PERSISTENCE OF GLYPHOSATE IN STREAMWATER FOLLOWING AERIAL APPLICATION WITH A MICROFOIL BOOM AT CARNATION CREEK, BRITISH COLUMBIA, 1984.

By

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ABSTRACT

Streams buffered and aerially oversprayed with glyphosate (N-phosphonomethylglycine) by a helicopter and MICROFOIL® boom equipped with 1.5 mm (0.06 inch) hayrack nozzles, were monitored for residue concentration as part of collaborative research trials undertaken at Carnation Creek, Vancouver Island, in September 1984. Integrated hourly water samples were collected during the first 3–8 h, and single L samples were collected at decreasing frequency up to 96 h after application from the main stream and from three tributaries with distinct characteristics or treatments. Long-term sample collection was carried out during and following storm events, and bi-weekly from 196 days to 1 year after application. Water samples were purified and quantified for glyphosate and its metabolite AMPA (aminomethylphosphonic acid) by Ion Exchange High Performance Liquid Chromatography (HPLC). The maximum glyphosate concentration detected [162 ppb (μg/L)] was found in an integrated sample from a rapidly flowing unbuffered and oversprayed tributary within 2 h after application. Residue concentration then declined rapidly to 37 ppb after 16 h, and rose again to 109 ppb during the first rainfall (39 mm) at 28 h after initial application. Residue concentrations decreased in the mainstream from dilution and residue interactions to a maximum of 1.4 ppb at 1100 m downstream 6 h after application, and rose to 3.2 ppb after 30 h, during the first rainfall. Glyphosate concentrations were greater in runoff from the first rainfall (144 ppb) than from initial application (1.5 ppb) in one oversprayed and slowly flowing tributary. Small amounts of glyphosate (0.8 ppb) were detected

in a small buffered tributary in the first hourly integrated sample, probably from inadvertent overspray of a stream channel obscured during application by dense riparian vegetation. Another late peak (2.5 ppb) detected 10 h after application was probably a delayed response to overspray of a middle section of the tributary which then flowed underground before re-emerging further downstream. Another small amount of glyphosate (0.6 ppb) was detected during the first rainfall at 20 h after application of this spray block. In long-term monitoring, glyphosate was detected in trace quantities between 0.5 and 0.1 ppb in stormflows up to 150 days after application in an unbuffered and oversprayed tributary. Residues were not detected in regular bi-weekly samples up to 1 year after application.

INTRODUCTION

Glyphosate (Roundup®) is a herbicide recently registered (1984) for Canadian forestry use, although some local regulatory agencies require further research for its operational use. Studies on several environmental aspects of glyphosate use, such as aquatic fate and impact, persistence, degradation patterns, leaching and lateral movement, are presently being undertaken to satisfy provincial regulatory agencies and federal Department of Fisheries and Oceans requirements for its operational use in different regions in Canada. Results of these studies are of particular interest in the coastal areas of British Columbia, where the current buffer width requirement (a 10 m 'pesticide free zone' plus a >100 m buffer) is considered impractical for effective forest management. A compromise between forestry and fishery interests may be reached regarding appropriate buffers, pending research results on off-target deposit using several new herbicide dispersal systems such as the MICROFOIL® boom (designed for increased drift control), and results on aquatic fate of glyphosate, should it enter a stream system.

Although many studies have investigated the aquatic fate of glyphosate (Comes et al. 1976; Rueppel et al. 1977; Edwards et al. 1980; Ghassemi et al. 1981; Norris et al. 1983; Newton et al. 1984), few results are applicable to forested west coast British Columbia streams. High rainfall in these areas (often exceeding 300 cm/year) may generate "flashy" stream conditions with rapid runoff through ephemeral stream channels. Herbicide residue persistence and transport patterns under runoff conditions, further influenced by undetermined residue input from detritus, overland flow and surface erosion, are most appropriately determined through a series of field investigations across a range of conditions likely to be encountered. An opportunity to monitor glyphosate residues in streams under conditions within the range of west coast areas requiring conifer release was presented at Carnation Creek in 1984.

