributary 750 were very low (<1.5 μg/L). The differences in initial residue response in the two oversprayed tributaries were attributed to differences in the degree of occlusion by riparian vegetation and general flow characteristics, as described previously.

In both oversprayed tributaries, glyphosate concentrations rose dramatically (100-fold) in response to the first rainfall event 27 h postapplication and then decreased rapidly, falling below detectable levels (LOD = 0.1 μg/L) within 96 h postapplication. The magnitude of the initial concentrations and rate of residue dissipation in tributary 1600 were comparable to those observed by Newton et al. (1984), who found maximum stream water concentrations of 270 μg/L following an aerial application of glyphosate at a rate of 3.3 kg/ha. Wan (1988) recently reported much lower initial levels (23 μg/L) in a stream unprotected by buffer zones. The increase in glyphosate stream water residues following the first rainfall event is consistent with previous research (Edwards et al., 1980; Newton et al., 1984; Wan, 1988) and may result from several sources of input including mobilization of residues

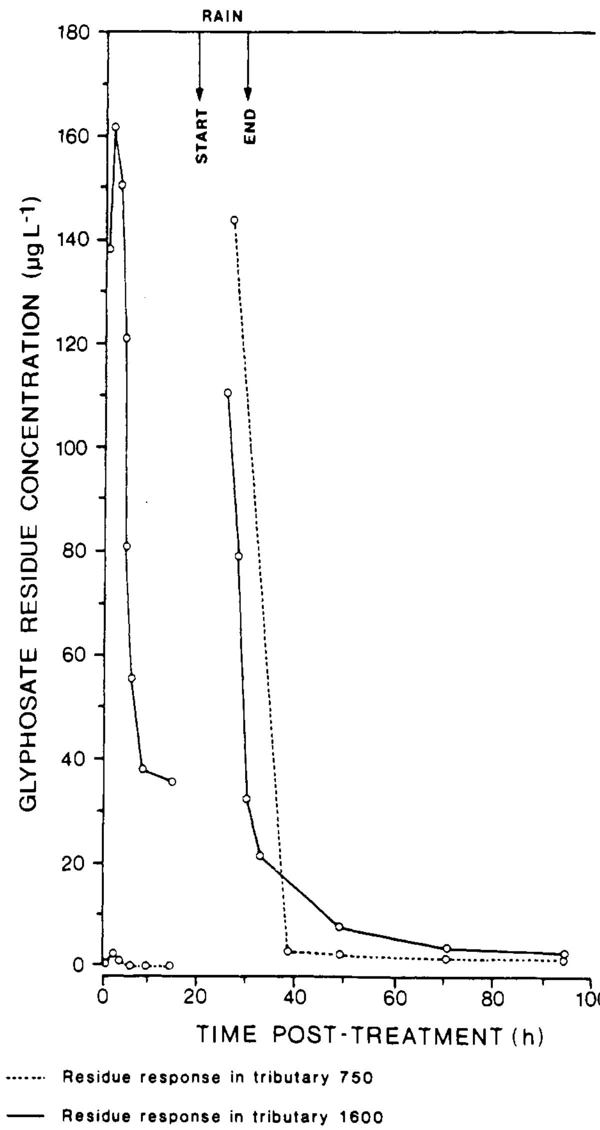

Figure 3. Glyphosate residues in stream water of directly oversprayed tributaries 750 and 1600 of the Carnation Creek watershed.

in ephemeral stream channels feeding the tributary, washoff of unabsorbed residues from overhanging vegetation, surface runoff, and subsurface flow. Concentrations of AMPA found in both tributaries 750 and 1600 were approximately 2% of concurrent glyphosate concentrations.

