FATE OF GLYPHOSATE IN A FOREST STREAM ECOSYSTEM

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ABSTRACT

Residues of glyphosate and its major metabolite aminomethyl phosphonic acid (AMPA) were monitored in stream water, bottom sediments and suspended sediments for a one year period following aerial application of glyphosate (2.0 kg/ha) to the Carnation Creek watershed of Vancouver Island, British Columbia. Analysis of deposit collector samples indicated an actual deposit of 1.88 kg/ha within the target zone and that less than 0.1% of the full rate impinged on surfaces beyond 8 m from the spray zone boundary. The highest concentrations of glyphosate (6.80 μg/g dry mass) were observed in bottom sediments of a directly sprayed tributary, with low residue levels (<0.2 μg/g) persisting in this substrate throughout the monitoring period. Suspended sediment samples collected from the main stream channel, indicated low levels of glyphosate input (0.10 μg/L) in conjunction with the first five storm events (23-66 days post application). The highest stream water residue observed (162 μg/L) occurred in a directly sprayed tributary, 2 h post-application and decreased rapidly to 37 μg/L after 16 h. Transient increases in glyphosate concentrations were associated with first rainfall event (39 mm) which occurred 23 h post-application. Subsequent dissipation of residues in the two tributaries receiving direct glyphosate applications was rapid, such that no quantifiable residues were found after 96 h post-application. No quantifiable residues were found in tributaries buffered with a 10-m vegetation strip during the monitoring period.

INTRODUCTION

Glyphosate (ROUNDUP[1]) is a forestry herbicide recently registered in Canada for site preparation and conifer release (Malik and Vanden Born 1986). Federal and provincial regulatory agencies require further research on the aquatic fate and persistence relevant to the operational use of glyphosate under local geographical and climatic conditions. Although 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), this aspect has not been studied in Canada. Research on the aquatic fate and impact of glyphosate is of particular importance in coastal temperate rainforest ecosystems of British Columbia. In such areas a number of factors, including steep-sloped terrain, high rainfall (>2000 mm), and proximity of treatment areas to salmon spawning streams, combine to approximate a worst case scenario with respect to aquatic ecosystem impacts following silvicultural chemical applications. The aquatic persistence and transport patterns of glyphosate under these situations are unknown. Also, the relative degree of stream contamination resulting from input sources such as direct over-spray of stream channels, off-target deposit, lateral movement and mass transfer from surrounding treated areas have not been quantified under these conditions.

[1]Registered trademark of Monsanto Co. Inc., St. Louis, Missouri

A vegetation buffer strip along streams may be used to reduce contamination via off-target drift and runoff. Current regulatory guidelines in British Columbia require the establishment of a 10-m pesticide-free zone with appropriate buffers, usually 100-m, to achieve this goal. These guidelines may unduly restrict silvicultural treatment of the highly productive forest lands that border the intensive network of streams in coastal regions.

Establishment of an effective buffer must balance environmental concerns with the need for maximum utilization of lowland forests. The goal of effective buffering has become feasible with the development of dispersal systems, such as the MICROFOIL BOOM[2], which are designed to reduce chemical drift and the width of buffer strips required to protect streams and lakes (Payne et al. 1986).

OBJECTIVES

The specific objectives of this study were:

1. To assess the on- and off-target deposit of glyphosate following an operational application for conifer release in a typical, coastal British Columbia watershed.

2. To determine the residue levels and subsequent dissipation of glyphosate and its major metabolite AMPA during the initial 96 hour period in four dissimilar streams following aerial application with a MICROFOIL BOOM.

3. To compare residue levels and dissipation rates of glyphosate and AMPA in water, stream bottom sediment and suspended sediment, of buffered and directly sprayed streams during fall and winter storm events.

4. To assess the long term (1 year) potential for stream contamination resulting from lateral movement and mass transfer in four streams typical of a coastal forest watershed.

5. To evaluate the effectiveness of a 10-m vegetation buffer in protecting forest streams from contamination via off-target drift resulting from applications with a MICROFOIL BOOM.

MATERIALS AND METHODS

Site Description

The study site was located in the Carnation Creek watershed on the west coast of Vancouver Island, British Columbia (48°50'N, 125°2'W), approximately 200 km west of Victoria (Fig. 1). Carnation Creek has been the focus of a 15-year investigation of the effects of logging on fish (Hartman 1982). The main stream and side channels support populations of coho (*Oncorhynchus kisutch* Walbum) and chum (*O. keta* Walbum) salmon.

The 10-km watershed is within a coastal hemlock and cedar ecozone (Krajina 1969). Following clear-cutting in 1975, the study area was site-prepared and planted in 1976 (Dryburg 1982). Shortly after planting, thick vegetation, dominated by salmonberry (*Rubus spectabilis* Pursh) and red alder (*Alnus rubra* Bong), covered the area (King and Oswald 1982). In September 1984, the ranges in height for salmonberry and alder were 1.5-2.5 m and 7-10 m, respectively. Weather stations and a broadcast weir (B weir) were established near the mouth of Carnation Creek to monitor precipitation and stream discharge (Fig. 1). The four tributaries involved in this study were