A collaborative research effort culminated in September 1984 with aerial application of glyphosate in the Carnation Creek watershed, British Columbia (Reynolds 1985)[1]. The multi-disciplinary study on efficacy, environmental impact and fate of aerially applied glyphosate was designed to satisfy some of the assessment requirements of regulatory agencies for forestry use of glyphosate. One component of this study was to investigate the aquatic fate of glyphosate in streams after aerial application under operational conditions typical of coastal British Columbia.

The specific objectives of this study were to:

1) Determine the initial (96 h) residue input and dissipation in streamwater following aerial overspray with glyphosate in four dissimilar streams.

2) Compare glyphosate residue input and dissipation in runoff during winter storm events between two buffered and two oversprayed streams.

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[1]P.E. Reynolds. 1985. Progress report. 1984 British Columbia cooperative herbicide research trials. Can. For. Serv., For. Pest Manage. Inst., P.O. Box 490, Sault Ste. Marie, Ont. P6A 5M7.

3) Assess the 1 year long-term potential for streamwater contamination in four streams through regular bi-weekly monitoring following an operational aerial application of glyphosate.

MATERIALS AND METHODS

General Site Description

Carnation Creek lies on the west coast of Vancouver Island, draining a 10 km^2 watershed (Fig. 1) in a coastal hemlock and cedar zone (Krajina 1969). Carnation Creek supports sizeable populations of coho [*Oncorhynchus kisutch* (Walbaum)] and chum [*O. keta* (Walbaum)] salmon and has been the focus of a 15 year investigation into the effects of logging on fish (Hartman 1982). Annual precipitation in the Carnation Creek watershed ranges between 250 and 390 cm and mainly occurred from October through March (Hetherington 1982). Weather stations and a broadcrest weir for monitoring stream discharge were located near the mouth of Carnation Creek (Fig. 1). Tributaries in the watershed were largely ephemeral, and started flowing with the first major seasonal rainfalls (60 mm) between 4-8 September 1984.

About 41% of the watershed was logged between 1975 and 1981 and reforestation has been extensive (Dryburg 1982). Rapid growth of shrubs followed logging. Salmonberry (*Rubus spectabilis* Pursh) initially dominated the vegetation (King and Oswald 1982), and later red alder (*Alnus rubra* Bong.) dominating in portions of the scarified valley bottom lands. In September 1984 the average heights of salmonberry and alder were 1.5-2.5 m and 7-10 m, respectively.