Initial Stream Water Residues in Buffered Tributaries. No quantifiable residues (LOQ = 1.0 μg/L) of glyphosate were found in tributaries buffered by a 10-m vegetation zone (C-Creek and 1450), with the exception of three samples from tributary 1450, which contained extremely low but quantifiable glyphosate residues. The maximum residue observed in this case was 2.47 μg/L at 10 h postapplication; the residue response observed in this tributary was attributed to unintentional overspray of the stream channel.

Stream water samples from Carnation Creek were

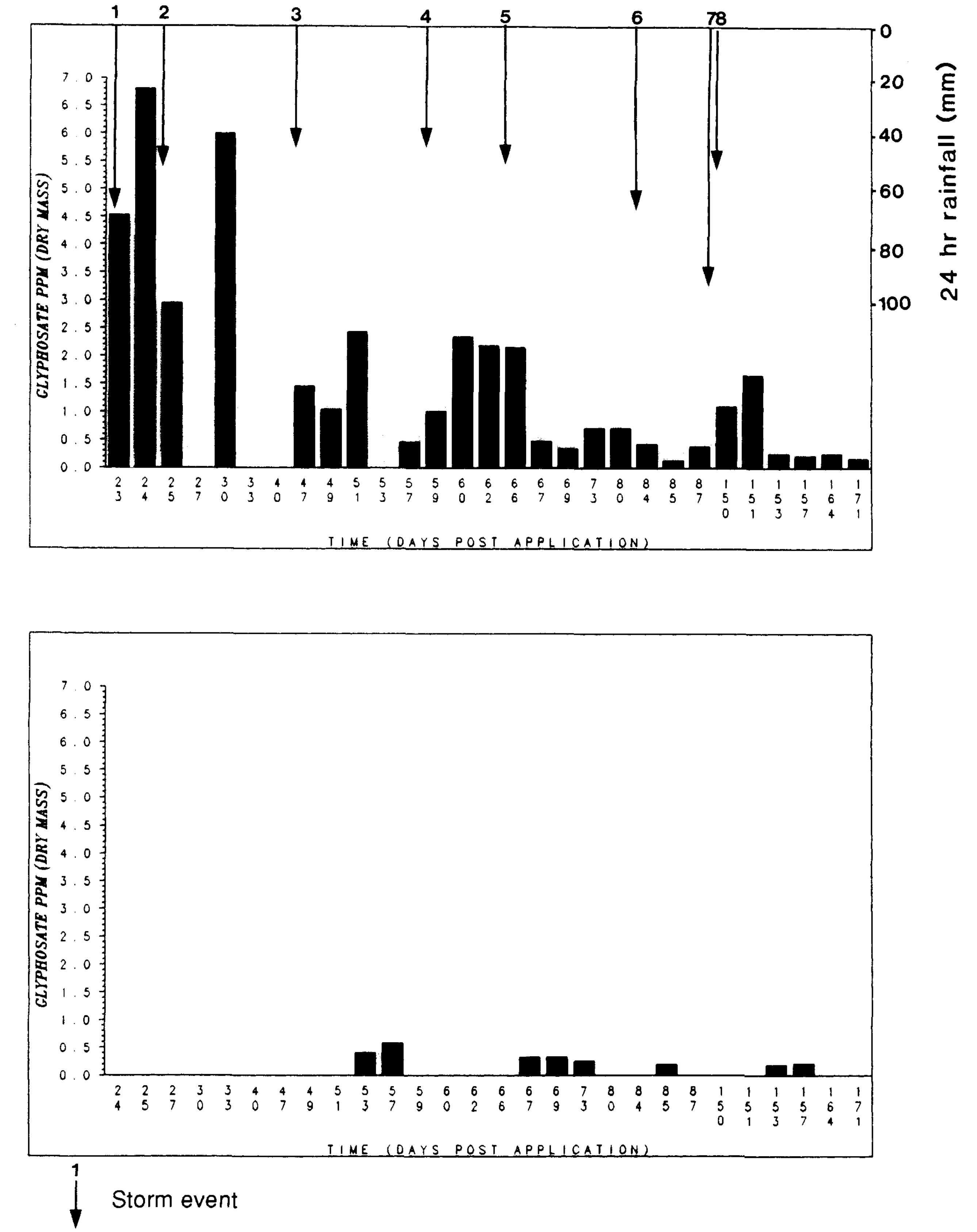

Figure 4. Glyphosate residues in bottom sediments of directly oversprayed tributaries 750 and 1600 of the Carnation Creek watershed.