[2] Registered trademark of Union Carbide Inc., Ambler, Pennsylvania

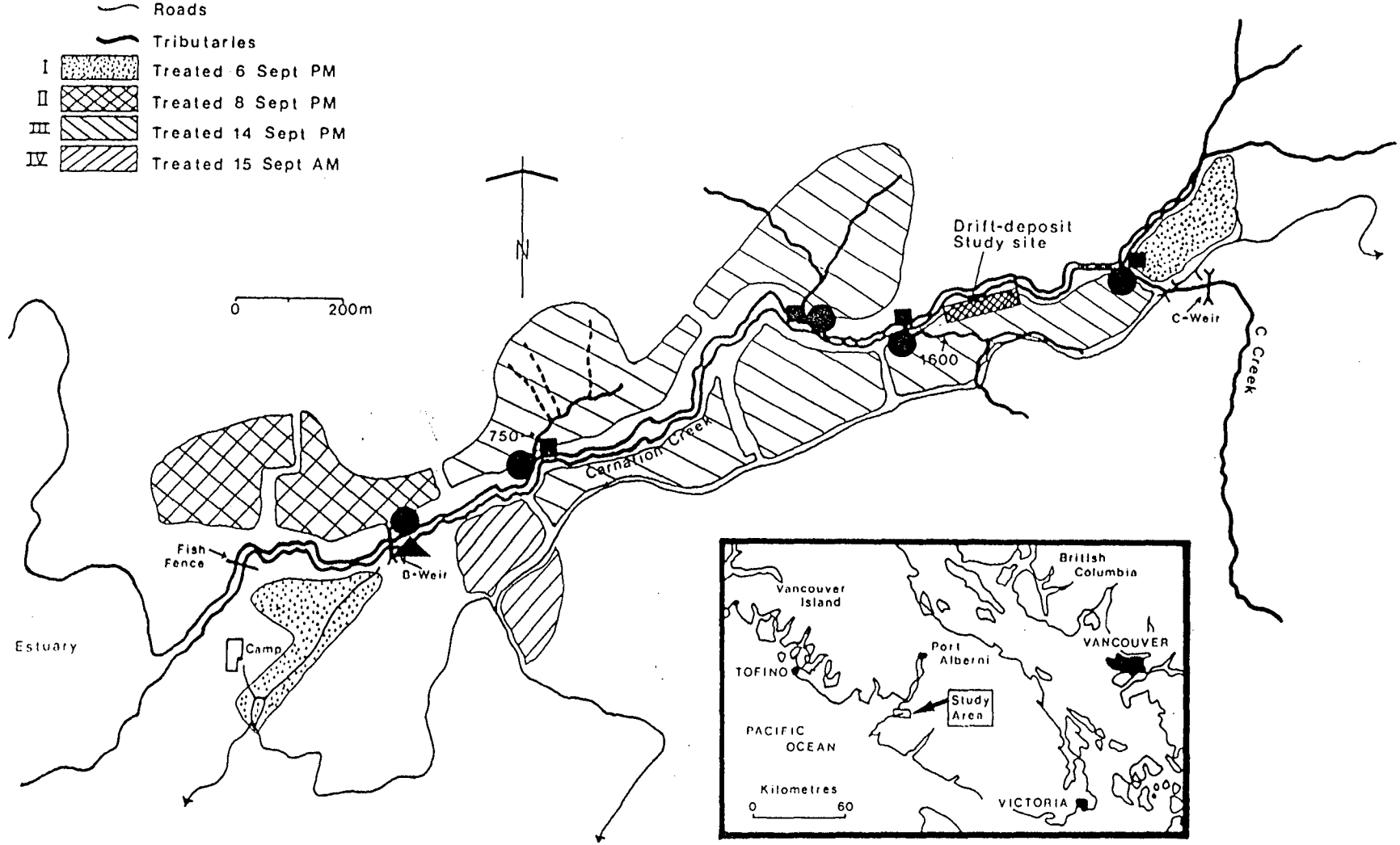


Figure 1. Location of the Carnation Creek Watershed Study Area and Stream Sampling Stations.

located at 750, 1450, 1600 and 2200 m upstream from the Carnation Creek estuary; they are referred to in this manuscript as tributaries 750, 1450, 1600 and C, respectively (Fig. 1). Annual precipitation at the study site ranges from 2500 to 3800 mm and occurs mainly from October through March (Hetherington 1982). Tributaries 750, 1450 and C are ephemeral and in 1984 started flowing with the first seasonal rainfall (35 mm) on September 04. Further details regarding site characteristics and description are reported by Hartman (1982) and King and Oswald (1982).

Herbicide Application

ROUNDUP (isopropylamine salt of glyphosate) was applied in the fall of 1984 at 2 kg active ingredient (a.i.) per hectare by a Bell-47 helicopter equipped with a MICROFOIL BOOM and 1.5-mm hayrack nozzles calibrated to deliver 258.25 L/ha. The main channel of Carnation Creek and tributaries 1450 and C (Fig. 1) were buffered with a strip of vegetation, approximately 10 m in width. Tributaries 750 and 1600 were directly treated. A total of 45 ha received herbicide application on four different days. Treatment Area I was sprayed on 06 September 1984 (1935 - 2005 h), Treatment Area II on 08 September 1984 (1416 - 1940 h), and Treatment Area III received application on 14 September 1984 (1430 - 1930 h). Meteorological conditions for specific spray periods as well as application system specifications are reported in Reynolds et al. (1989).

Site Preparation for Deposit Study

The study area prepared for determination of initial deposit levels was located on the southern bank of Carnation Creek about 2000 m upstream from the estuary (Fig. 1). The deposit study area measured 100 x 20 m, including 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) (Fig. 2). Within the deposit-study area six transects, each 20 m apart and 20 m long, were established at right angles to the stream bank (Fig. 2). Three transect lines were located in the salmonberry area and three in the alder area. The deposit collectors were located at 5-m spacing from the stream bank at -5, 5, 10 and 15 m along each transect (Fig. 2). The outermost deposit collectors were located 5 m inside the stream channel.

Sampling Methodologies

Deposit collector sampling

Deposit collectors were arranged within the off-target deposit study site as described above. In open areas, deposit collection plates (400 cm^2) were placed 20 cm above either ground or water level. In areas of vegetation, collectors were raised 170 cm above ground level, roughly corresponding to the height of salmonberry but below the alder tree canopy. The actual swath edge (Fig. 2) was determined by assessing phytotoxicity 10 months post-application. The swath edge was defined as the line demarcating the zone of 100% injury to salmonberry. The distances of the deposit collectors to the actual swath edge were measured and used for subsequent interpolation of glyphosate deposit at various distances from the target area. Detailed descriptions of deposit collection procedures have been reported previously (Feng and Klassen 1986).