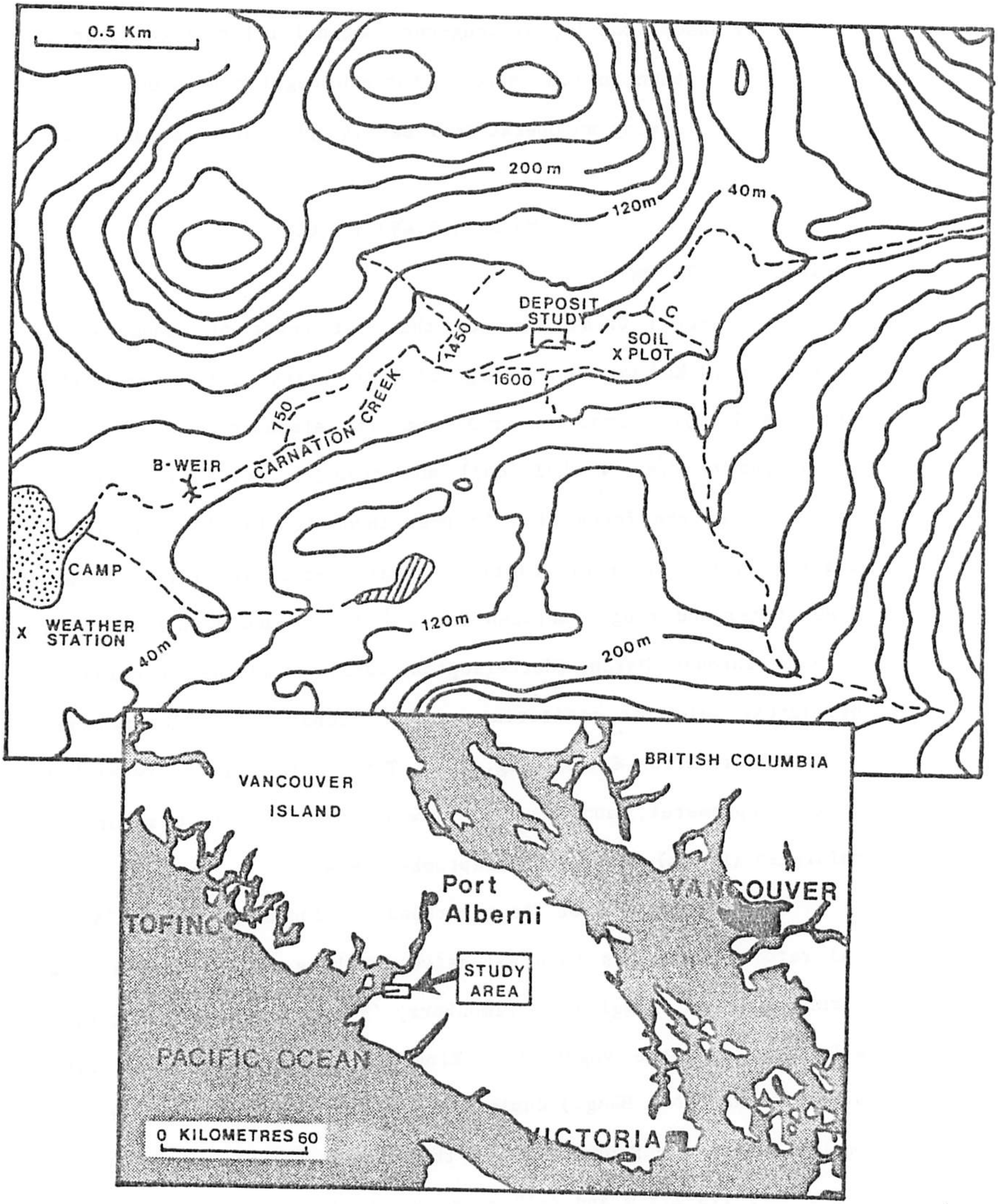

Figure 1. The study area at Carnation Creek.

Application

Eleven operational spray blocks were selected in the lower 2.5 km of the Carnation Creek watershed (Fig. 2) to represent typical B.C. coastal sites requiring conifer release. Glyphosate was applied to the spray blocks over a 9-day period (Table 1), owing to periods of inclement weather. A total of 41.7 ha was treated at 2.0 - 2.1 kg/ha Roundup [2] formulation (Table 1). Glyphosate was applied with a Bell-47 helicopter and a MICROFOIL boom[3] equipped with 1.5 mm (0.06 inch) hayrack nozzles. The dispersal system was calibrated at an application rate of 252 L/ha. Spray boundaries were marked with plastic flags on a 10-m high pole up to 10 m in height for clear identification above the canopy.

Site Selection

Five water collection stations were selected to monitor glyphosate concentrations in four tributaries and the main stream of Carnation Creek. Two tributaries were oversprayed and a 10 m buffer was flagged along the other tributaries and the main stream. About two thirds (600 out of 800 m) of oversprayed 1600-tributary (1600 m upstream from the estuary) flowed through the alluvial floodplain of Carnation Creek and was included within 8.9 ha spray block No. 5 (Fig. 2). Riparian vegetation along 1600-tributary was largely salmonberry with portions dominated by alder, typical of the alluvial flood plain. The width of the exposed stream channel ranged from 1 to 3 m. Stream discharge was about 0.016 m^3/sec at the time of application. Pools 0.5 - 1 m deep along

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[2]Registered trademark of Monsanto, St. Louis, Mo.
[3]Registered trademark of Union Carbide, Ambler, Pa.