obtained at B-weir and thus reflected residue inputs from the entire watershed. Initial samples were taken in association with all chemical applications (treatment areas I–IV, Figure 1). Only samples collected following application to treatment area III showed quantifiable glyphosate concentrations, with residue levels <1.5 μg/L. An increase in stream water residues (maximum 3.2 μg/L) in Carnation Creek subsequent to the first rainfall event was attributed primarily to mobilization of residues associated with oversprayed tributaries 750 and 1600 as discussed previously.

In general, these results corroborate other research indicating rapid dissipation of glyphosate in both lentic surface waters (Legris et al., 1985) and lotic systems (Comes et al., 1976; Norris et al., 1983; Legris et al., 1985) as the result of degradation, dilution, adsorption to organic substrates, or uptake by biota.

These results are also consistent with the observations of other workers (Kimmins, 1975; Newton et al., 1984; Wan, 1988; Edwards et al., 1980), who have previously reported that the first rainfall after treatment generates the highest residue concentrations in stream water and runoff water.

Storm Event and Long-Term Stream Water Residues. During the study, seven rainfall events resulting in mainstream flows above 3 m^3/s were identified as major storms (Table II). Stream flows observed in Carnation Creek for these storm events were 13.1, 8.3, 10.0, 5.3, 3.0, 4.0, and 4.4 m^3/s, with cumulative rainfall for the period being 1490 mm. A total of 120 water samples were collected from the main channel and three tributaries (750, 1600, and C). Although trace levels of glyphosate (<1 μg/L) were occasionally detected in the main channel and two oversprayed tributaries, no quantifiable residues (<1 μg/L) of glyphosate or AMPA were found in any stream water samples associated with storm events. Similarly, biweekly samples taken from the main stream and tributaries 750, 1600, and C during the long-term monitoring period (196–364 days) after treatment contained no detectable residues (LOD = 0.1 μg/L).

Residues in Bottom and Suspended Sediments. A total of 120 samples of stream bottom sediments were collected in conjunction with storm events. No quantifiable amounts of glyphosate or AMPA were found in buffered tributary 1450 or the main channel during the storm event monitoring period.

The highest residue levels observed in the aquatic compartments of the ecosystem were associated with bottom sediments of the oversprayed tributaries (1600 and 750), indicating that bottom sediments were the major sink for glyphosate residues. Peak concentrations of glyphosate in bottom sediments (6.80 and 6.34 μg/g dry mass) occurred in tributary 1600. Concentrations of glyphosate in bottom sediments of tributary 750 were substantially lower (0.44 and 0.58 μg/g dry mass). In both cases, peak glyphosate concentrations in bottom sediments appeared following major storm events (Figure 4). In both tributaries, glyphosate and AMPA residues in bottom sediments persisted throughout the storm event monitoring period.

We suggest that differences observed in glyphosate residues associated with bottom sediments of the two oversprayed tributaries may be interpreted on the basis of stream flow dynamics. In meandering streams with slow flow rates, as is the case for tributary 1600, deposition of fine-textured organic sediments is common. In contrast, fast-flowing streams such as tributary 750 inherently have little sediment deposition and are regularly flushed out during storm events; bottom sediments that accumulate are typically coarser in texture, resulting in lower surface area and sorptive capacity for chemical residues.