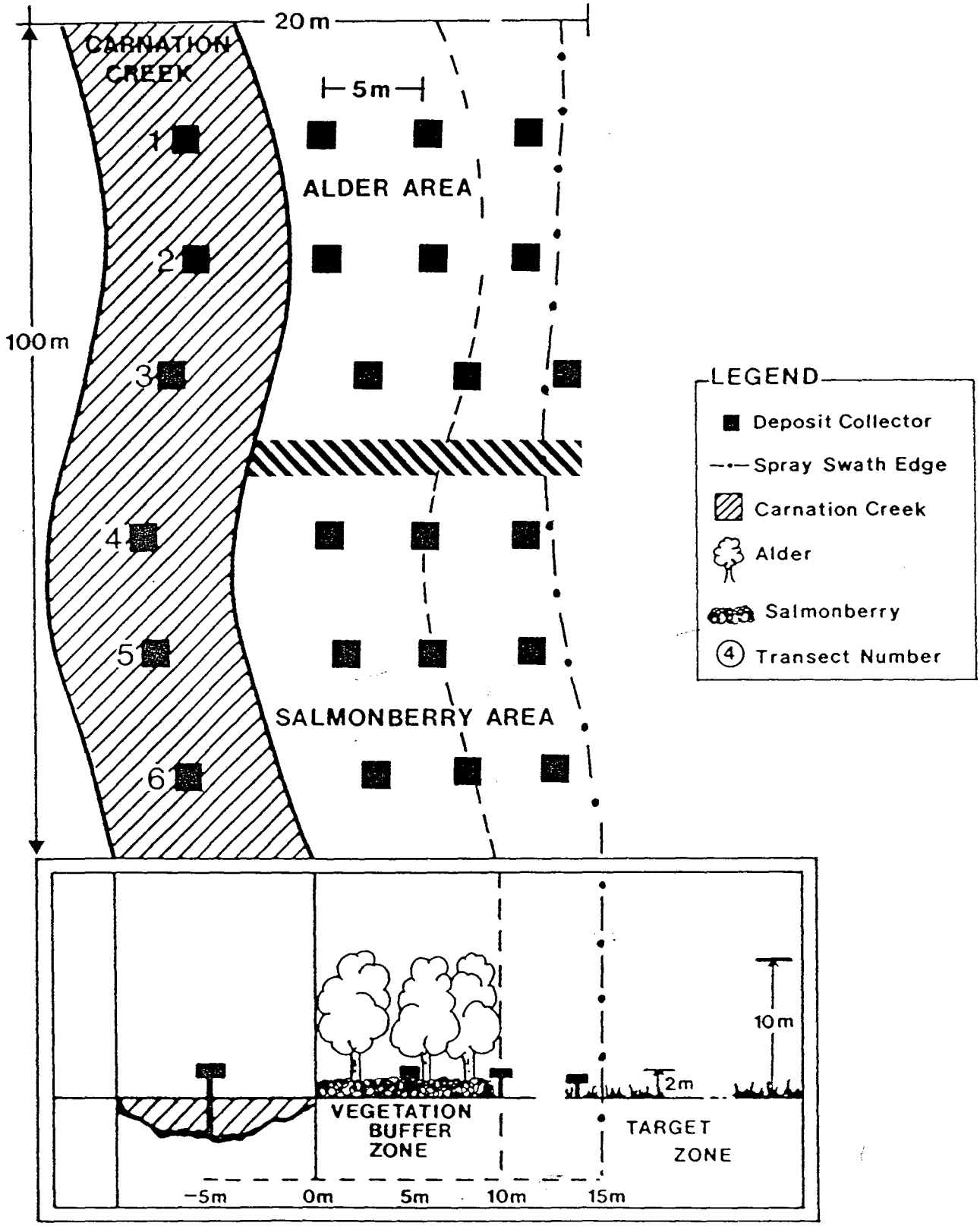


Figure 2. Experimental Design of the Off-Target Deposit Study at Carnation Creek Watershed.

Initial (96-h) intensive sampling program for water residues

Water samples were collected intensively during the first 96-h period after treatment, at tributaries 750, 1450 and 1600 as well as in Carnation Creek (Fig. 1). The 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 Treatment Area III. Water samples were collected using techniques described by Feng and Klassen (1986). The sampling protocol involved an initial, short-term, intensive sampling period during which integrated samples were collected hourly for the first 96 hours post treatment (Table 1). Integrated samples (IS) were obtained initially by collecting six samples of 150 mL at 10-minute intervals, thus yielding an hourly integrated sample with total volume of 900 mL. Following the intensive sampling period, point samples (PS) of 900 mL were collected according to the schedule as outlined in (Table 1).

Table 1. Sampling schedules for the Carnation Creek watershed study

Sampling Site	Sampling Schedule (time post-application)
Intensive (96-h) Sampling Schedule For Water (Time in Hours)	
Carnation Creek	(IS) 0 1 2 3 4 5 6 7 8
(B weir)	(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 16 28 30 32 34 48 72 96
Storm Event Sampling Schedule For Water, Bottom and Suspended Sediments (Time in Days - Bold Values Denote Major Storm Events)	
Carnation Creek (B weir),	23 24 25 27 30 33 40 47 49 51 53 57 59 60 62
750,1600 & C tributaries	66 67 69 73 80 84 85 87 150 151 153 157 164 171
Long Term Sampling Schedule (Water and Bottom Sediments) (Time in Days)	
Carnation Creek (B weir),	196 210 224 238 252 263 280 297 311 326
750, 1600 and C tributaries	339 355 364

IS = Integrated Sample
PS = Point Sample

Storm event sampling

Water samples were collected in conjunction with major storm events at B weir in Carnation Creek, and at tributaries C, 750 and 1600. Suspended sediment samples were taken at B weir only, during and after major storm events (Table 1). Methods used to obtain suspended sediment samples are presented in detail by Feng and Klassen (1986). In brief, the technique involves collection and filtration of 20 L of water during each storm event; the residues in filtered sediments are quantified and reported on a μg/L basis. Storm event samples were obtained during a major storm

event when the instantaneous discharge of Carnation Creek at B weir reached a threshold level of 7 m^3/s. Post-storm sampling commenced when the discharge decreased to below the same threshold, with collections at 1, 3, 7, 14 and 21 days after a storm or until a new storm began. Peak discharges were recorded in conjunction with each storm event, while daily rainfall and average discharge were measured throughout the sampling program.

Long term sampling

Long term water and bottom sediment point samples were obtained from Carnation Creek (at B weir) and from tributaries 750, 1600 and C. The sampling schedule was biweekly, totaling thirteen sampling dates. Methods used to obtain water and sediment samples were described by Feng and Klassen (1986).

Residue Analysis

Formulation analysis

Samples of ROUNDUP formulation (356 g a.i./L) were collected before mixing for application and kept at ambient temperature. Quadruplicate 1 mL aliquots were serially diluted (10^5 X) with KH_2PO_4 buffer solution (mobile phase) as described in Table 2. The diluents were filtered with Millipore filter units (Millex HV, 0.45 μm) and subjected to HPLC analysis for glyphosate and AMPA, as described above and in Table 2.

Table 2. Specifications of HPLC instrumentation

Component	Specification
HPLC System:	Varian Model 5560 Ternary HPLC, Model 8085 autosampler
Detector:	UV-200 variable wavelength detector set at 570 nm
Derivatization System:	Ninhydrin post column reactor (100°C) System V Model 5000 (Varian Inc.)
Analytical Column:	Bio-Rad Aminex A-9 10 cm X 4.6 mm i.d.
Guard Column:	Bio-Rad Aminex A-9 (K^+ form cartridge)
Mobile Phase:	0.005 M KH_2PO_4 buffer in 4% methanol pH = 1.9
Flow Rate:	0.5 mL/min (iso-cratic)
Column Temperature:	50°C

Tank mix analysis

Tank-mix samples (400 mL) collected immediately prior to application to Treatment Area III were stored frozen prior to analysis. Duplicate 1 mL aliquots were diluted (10^{-3} X) in buffer solution and filtered and analyzed as described above.

Deposit collector sample analysis

Residues of glyphosate and AMPA were extracted from the deposit collecting sheet by a multiple rinsing/shaking and sonicating procedure using 0.1 N HCl as the extraction solvent (Feng and Klassen 1986). The extracts were then subjected to cation and anion exchange column cleanup prior to quantification by HPLC analysis (Table 2). Herbicide quantities (glyphosate plus AMPA as glyphosate equivalent) on the deposit plates, were converted to kg/ha rates using the equation:

$$kg/ha = 2.5 \times 10^{-4} \times R$$

where R = total residue (μg) per deposit collector (400 cm^2). The off-target deposit residue data were subjected to linear regression analysis, using the logarithms of distance off-target in meters (X) and rate (kg/ha) of glyphosate deposited (Y) for both conditions (alder area and salmonberry area) and for the pooled data of the six replicates ($\log Y = a + b(\log X)$). 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. Since deposit estimates were measured over a limited distance, and since distance to off-target deposit relationships are generally exponentially related over larger distances, regression equations could not be used for extrapolation beyond the furthest distance at which deposits were empirically determined. The regression equations developed to interpolate off-target deposit are specific for the application, meteorological and physical conditions of the Carnation Creek site. Since this off-target deposit study was conducted once only and conditions are not representative of worst-case scenarios, regression equations are neither accurate or useful models for purposes of prediction or establishment of buffer zone requirements.