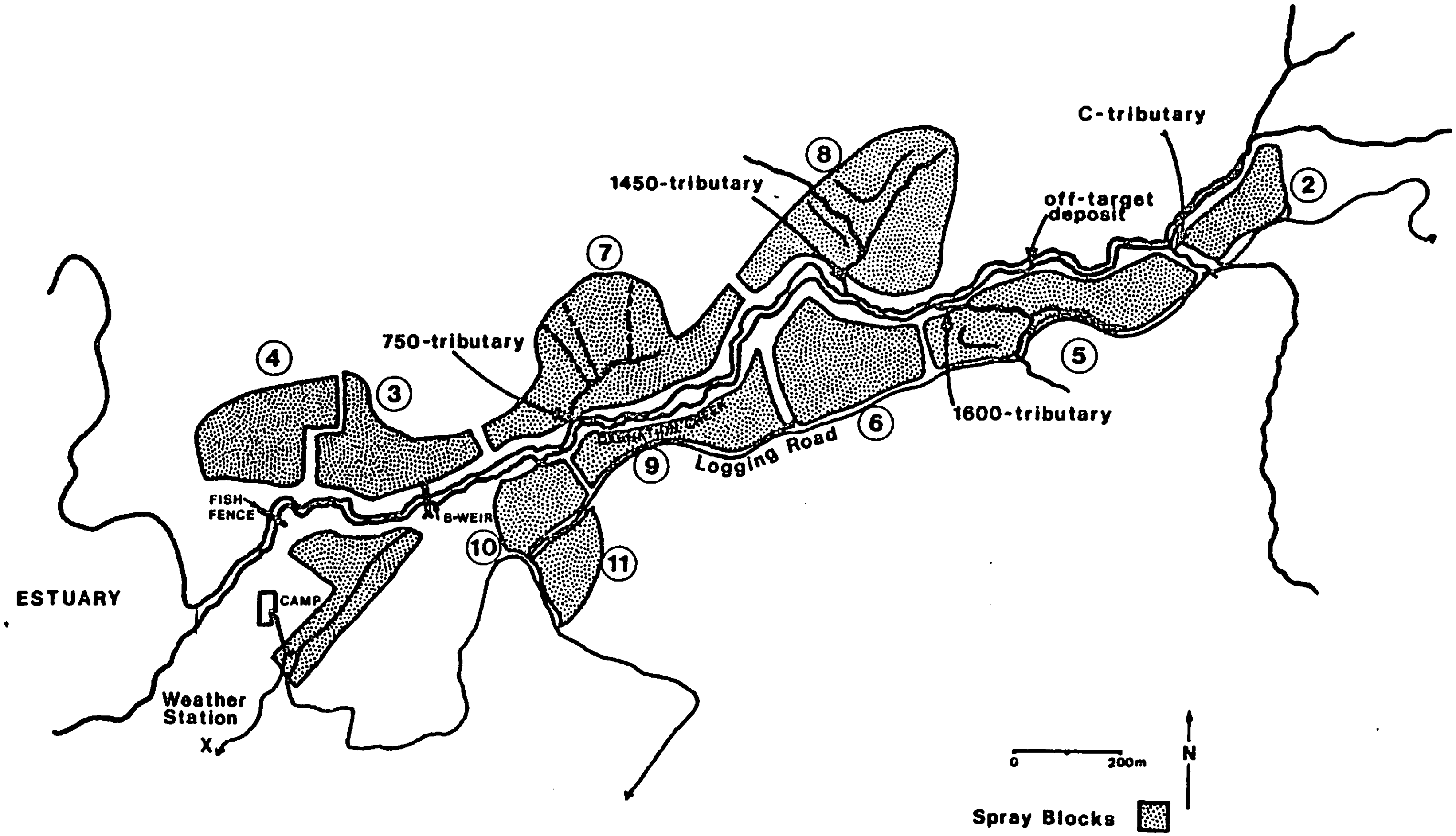

Figure 2. Locations of glyphosate spray blocks and streamwater sample collection stations at Carnation Creek.