Analyses of 49 bottom sediment samples taken between 196 and 364 days showed no quantifiable residues in sediments of the Carnation Creek main channel or tributary 1450. However, quantifiable residues (0.14–1.92 μg/g dry mass) were observed in bottom sediments of directly sprayed tributaries 750 and 1600. Glyphosate residues in bottom sediments were persistent in comparison to stream water residues but declined over time so that glyphosate concentrations were less than 0.2 μg/g dry mass by the end of the long-term monitoring period.

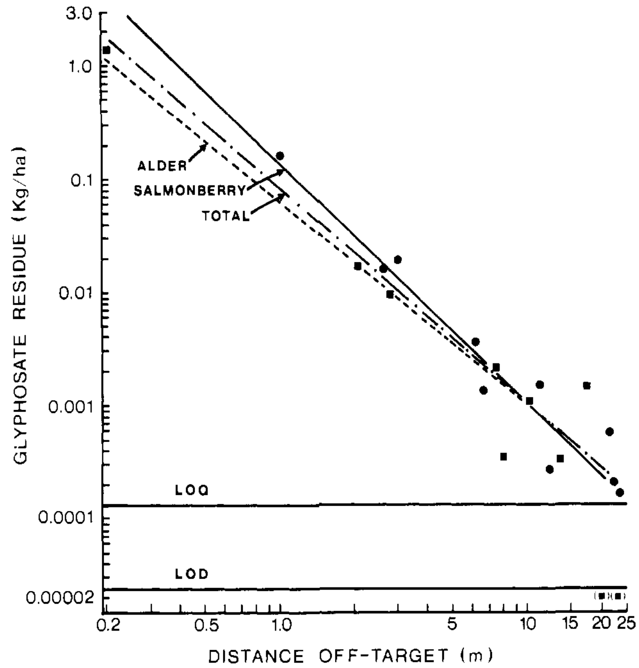

Figure 5. Off-target deposit of glyphosate at the Carnation Creek watershed.

A total of 29 suspended sediment samples were collected at B-weir during the seven storm events that occurred during the study. Quantifiable glyphosate residues were found in only four of the 29 samples collected. The highest concentrations detected in suspended sediments (0.060 μg/L) were observed 23 days postapplication, following the first major storm event.

Off-Target Deposit Assessment. The highest deposit rate observed (1.882 kg/ha) was found 2.9 m within the target area and equated to 6% less than the nominal application rate for the study. The lowest quantifiable deposits off-target (0.001 55 and 0.000 176 kg/ha) were found 17.2 and 23.1 m off-target for the salmonberry and alder areas, respectively. Statistical analysis of the deposit data indicated a significant ($P < 0.05$) linear regression of log-transformed data with coefficients of determination (r^2) values of 0.89 and 0.94 for the alder and salmonberry areas with slopes of −1.82 and −2.13, respectively. Based on a lack of significant differences between slopes (t = 1.09, df = 15) and elevations (t = −0.178, df = 16) for the two regression lines, data were pooled to allow calculation of a general extinction rate (Figure 5). The regression of pooled data was characterized by an r^2 value of 0.91 and a slope of −1.05. On the basis of regression of pooled data and a calculated extinction rate equivalent to the slope of this line (−1.05 kg ha^{-1} m^{-1}), the distances from the spray boundary at which 10%, 1%, and 0.1% of the full deposit were interpolated as 0.7, 2.2, and 7.4 m, respectively (Figure 5). The regression equations derived from off-target deposit measurement data indicate that vegetation buffer zones of 10 m should effectively eliminate chemical drift into streams under the specific application, meteorological, and physical conditions of the Carnation Creek site. This hypothesis was borne out by the general lack of glyphosate residues in stream water of buffered tributaries C-Creek and 1450.