Water samples

Frozen water samples were thawed, acidified with HCl to pH 2 and filtered through a Millipore filtering apparatus (0.45 μm HA disc filters), prior to concentration of the analytes on cation exchange resin (Chelex, Fe^{+++} form) and subsequent cleanup on anion exchange resin (AG1-X8, HCO_3^- form). Extraction and cleanup procedures based on those of Cowell et al. (1986) were used, with slight modification to provide samples for HPLC analysis. The cleanup procedure was altered by increasing the concentration (6.0 to 6.5 N) of HCl used to elute the analytes from the cation exchange column. An additional modification involved final recovery of glyphosate and AMPA using mobile phase solution (as described in Table 2) rather than distilled water.

Bottom and suspended sediment sample analysis

Residues of glyphosate and AMPA in bottom and suspended sediments were quantified using the method as described by Thompson et al. (1989). The method involves extraction of the substrate with 0.5 M NH_4OH, pre-concentration on AG1-X8 (HCO_3^- form) anion exchange resin, cleanup via cation exchange (Dowex 50W-X8, H^+ form) and HPLC analysis as described below and in Table 2.

For bottom sediment samples, aliquots (20 g, air dry mass) were taken for analysis. Percent moisture was determined in duplicate aliquots for each sample so that residue levels could be calculated on μg/g dry mass basis. For suspended sediment samples the entire sample (including filter paper), as obtained from the field was weighed, homogenized and extracted. Residue results were calculated as μg/L of filtered water.

High performance liquid chromatography

High Performance Liquid Chromatography (HPLC) coupled with post-column ninhydrin derivatization and absorbance detection (specifications as listed in Table 2) was utilized for separation and quantification of glyphosate and AMPA. Use of the short (10 cm) analytical column resulted in short retention times (7 min), improved peak shape and increased sensitivity compared to systems employing a longer (30 cm) column (Cowell et al. 1986).

Validation data for analytical methods

Data indicating the accuracy and precision of analytical methods used for quantification of glyphosate and AMPA are presented in Table 3 for each substrate.

Table 3. Validation data for analytical methods

Substrate Type	Fortification Level	N	Analyte	Mean ± s.e. (cv%)	LOD[a] (ppm)[3]	LOQ[b] (ppm)[c]
Deposit Collector[d]						
Water	1.0-40.0 μg/L	25	GLYPH	99 ± x.x (5.0)	0.10	1.00
			AMPA			
Bottom Sediment	0.05-0.8 μg/g	36	GLYPH	79.7 ± 6.3 (7.9)	0.03	0.10
			AMPA	64.0 ± 10.1 (15.4)	0.01	0.03
Suspended Sediment	0.50-4.0 μg	14	GLYPH	65.5 ± 9.1 (13.9)	0.03	0.10
			AMPA	54.3 ± 8.5 (15.7)	0.01	0.03

[a] LOD = limits of detection = detector response equivalent to 2X S:N ratio.
[b] LOQ = limits of quantification = detector response 6X S:N ratio.
[c] ppm = mg/L for formulation, tank mix and water
= ng/kg dry mass for bottom and suspended sediments.
[d] LOD and LOQ values for deposit collectors equate to 2.5×10^{-5} and 1.25×10^{-4} kg/ha respectively.

RESULTS AND DISCUSSION

Formulation Analysis

Analyses of the ROUNDUP formulation used for the herbicide application in this study indicated that the amount of active ingredient (glyphosate) was 363 g/L ± 2% cv, approximately 2%

in excess of the label concentration (356 g/L). No AMPA was detected in the formulation, which had been stored at ambient temperature for 3 months.

Tank Mix Analysis

Results of the analyses conducted on the tank mix showed concentrations of 7889 and 58 μg/L of glyphosate and AMPA respectively. There was a 6% v/v contamination of the tank-mix from a six-day old mixture used to spray adjacent areas of the watershed. The amount of AMPA detected (0.7% of glyphosate concentration in the tank mix), indicated a 13% degradation of glyphosate in the previous mixture after six days of storage at ambient temperature. The initial concentration of the tank mix was corrected by converting the AMPA concentration to a glyphosate equivalence. The corrected value was 103% of the concentration required to yield an application rate of 2 kg a.i/ha.

Off-Target Deposit Study Results

Analysis of 20 deposit collector samples indicated that the concentration of AMPA (relative to glyphosate) was 1.5%, slightly higher than the ratio for the tank mix. The highest deposit rate, which was found 2.9 m within the target area, was 1.882 kg/ha. This empirical value was 6% less than the nominal application rate for the study. The lowest quantifiable deposition rates (0.00155 and 0.000176 kg/ha) were found 17.2 and 23.1 m off-target for the salmonberry and alder areas respectively (Table 4).

Table 4. Off-target deposit of glyphosate monitored at Carnation Creek watershed

Alder Area		Salmonberry Area	
Distance (m) off-Target	Glyphosate deposit (kg/ha)	Distance (m) Off-Target	Glyphosate deposit (kg/ha)
-2.9	1.8820	1.0	0.1786
0.2	1.5093	2.6	0.01687
2.1	0.01934	3.0	0.02096
2.8	0.01025	6.2	0.00383
7.2	0.00239	6.5	0.00145
7.8	0.000364	11.1	0.00162
10.0	0.00115	12.0	0.000281
12.9	0.000337	13.1	0.000351
17.2	0.00155	21.1	0.000600
20.0	<0.000025	22.0	<0.000216
22.9	<0.000025	23.1	<0.000176

Note: Limit of detection (LOD) = 0.000025 Kg/ha
Limit of quantification (LOQ) = 0.000125 Kg/ha.

Statistical analysis of the deposit data indicated a significant ($P < 0.05$) correlation between the log of glyphosate deposited and the log of distance off-target. Linear regression on log-log transformed data yielded correlation coefficients of -0.95, -0.97 and -0.95 for the mean

data values of 3 replicate transects in the alder, salmonberry and for the pooled data, respectively. The corresponding regression equations accounted for 89%, 94%, and 91% of the variation within the data, respectively. Non-significance in differences between regression lines for the salmonberry and alder areas allowed calculation of a general extinction rate from pooled data. The general extinction rate was used to estimate distance downwind from the spray boundary at which 10%, 1% and 0.1% of the full deposit would be found (Table 5). The results show a very rapid decline in glyphosate deposit with increasing distance off-target.

Table 5. Glyphosate distance:deposit relationships as calculated for the Carnation Creek study site.

Calculated Distance Off-Target (m)		Estimated Deposit Rate	
Alder Area	Salmonberry Area	(Kg/ha)	(% of Full Rate)
0.2	0.3	2.0	100
0.6	0.9	0.2	10
2.0	2.7	0.02	1
7.2	7.8	0.002	0.1

Note: Off-target deposit estimates as shown in Table 5, were interpolated using the regression equations:

Alder: $\text{Log } Y = a + b \text{ (log } X); \; r^2 = 0.89$
where: X = distance off-target (m)
Y = amount of glyphosate deposited on collectors (kg/ha)
a = -1.17
b = -1.82

Salmonberry: $\text{Log } Y = a + b \text{ (log } X); \; r^2 = 0.94$
where: X = distance off-target (m)
Y = amount of glyphosate deposited on collectors (kg/ha)
a = -0.82
b = -2.13

Vegetation assessment indicated the average off-target distance between spray boundary and zone of 100% healthy salmonberry was 2 m. However, several pockets of partially damaged salmonberry were found up to 5 m from the spray boundary in association with scattered clumps of alder. Results of the vegetation assessment indicated that deposit rates of <0.02 kg/ha (i.e., approximately 0.01% of full application rate) would be required to ensure no phytotoxicity to salmonberry.