Table 1. Application data for Carnation Creek watershed*

Spray Block Number	Associated Water Collection Station**	Spray Date (Sept. 1984)	Time Period (PDST)	Nominal Application Rate (kg/ha)	Block Size (ha)
1	---	6	1900-1925	2.0	2.5
2	B,C	6	1935-2005	2.0	3.1
3	B	8	1416-1445	2.0	5.3
4	---	8	1913-1940	2.0	3.2
5	B,C,1600	14	1430-1539	2.1	8.9
6	B	14	1646-1715	2.1	4.1
7	B,750	14	1730-1814	2.1	5.1
8	B,1450	14	1840-1849	2.1	1.1
9	B	14	1900-1931	2.1	5.0
10	B	15	1041-1050	2.1	1.7
11	—	15	1055-1101	2.1	1.7
Total					41.7

*From P.E. Reynolds. 1985. Progress Report. 1985 British Columbia cooperative herbicide research trials. Can. For. Serv., For. Pest Manage. Inst., P.O. Box 490, Sault Ste. Marie, Ont. P6A 5M7.

**B = B-weir; C = C-tributary; 750 = 750-tributary; 1450 = 1450-tributary; 1600 = 1600-tributary.

1600-tributary provided suitable overwinter habitat for juvenile coho salmon (Tschaplinski and Hartman 1982).

The other oversprayed 750-tributary (750 m upstream from the estuary) was a small ephemeral channel and had all of its 400 m length included within 5.1 ha spray block No. 7 (Fig. 2). Riparian vegetation (7-10 m alder) completely covered 750-tributary along most of its length. The streambed was dry before the first seasonal rainfall 6 days before application, and discharge was estimated at about 0.001 m^3/sec at the time of application. During storm events, the lower 50 m of 750-tributary formed a sidechannel of the mainstream of Carnation Creek.

Carnation Creek was monitored further downstream, near B-weir (500 m upstream from the estuary), to detect overall glyphosate concentrations from the operational application (Fig. 2). The stream discharge at the time of application was 0.26 and 0.16 m^3/sec on 6 and 14 September, respectively.

Buffered 1450-tributary (1450 m upstream of the estuary) was selected to represent a difficult situation during an operational application and to contest the accuracy of aerial application in maintaining a designated buffer without the intensified boundary marking associated with a precisely controlled experimental spray. A dense 2 m salmonberry canopy overhanging a network of branching 1450-tributary stream channels and a discontinuous flow where streamwater flows underground in a middle portion of the stream prevented the channel boundary from being clearly identifiable from the air. About two-thirds of its length (600 out of 800 m) was bordered by spray block No. 8 (Fig. 2). Flow was minimal

(0.01 m3/sec) at the time of application. The 1450-tributary was monitored only over the first 96 h after application.

Buffered C-tributary (2200 m upstream of the estuary) was selected to compare long-term herbicide residue input with the similar but oversprayed 1600-tributary. The lower 10% (100 out of 1000 m) of C-tributary flowed through the aluvial floodplain adjacent to spray blocks No. 2 and 5 (Fig. 2).

Water sample collection stations of the four tributaries were located about 5 m upstream from the confluence with Carnation Creek, and 5 m downstream from the spray boundary in oversprayed 750- and 1600 tributaries. The water collection station for the main channel was near the south streambank and 20 m upstream of B-weir. Streamflow was turbulent at and upstream of the B-weir station, and streamwater was assumed to be well-mixed.

Sample Collection

Water samples were collected in 1 L Nalgene (Nalge 2002) bottles. Samples collected within the first 3 hours after application, and the first 8 hours at B-weir and 1600-tributary, were time-integrated to smooth glyphosate pulses. Samples (150 mL) were collected at 10 min intervals and combined to yield one pooled sample (900 mL) per hour. Point samples (900 mL) were collected approximately every 3 h with sample frequency decreasing to daily up to 95 - 99 hours after application. Between 10 - 15 samples were collected from the tributaries, and 32 from B-weir.