Relationship of Environmental Residues to Aquatic Toxicity Data. A relatively large database currently exists with respect to the toxicity of ROUNDUP and/or glyphosate to aquatic biota, the investigation conducted by

Table IV. Toxicity and Calculated Relative Safety Factor Values for ROUNDUP and Glyphosate in Freshwater Aquatic Organisms

organism[c]	LC_{50},[a] mg/L	RSF[b] 1450	RSF[b] CC	reference
		ROUNDUP		
D. magna	25.5	3188	2383	Servizi et al., 1987
O. nerka	26.7	3338	2495	Servizi et al., 1987
P. promelas	2.4 (a)	300	224	Folmar et al., 1979
G. pseudolimnaeus	43	5375	4019	Folmar et al., 1979
L. macrochirus	6.4 (a)	800	598	Folmar et al., 1979
S. gairdneri	8.3 (a)	1038	776	Folmar et al., 1979
S. gairdneri (eggs)	46.0 (a)	5750	4299	Folmar et al., 1979
S. gairdneri (sac-fry)	11.0 (a)	1375	1028	Folmar et al., 1979
S. gairdneri (swim-up fry)	2.4 (a)	300	224	Folmar et al., 1979
S. gairdneri (fingerling)	1.3	163	122	Folmar et al., 1979
S. gairdneri (fingerling)	2.2 (a)	275	206	Folmar et al., 1979
S. gairdneri	32.4	4050	3028	Wan et al., 1988
S. gairdneri	54.8	6850	5121	Hilderbrand et al., 1982
O. kisutch	42.3	5288	3953	Wan et al., 1988
		Glyphosate		
L. macrochirus	24	10000	7500	USDA, 1981
L. macrochirus	150 (a)	62500	46875	Folmar et al., 1979
S. gairdneri	140 (a)	58333	43750	Folmar et al., 1979
S. gairdneri	86	35833	26875	Monsanto, 1985c
P. promelas	97 (a)	40417	30313	Folmar et al., 1979
I. punctatus	130	54166	40625	Folmar et al., 1979

[a] LC_{50} values are for 96-h exposure periods except those values denoted by (a) for which exposure periods are 24 h. [b] Relative safety factor calculated as the ratio of reported toxicity value to the maximum concentration observed in tributary 1450 (0.0024 mg/L glyphosate; ROUNDUP equivalence, 0.008 mg/L) and the main channel of Carnation Creek (CC) (0.0032 mg/L; ROUNDUP equivalence, 0.0107 mg/L). ROUNDUP equivalence calculated based on guarantee of 356 g of acid/L of ROUNDUP formulation with a specific gravity of 1.17 (Monsanto, 1985a). [c] Genus names: *D* = *Daphnia*, *O* = *Oncorhyncus*, *G* = *Gammarus*, *L* = *Lepomis*, *S* = *Salmo*, *P* = *Pimephales*, *I* = *Ictalurus*.

Folmer et al. (1979) being the most comprehensive (Table IV). These data indicate that ROUNDUP is substantially more toxic than technical glyphosate and that toxicity was greatest in sac-fry and early swim-up life stages. Duration of exposure (24–96 h) generally resulted in only marginal effects on LC_{50} values.

In Canada, the use of pesticides in forest management requires establishment of buffer zones (ranging from 60 to 100 m) to reduce or eliminate pesticide input into aquatic systems. Risk assessments for aquatic organisms are based on the relationship between the expected environmental concentration (EEC) calculated from a worst case scenario of direct application of the pesticide at the maximum rate of application to a body of water 0.5 m deep. The EEC is then compared to data derived from standard laboratory toxicity protocols (i.e., 96-h LC_{50} values), in order to determine the margin of safety. We contend that this approach may vastly overestimate the true risk under natural stream conditions, because organisms in lotic systems are typically not exposed to continuous static concentrations for periods of 96 h and because buffer zones required around aquatic habitats effectively eliminate inputs of glyphosate to stream systems.