Dissipation of Glyphosate and AMPA in Stream Water and Sediments

Results of short-term intensive sampling program

Initial residue response differed in buffered and unbuffered streams. Rainfall (39 mm) occurred one day after treatment of Treatment Area III and lasted for 8 h. In streams receiving

direct application, stream response was characterized by rapid decrease in residue concentrations, both immediately post-application and in response to the rainfall.

Direct treatment of tributary 750 resulted in quantifiable glyphosate concentrations (1.5 μg/L) at 1 and 2 h post-application (Fig 3). Glyphosate concentrations rose to 144 μg/L at 27 h post-application in response to the rainfall event and decreased rapidly to 2.2, 1.3 μg/L and non-detectable levels at 36, 72 and 96 h post-application, respectively. Tributary 750 was a small, ephemeral stream covered by riparian vegetation for most of its length. At the time of application it exhibited a slow flow rate (0.001 m^3/s). As compared to the inital stream response to direct over-spray, longer periods of time (>45 h vs. <5h) were required for residues to dissipate below detectable levels. The 100-fold increase in concentrations of glyphosate in stream water following the first rainfall event may have been the result of several sources of input including mobilization of residues in ephemeral stream channels feeding the tributary (Norris et al. 1983), washing of residues from leaves of overhanging vegetation, surface movement and subsurface flow. Norris et al. (1983) noted that mobilization of residues in runoff may yield longer lasting effects than direct application. In a study of agricultural watersheds, Edwards et al. (1980) showed that residues of glyphosate were transported mainly via overland (surface) runoff, rather than through subsurface flow.

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. Residues were detected in water samples immediately following direct deposit of glyphosate, concentrations peaked at 162 μg/L within 2 h and decreased rapidly to 54.4 and 36.5 μg/L at 7 and 16 h, respectively (Fig. 3). The magnitude of the initial concentrations and rate of residue dissipation in this stream were comparable to those observed in a similar forest stream in Oregon (Newton et al. 1984). Following the first rainfall, concentrations of glyphosate in the water rose to 109 μg/L at 28 h and decreased rapidly thereafter to 1.3 μg/L at 96 h (Fig. 3). Concentrations of AMPA found in both tributaries 750 and 1600 were about 2% of corresponding glyphosate concentrations.

The buffered tributary 1450 was selected to represent a worst-case situation for operational spraying and to determine the accuracy of aerial application while maintaining a designated buffer without an intensive boundary marking system. This tributary consisted of a network of branching stream channels, mid-portions 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) were adjacent to Treatment Area III (Fig. 1). Stream flow at the time of application was 0.01 m^3/s. No quantifiable residues were found in the first 7 h of the intensive sampling program. The rainfall that occurred at 20 to 28 h post application did not mobilize significant quantities of glyphosate into this stream during the first 16 to 96 h post-application. These results indicate that a 10-m wide vegetation buffer is adequate to prevent stream contamination from either direct aerial application, drift or from subsequent inputs in the first 96 h. One anomalous sample (10 h post-application) was identified, having a concentration of 2.5 μg/L of glyphosate. This delayed response may be the result of an accidental spray over a middle section of the tributary, which eventually flowed underground. The slower water velocity, which would be expected in subterranean flow, may be responsible for the delay of residue response to 10 h post application.

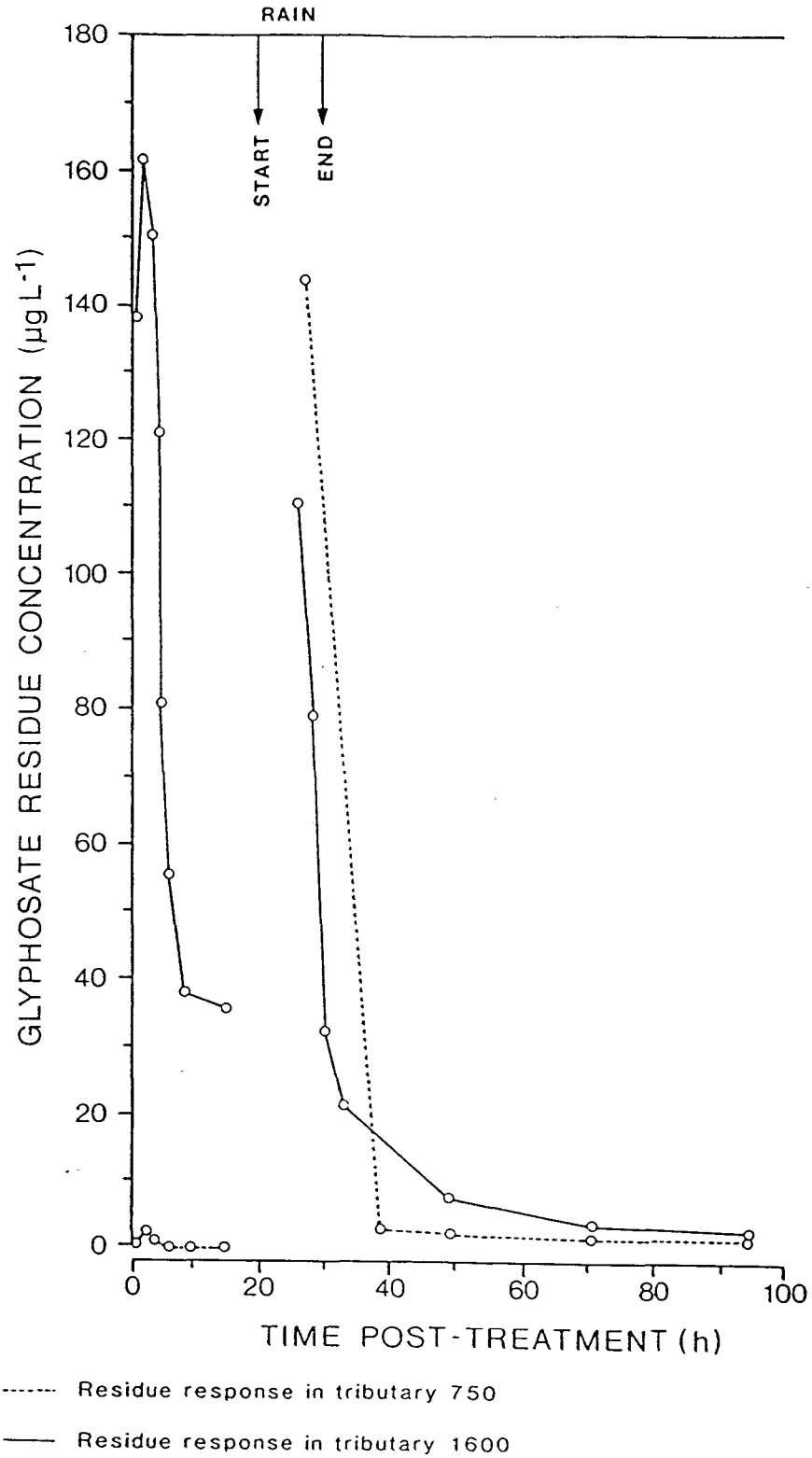


Figure 3. Short-term Streamwater Residues of Glyphosate in Carnation Creek Watershed Tributaries 750 and 1600.