Water sample collection to monitor storm events was initiated when the instantaneous discharge of Carnation Creek at B-weir reached a

7.0 m^3/sec (250 cfs) threshold level, equivalent to an average frequency of 14 storms per 7 month period (September to March), based on 10 years of discharge records. Samples (900 mL) were collected every 24 hours during a storm event. Post-storm event sampling commenced when 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 for each storm event, and daily rainfall and average discharge were measured throughout the sample program.

To ensure that water samples were representative of the stream water, samples were depth-integrated from top to bottom of the water column. Precautions were followed to prevent contamination of the samples (Feng and Klassen 1986). Samples were chilled immediately and frozen within 1 h of collection. Storage was at -5°C in the field freezers and -14°C at the analytical laboratory. Samples were kept frozen during transport by packaging them in insulated cardboard boxes lined with extra 2.5 cm styrofoam and covered with a layer of frozen cooler packs.

Residue Analysis

The analytical procedure described by Monsanto (Monsanto 1985)[4] was modified for the extraction and analysis of glyphosate and AMPA, its major metabolite (Rueppel et al. 1977). Samples were acidified to pH = 2 and filtered through a Millipore filtering apparatus equipped with Millipore (0.45 μm HA) discfilters. Residues of glyphosate and AMPA were trapped on Chelex - FE+++ (Bio-Rad) cation exchange columns while

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[4]Monsanto. 1985. Analytical methods for the determination of glyphosate and AMPA by high-performance liquid chromatography. Monsanto Agricultural Products Co., St. Louis, Mo. in press.

anion and neutral coextractives were washed off. Residues were then eluted from the cation exchange resin with 6.5 N HCl. The eluents were further acidified with 12 N HCl to free ferric ions that were trapped on AG1-X8 (Bio-Rad) anion exchange columns. The eluents were flash-evaporated to dryness with a rotary evaporator under reduced pressure at 60°C. Residues were re-dissolved in 2 mL of HPLC buffer solution (0.005 M KH2PO4 in 4% methanol - water), and filtered with a Millex-HV 0.45 μm filter unit before HPLC analysis. The analysis of glyphosate and AMPA by ion exchange HPLC involved the use of a cation exchange column and ninhydrin post-column reactor similar to amino acid analysis with a UV/VIS detector setting at a wavelength of 570 μm. Peak heights of glyphosate or AMPA within a pre-determined working range were used for the quantification of residues by comparing with the average peak height of the two corresponding reference standards analyzed immediately prior to and after the sample analysis.

RESULTS AND DISCUSSION

Results on the three components of this study are presented separately, with the initial 96 h short-term residue response followed by storm event monitoring and long-term (1 year) residue persistence from bi-weekly samples.

Short-Term Residue Response

Initial pre-rainfall response to application

Direct application of glyphosate on oversprayed 750-tributary resulted in maximum glyphosate concentrations (1.5 ppb) in an integrated sample at 2 h, which decreased to below detectable quantities[5] within 6 h of application (Fig. 3). AMPA remained undetectable during this initial period. Glyphosate concentrations in 1600-tributary exceeded 160 ppb, and AMPA exceeded 4 ppb in the first 2 h as an initial response to direct overspray (Fig. 4). Concentrations decreased rapidly to 54.4 and 1.3 ppb by 6.4 h, and 36.5 and 0.84 ppb by 15.4 h after application, respectively. This magnitude and rate of residue decrease is comparable to that found in an Oregon study monitoring glyphosate residue after overspray of a small forest stream (Newton et al. 1984).

The higher initial glyphosate concentrations found at 1600-tributary after overspray compared with those from 750-tributary may have been from greater stream surface exposure to spray deposit at 1600-tributary. Overhanging 7-10 m alder riparian vegetation along most of 750-tributary may have intercepted a higher proportion of the glyphosate applied, whereas salmonberry dominated riparian vegetation along most of the wider 1600-tributary, leaving greater water exposure to spray deposit.