Our experimental research results, as well as monitoring of operational spray programs (Wan et al., 1988; Eremko, 1986; Gluns, 1989), consistently indicate that establishment of appropriate buffers effectively eliminates stream contamination resulting from off-target deposits of glyphosate. Infrequently, very low residues have been observed in protected streams, and these are generally associated with storm events occurring soon after chemical application. In an effort to estimate realistic margins of safety for organisms in buffered streams, relative safety factors (RSF) have been calculated as the ratio of toxicity end points presented in Table IV to maximum residues observed in buffered streams of the Carnation Creek watershed study. As such, the RSF values may still substantially overestimate risk owing to differences in mode and duration of exposure as discussed previously. The maximum stream water concentration of glyphosate in buffered tributary 1450 was 0.024 mg/L, while that of the main channel of Carnation Creek was 0.0032 mg/L. On the basis of glyphosate acid content of 365 g of acid/L in ROUNDUP formulation with a specific gravity of 1.17 (Monsanto, 1985a), the ROUNDUP equivalences for these maximum observed concentrations are 0.008 and 0.0107 mg/L, respectively. The lowest RSF values calculated in this manner were 122 for ROUNDUP and 7500 for glyphosate. This analysis suggests that residue levels, as typically observed under actual operational conditions, pose essentially no risk to aquatic organisms in terms of acute toxicity.

Stream water residues observed in oversprayed tributaries in this study exhibit a dual-pulse pattern of exposure that may be considered typical for glyphosate/ROUNDUP. The pulse exposures result from an initial direct input due to overspray and a subsequent input associated with mobilization of terrestrial residues with the first storm event following application. The data clearly show (Figure 3) that exposures to peak concentrations of glyphosate or ROUNDUP would be in the order of a few hours; other researchers have observed similar patterns in lotic systems (Wan et al., 1988; Newton et al., 1984). Realistic estimates of risk to aquatic organisms exposed in this manner are difficult, owing to the general lack of toxicity testing conducted with pulse modes of exposure. Folmer and co-workers (1979) conducted tests designed to simulate actual field exposures in which sac-fry of rainbow trout was exposed to ROUNDUP for 6 h. Results of these tests indicated that statistically significant reduction in survival occurred at concentrations of 5 mg/L. On the basis of this value and the maximum concentration of glyphosate observed in the two oversprayed tributaries of the Carnation Creek study (tributary 1600 peak concentration of glyphosate, 0.162 mg/L; ROUNDUP equivalence, 0.540 mg/L), the calculated RSF values for a worst case scenario of direct overspray would be 31 and 9.26 for glyphosate and ROUNDUP, respectively. This assessment would suggest that even under worst case conditions of direct overspray residues of ROUNDUP or glyphosate would not be sufficient to elicit a significant toxic response in aquatic organisms. The highest concentrations observed in oversprayed tributaries were also well below sublethal, no-effect levels (2.78 mg/L) for coho salmon smolt osmoregulation or growth as reported by Mitchell et al. (1987).

Maximum glyphosate residues in bottom sediments were 6.80 μg/g dry mass, and these residues were relatively persistent compared to stream water residues. However, glyphosate residues are known to sorb strongly to organic matter (K_{oc} = 30 000), and its sorption to natural organic substrates is well documented (Sprankle et al., 1975; Wan, 1988). Thus, we suggest that glyphosate residues in bottom sediments are unlikely to be biologically available. A paucity of information on the toxicity of bound sediment residues of glyphosate precludes assessment of potential impacts relating to residues in this compartment of the aquatic ecosystem.

CONCLUSIONS

Glyphosate residues in the aquatic compartments of the watershed were primarily associated with bottom sediments and were more persistent and greater in magnitude compared to stream water residues. These results suggest that the bottom sediments act as a primary sink for glyphosate residues, however, based on the documented tendency of glyphosate to sorb strongly to soils, suggest that such residues are tightly bound and not biologically available. Suspended sediments did not represent a major mechanism for export of aquatic residues from the treated watershed. The stream water residue data confirm the results of the off-target deposit assessment and indicate that, under the conditions of this study, 10-m vegetation buffer zones effectively eliminated direct chemical inputs into protected streams. The low magnitude and transient nature of glyphosate/ROUNDUP residues observed in stream water result in margins of safety ranging from 10 for directly oversprayed streams to >100 for buffered streams.