The buffered main stream (Carnation Creek) was monitored at B weir, both following application to Treatment Area I and Treatment Area III. No residues were found in any of the 12 samples collected after application to Treatment Area I. Results of samples associated with application to Treatment Area III, showed that the main stream responded with quantifiable glyphosate concentrations only following the direct treatment of tributary 1600. Glyphosate (1-1.5 μg/L) was found in only two samples, 4 and 6 h after treatment. In general, these results corroborate other studies, which indicate 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). In lotic systems such as Carnation Creek, this effect may be the result of degradation, dilution, adsorption to organic substrates or uptake by biota. Glyphosate concentrations in five samples collected between 29 and 33 h rose to 1.7-3.2 μg/L in response to the rainfall. The 2-fold increase in main stream water residues further indicated input of chemical from non-point sources such as charged ephemeral tributaries.

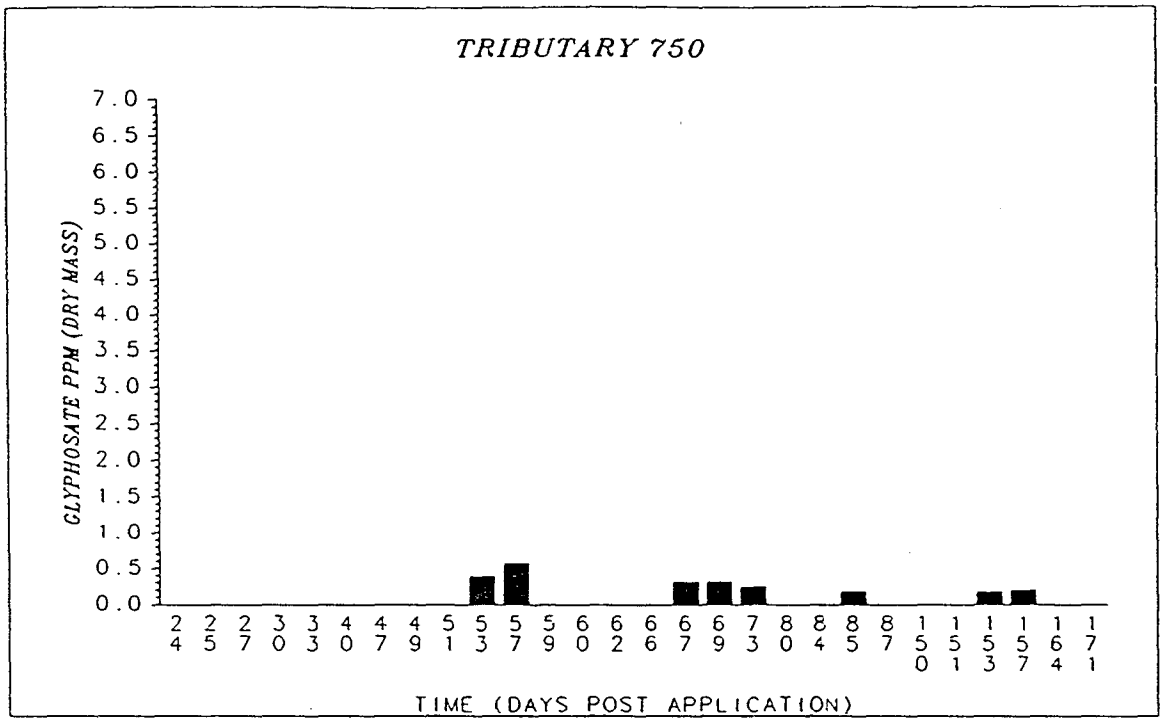
Results of Storm Event Monitoring

During the observation period, seven storm events above 3 m^3/s were identified as major storms (Table 1.). Stream discharges monitored in Carnation Creek for these seven events were: 13.1, 8.3, 10.0, 5.3, 3.0, 4.0, and 4.4 m^3/s, respectively. Cumulative rainfall was 1490 mm during this period. As a result, a total of 120 water samples (900 mL PT) were collected on 30 different days from the main channel and three tributaries (750, 1600 and C) (Table 1). No quantifiable residues of glyphosate or AMPA were found in any of the water samples. Trace amounts (<1 μg/L) of glyphosate were detected in one sample from the main channel following storm event 7 and in one water sample from tributary 750 following the first storm event. Similarly, transient indications of trace residues were observed in tributary 1600 in five of seven major storm events (i.e. on days 23, 25, 49, 59 and 150 post-application). Glyphosate concentrations observed 23 days after treatment were approximately 1000-fold lower than those found after the rainfall (39 mm) event 27 h post-application. These results are consistent with the observations of other workers (Kimmins 1975; Edwards et al. 1980), that the first rainfall after treatment generates the highest residue concentrations in stream water.

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 the buffered tributary C and main channel during the storm-event monitoring period. In the directly treated Tributaries 750 and 1600, glyphosate and AMPA residues in bottom sediments persisted throughout the storm-event monitoring period (Fig.4). The highest bottom sediment concentrations of glyphosate (0.44 and 0.58 μg/g dry mass) found in tributary 750 were in conjuction with the third major storm event, 53 and 57 days post-application, respectively. In tributary 1600, peak bottom sediment concentrations (6.80 and 6.34 μg/g dry mass) were observed 24 and 30 days post-application, respectively (Fig. 4).

A total of 29 suspended sediment samples were collected at B weir during 8 storm events that occurred between 23 and 171 days post-treatment (Table 1). Quantifiable glyphosate residues were found in only four of the 29 samples collected. The highest concentrations detected in suspended sediments (0.060 μg/L) occurred in conjunction with the first storm event, 23 days post-application.

Monitoring in conjunction with major storm events indicated that residues of glyphosate and AMPA are associated primarily with bottom sediments, with no quantifiable residues being observed in stream water. Highest concentrations were found in the slow-flowing tributary 1600, which meanders through the floodplain, while the swift-flowing 750 tributary had much lower con-



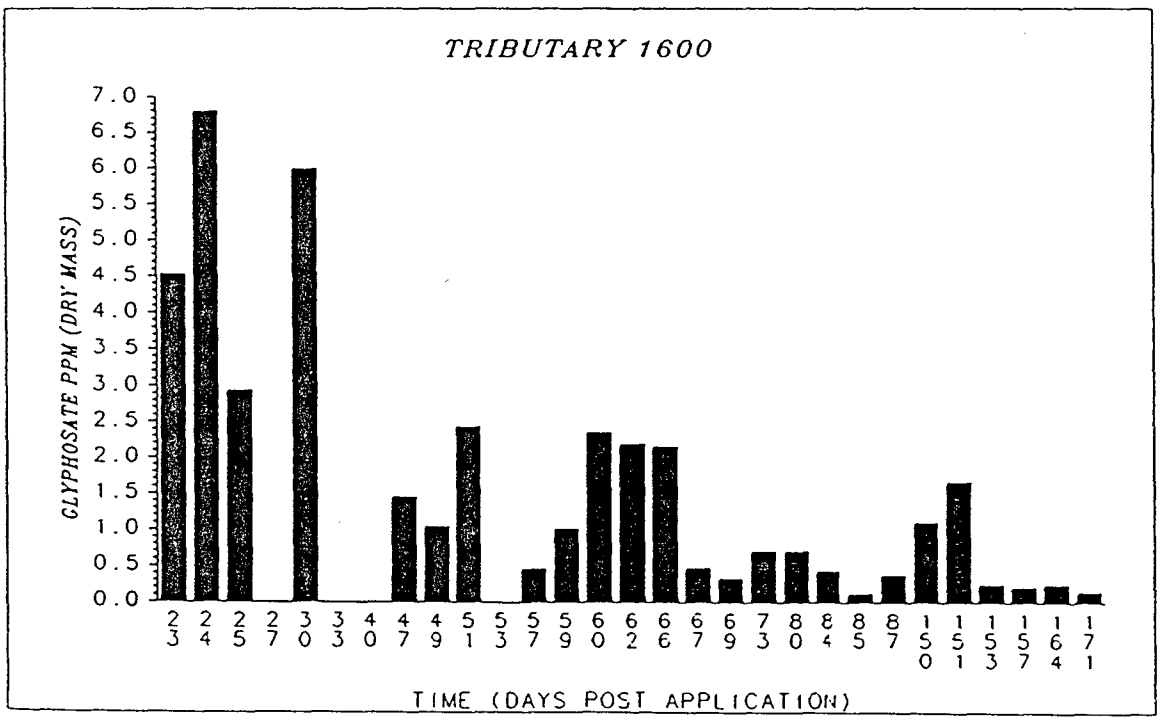


Figure 4. Residues of glyphosate in bottom sediments of directly oversprayed tributaries at Carnation Creek, British Columbia.

centrations. Levels of glyphosate residue associated with bottom sediments appear to depend largely on stream flow dynamics. In slow-flowing, meandering streams deposition of contaminated sediment may result in transient increases in residue concentrations. In contrast, fast-flowing streams inherently have little sediment deposition and are regularly flushed-out during storm events, resulting in bottom sediment concentrations being somewhat lower.

Results of Long Term Dissipation Study

Biweekly samples of both water and bottom sediments were taken from the main stream and tributaries 750, 1600 and C during the period 196 to 364 days after treatment (Table 2). No detectable residues (detection limit = 0.1 μg/L) were found in any of the 48 scheduled water samples. Analyses of 49 bottom sediment samples taken during this period showed no quantifiable residues in sediments of the Carnation Creek main channel or C-tributary (Fig. 4). Quantifiable residues (1.92 to 0.14 μg/g dry mass) were observed in bottom sediments of directly sprayed tributaries 750 and 1600 during the long term monitoring period (196-364 days post application). The data indicate that residues in bottom sediments were comparatively persistent, with levels variable but generally declining over time. By the end of the long term monitoring period, residue levels were less than 0.2 μg/g dry mass. Results of the long term monitoring program provide no evidence of glyphosate or AMPA accumulation in either bottom sediments or water and no quantifiable residues in stream water resulting from inputs via mass transfer or lateral movement mechanisms.

Relationship of Observed Residue Concentrations to Toxicological Data

Application of glyphosate to the Carnation Creek Watershed approximates a worst-case scenario for the silvicultural use of this herbicide. As would be expected, the highest residue concentrations were observed in water samples taken immediately after direct application to tributaries 750 and 1600. Residues dissipated rapidly from water and tended to be sorbed by bottom sediments. No evidence of accumulation of glyphosate or its metabolite AMPA in sediments was observed.

Although it is beyond the scope of this paper to draw absolute conclusions regarding the potential for aquatic impacts as a result of silvicultural applications of ROUNDUP, it is of interest to compare actual environmental concentrations of glyphosate observed in this study with those concentrations of the active ingredient known to elicit acute toxic response. Servizi et al. (1987) have recently reported on the acute toxicity of ROUNDUP, the active ingredient glyphosate and the surfactant MON0818 to four aquatic organisms including *Onchorhyncus* sp. fry. The data indicate that all four species show similar sensitivities to these materials. Mitchell and Chapman (1986) reported that environmental concentrations resulting from aerial spraying of ROUNDUP herbicide are 100-fold less than levels found to be acutely toxic to salmonids in 96 h LC_{50} tests. The highest streamwater concentrations observed in this study (162 μg/L in directly oversprayed tributary 1600) is approximately 80-fold less than the 96 hour LC_{50} reported for coho salmon (Wan et al. 1988), when corrected for glyphosate equivalence (30% a.e.). Similarly, the highest concentrations observed in our study were well below sub-lethal no-effect levels for coho salmon smolt osmoregulation or growth as reported by Mitchell et al. (1987).

With respect to toxicity of glyphosate to organisms other than fish, direct observation indicated that residue concentrations at B Weir and tributaries 1600 and C induced a minimum response in drift of aquatic invertebrates (Kreutzweiser and Kingsbury 1989).

Thus, the results of this study generally indicate a large safety margin between stream water concentrations of glyphosate resulting from forest applications and known acute and sub-acute toxicological endpoints.

CONCLUSIONS

In relation to the objectives of the study, the following conclusions may be drawn:

a) Results of the off-target deposit collector experiment indicate that the herbicide application was reasonably accurate in that the empirical value for application rate was within 6% of the nominal rate for target area. The data also showed that use of the MICROFOIL BOOM under operational spraying conditions results in very little off-target deposit. Estimated deposit at distances greater than 8 m off-target were less than 0.1% of full application rates in this study. Results of the off-target deposit study conducted at Carnation Creek suggest that under the specific application and meteorological conditions of this study, a 10-m wide vegetation buffer zone of either salmonberry or alder, effectively protected streams from herbicide contamination following application of the herbicide ROUNDUP with a MICROFOIL BOOM.

b) Initial residue levels in stream water were correlated with a variety of factors including; stream flow rate and volume, occlusion of water surface by overhanging vegetation, and degree of input from intentional direct treatment. Directly treated tributaries contained the highest concentrations of the active ingredient, these levels were well below concentrations known to be acutely toxic to sensitive aquatic organisms. Residues in stream water dissipated rapidly, so that chemical concentrations were below detection limits (0.1 ppb) within 96 h of the application. Dissipation was more rapid in a fast flowing tributary than in a slow-flowing, meandering tributary in the floodplain.

c) Storm-event monitoring showed that no quantifiable residues of glyphosate occurred in stream water in conjunction with storm events. Bottom sediments appeared to be the major sink for glyphosate residues with high concentrations correlated to storm events. Residues associated with bottom sediments persisted throughout the monitoring period, the degree of contamination appears to be related to stream dynamics and location.

d) Results of the long-term dissipation monitoring study indicated no potential for persistence of residues of either glyphosate or AMPA in stream water. Long-term residues were associated predominantly with bottom sediments, indicating that this substrate attenuated residues from stream water by sorption processes. In contrast with the rapid dissipation of residues in stream water, sediment residues were relatively persistent. The slow rate of glyphosate degradation in bottom sediments, coupled with the known chemical behavior of glyphosate on organic substrates indicates that these residues are strongly sorbed to this substrate and thus unlikely to be biologically available.