In summary, the results of the aquatic environmental fate research conducted at Carnation Creek are consistent with previous studies and suggest that, even under worst case conditions of direct overspray, chemical concentrations would be insufficient to result in a significant toxic impact to aquatic organisms. The results support the continued use of glyphosate as environmentally acceptable chemical herbicide for use in forest renewal programs.

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Fate of Glyphosate in a Canadian Forest Watershed. 2. Persistence in Foliage and Soils

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Residues of glyphosate [*N*-(phosphonomethyl)glycine] and the metabolite (aminomethyl)phosphonic acid (AMPA) were monitored in foliage, leaf litter, and soils following aerial application of ROUNDUP herbicide (nominal rate 2.0 kg/ha AI) to the Carnation Creek watershed of Vancouver Island, British Columbia. Glyphosate deposit was variable, ranging from 1.85 to 2.52 kg/ha AI, depending upon location within the watershed. Foliar residues in red alder and salmonberry were 261.0 and 447.6 μg/g, respectively, indicating good impingement on the target foliage. Leaf litter residues, which averaged 12.5 μg/g for red alder and 19.2 μg/g for salmonberry initially, declined to less than 1 μg/g within 45 days postapplication (DT_{50} < 14 days). In soils, glyphosate and AMPA residues were retained primarily in the upper organic layers of the profile, with >90% of total glyphosate residue in the 0–15-cm layer. Distribution data for both glyphosate and AMPA suggested strong adsorption and a low propensity for leaching. Glyphosate soil residues dissipated as a function of time with an estimated DT_{50} of 45–60 days. After 360 days, total soil residues of glyphosate were 6–18% of initial levels.

The use of glyphosate (ROUNDUP, VISION (Monsanto Corp., St. Louis, MO)) in Canadian silvicultural management has been increasing steadily since its federal registration in 1984. The environmental fate of glyphosate in soils has been investigated primarily in relation to agricultural use patterns and environmental conditions of the United States (Rueppel et al., 1977; Edwards et al., 1980; Hance 1976; Sprankle et al., 1975; Muller et al., 1981; Moshier and Penner, 1978). The database pertinent to forest use patterns is more limited, although Newton et al. (1984) and Torstensson and Stark (1981) have reported on the fate and behavior of glyphosate in forest soils of the United States and Sweden, respectively. The fate of glyphosate in Canadian forest ecosystems has not been widely studied, and reports have been primarily restricted to government documents (Dotsie et al., 1988; Legris and Couture, 1988). Information pertaining specifically to the environmental fate of glyphosate in soils of Canadian western coastal watersheds is lacking. Similarly, although a relatively large amount of information is available with respect to the fate of glyphosate in agricultural crops or weed species, little information pertaining to the behavior of glyphosate residues in forest brush species is available. Newton et al. (1984) monitored the persistence of glyphosate in red alder and other forest hardwood species. Lund-Hoie (1985a) reported on the uptake, distribution, and metabolism of this herbicide in spruce and later in two brush species—ash and birch (Lund-Hoie, 1985b). Most recently, the persistence of glyphosate residues in foliage (raspberry, grasses, balsam fir, red maple) and in litter (white spruce, red maple) has been reported (Freedman et al., 1988).

In the coastal area of British Columbia, climatic conditions frequently include autumn and winter rainstorms: annual rainfall often exceeds 2000 mm. Winter temperatures are cool, with snowpack occurring in the upper reaches. Under such conditions, watersheds with areas of high water table, seasonally saturated soils, and frequent surface runoff events following major storms are common. Soil profiles in the flood plain of coastal forest watersheds are often highly stratified into organic rich (30% or greater organic matter content) upper horizons,

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