The residue data resulting from this study support the conclusion of Tooby (1985), who stated that "...it is unlikely that glyphosate will affect aquatic organisms at the concentrations found in the environment after use at the recommended rates." Given the rapid dissipation of this chemical in forest stream ecosystems, its susceptibility to biodegradation and its tendency to sorb strongly to organic substrates, significant biological impact to aquatic organisms as the result of silvicultural applications at recommended rates would be highly unlikely.

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REFERENCES

Comes, R.D., V.F. Bruns and A.D. Kelly. 1976. Residues and persistence of glyphosate in irrigation water. Weed Sci. 24(1):47-50.

Cowell, J.E., J.L. Kunstman, P.J. Nord, J.R. Steinmetz and G.R. Wilson. 1986. Validation of an analytical residue method for analysis of glyphosate and metabolite: An interlaboratory study. J. Agric. Food Chem. 34:955-960.

Dryburg, J.G. 1982. Carnation Creek logging and silvicultural treatment program. pp. 36-43 In G.F. Hartman (ed.) Proceedings of the Carnation Creek workshop, a 10-year review . February 24-26, 1982. Malaspina College, Nanaimo, B.C.

Edwards, W.M., G.B. Triplett and R.M. Kramer. 1980. A watershed study of glyphosate transport in runoff. J. Environ. Qual. 9(4):661-665.

Feng, J.C., and H.D. Klassen. 1986. Forestry field and laboratory manual for herbicide residue sampling, sample processing and reporting. Can. For. Serv., For. Pest Manage. Inst., Sault Ste. Marie, Ont. Inf. Rep. FPM-X-72.

Ghassemi, M., L. Fargo, P. Painter, S. Quinlivan, R. Scofield and A. Takata. 1981. Environmental fates and impacts of major forest use pesticides. EPA Contract No. 68-02-3174, U.S. Environ. Prot. Agency, Off. Pestic. Toxic Subst., Washington, D.C.

Hartman, G.F. 1982. [ed.]. Proceedings of the Carnation Creek workshop, a 10-year review. February 24-26, 1982. Malaspina College, Nanaimo, B.C.

Hetherington, E.D. 1982. A first look at logging effects on the hydrologic regime of Carnation Creek experimental watershed. pp. 11-15 In G.F. Hartman (ed.) Proceedings of the Carnation Creek workshop, a 10-year review. February 24-26, 1982. Malaspina College, Nanaimo, B.C.

Kimmins, J.P. 1975. Review of the ecological effects of herbicide usage in forestry environment. Can. For. Serv., Pac. For. Res. Cent., Victoria, B.C. Inf. Rep. BC-X-139.

King, R.K. and E.T. Oswald. 1982. Revegetation of Carnation Creek watershed. pp. 110-128 In G.F. Hartman (ed.) Proceedings of the Carnation Creek workshop, a 10-year review. February 24-26, 1982. Malaspina College, Nanaimo, B.C.

Krajina, V.J. 1969. Ecology of forest trees in British Columbia. pp. 1-146 In V. Krajina and R. Brooks (eds.) Ecology of western North America. Vol. 2, Nos. 1 and 2. Dept. Botany, Univ. B.C., Vancouver, B.C.

Kreutzweiser, D.P. and P.D. Kingsbury. 1989. Drift of aquatic invertebrates in a glyphosate contaminated watershed. This proceedings.

Legris, J., G. Couture, L. LaBerge et G. Mamarbachi. 1985. Concentrations residuelles de glyphosate dans l'eau de surface en milieu forestier suite a des pulverisations terrestres, 1985. Governement du Quebec, ministere de l'Energie et des Ressources. Service des etudes environmentales, #3315. pp. 35.

Malik, N., and W.H. Vanden Born. 1986. Use of herbicides in forest management. Can. For. Serv., North. For. Cent., Edmonton, Alberta. Inf. Rep. NOR-X-282.

Mitchell, D.G. and P.M. Chapman. 1986. Acute toxicity of Roundup herbicide to coho salmon, chinook salmon and rainbow trout. Report prepared for Monsanto Co., St. Louis, Missouri, by E.V.S. Consultants, Vancouver, B.C. (as cited in Mitchell et al. 1987).

Mitchell, D.G., P.M. Chapman and T.J. Long. 1987. Seawater challenge testing of coho salmon smolts following exposure to Roundup herbicide. Environmental Toxicology and Chemistry, 6:875-878.

Newton, M., K.M. Howard, B.R. Kelpsas, R. Danhaus, C.M. Lottman and S. Dubelman. 1984. Fate of glyphosate in an Oregon forest ecosystem. J. Agric. Food Chem. 32:1144-1151.

Norris, L.A. H.W. Lorz and S.V. Gregory. 1983. Forest chemicals. In W.R. Meehan (ed.) Influence of forest and rangeland management on anadromous fish habitat in western North America. USDA For. Serv., Gen. Tech. Rep. PNW-149.

Payne, N., J. Feng, and P. Reynolds. 1986. Off-target deposit measurement and buffers required around water for aerial glyphosate application. Can. For. Ser., For. Pest Manage. Inst., Sault Ste. Marie, Ont. Inf. Rep. FPM-X-80.

Reynolds, P.E., J.C. Scrivener, L.B. Holtby and P.D. Kingsbury. 1989. An overview of Carnation Creek herbicide study: historical perspective, experimental protocols, and spray operations. This proceedings.

Rueppel, M.L., B.B. Brightwell, J. Schaefer and J.T. Marvel. 1977. Metabolism and degradation of glyphosate in soil and water. J. Agric. Food Chem. 25:517-528.

Servizi, J.A., R.W. Gordon and D.W. Martens. 1987. Acute toxicity of GARLON 4 and ROUNDUP herbicides to Salmon, Daphnia, and Trout. Bull. Env. Contam. Toxicol. 39:15-22.

Thompson, D.G., B.J.E. Cowell, R.J. Daniels, B. Staznik and L. MacDonald. 1988. An alternative method for quantification of glyphosate and AMPA residues in organic and mineral soils, stream sediments and hardwood foliage. J. Assoc. Off. Anal. Chem. (in press).

Tooby, T.E. 1985. Fate and biological consequences of glyphosate in the aquatic environment. pages 206-217 In E. Grossbard and D. Atkinson (eds.) The Herbicide Glyphosate. Butterworths, London, U.K.

Wan, M.T. et al. 1988. Toxicity of the herbicide glyphosate (ROUNDUP) and its surfactant to salmonids. p. 41 In Environment Canada-Pesticides Research and Monitoring Annual Report: 1986-87. Ministry of Supply and Services. Canada.

Zar, J.H. 1984. Biostatistical analysis. 2nd edition. Prentice-Hall, Inc., Englewood Cliffs, N.J. pp. 292-298.

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