Glyphosate concentrations in buffered 1450-tributary were quantifiable in three samples and AMPA remained non-detectable throughout the 95 hour sample period (Fig. 5). The initial response to application was 0.75 ppb glyphosate in the first hour, decreasing below the LOD from 2-7.5 hours after the first spray swath. At the time of application, 1450-tributary was flowing through several ephemeral stream channels across the alluvial fan under a dense (100% coverage) 2-2.5 m salmon-

[5]The limits of quantitation (LOQ) were 0.5 and 0.2 ppb, and the limits of detection (LOD) were 0.1 and 0.05 ppb for glyphosate and AMPA, respectively. Trace values between the LOQ and LOD were not replicable. All values reported were corrected for recoveries (98.4 % with 7.8 % CV for glyphosate, and 86.4 % with 7.3 % for AMPA).

berry canopy. The small, short-lived initial response to application at 1450-tributary was similar to that of oversprayed 750-tributary (Fig. 3, 5) and suggests that water in the system was inadvertently oversprayed. In a nearby off-target deposit study using the same dispersal equipment, Feng et al. (1986) found a rapid rate of extinction from the swath edge (1% of application within 2-3 m). At this extinction rate, if a channel of 1450-tributary was not directly oversprayed, the swath edge probably was within several meters of a stream channel and well within the intended 10 m buffer to generate the indicated response.

A peak concentration of 2.47 ppb at 10 hours after treatment at 1450-tributary decreased to non-detectable levels by the next sample at 16 hours. However, no similar increases in residue were detected at this time at the 750- and 1600-tributaries and no residues were detected in the next sample 6 hours later. This 10 h delayed residue peak was probably from streamwater in a middle section of 1450-tributary flowing underground. The slower water velocity underground may be responsible for the delay of residue reaching the sample collection station near the confluence from upstream sources, such as inadvertent overspray of a stream channel sections having a dense overhanging riparian canopy.

Glyphosate concentrations were monitored at B-weir, 1100 m downstream from the confluence of 1600-tributary, to determine overall residue levels in the system. All 12 samples collected at B-weir prior to the major glyphosate application on 14 September (Appendix 1) contained no detectable residues. At 1600-tributary, glyphosate was detected within 1 h and peaked within about 2 h from the first spray swath on 14 September (Fig. 4), whereas at B-weir glyphosate was not detected by 3.8

hours and peaked at about 5.8 hours (Fig. 6). Hence the lag time here was about 4 h. The dilution factor based on relative stream discharges was 1:10, but pools were more substantial in the mainstream than in 1600-tributary. Glyphosate concentrations from the initial overspray of 1600-tributary were about 100-fold higher and persisted longer than those detected at B-weir. The difference between the dilution factor and relative residue values suggests that some loss of glyphosate from streamwater may have occurred in the 2-4 hour period it took to travel the 1100 m from 1600-tributary to B-weir. Glyphosate residue concentrations were found to decrease with distance downstream in other studies as well, owing to dilution, and physical and biological interactions of the residues (Comes et al. 1976; Norris et al. 1983).

Residue response to the first rainfall after application

The first rainfall in the short-term sample collection period started at 1435 on 15 September and lasted about 8 h. Glyphosate concentrations responded to the 39 mm of rain, which started 21 and 24 hours after overspraying 750- and 1600-tributaries, respectively. At 750-tributary, glyphosate concentrations rose to 144 ppb at 27 h before decreasing to non-detectable levels at 96 h after application (Fig. 3). AMPA concentrations of 3.6 ppb at 750-tributary were recorded during the first rainfall but decreased to non-detectable levels by the next scheduled sample at 37 h after application and 8 h after the rain stopped. Glyphosate residue in 1450-tributary showed a minor response (to 0.64 ppb) within the first 0.5 h into the first rainfall at 20.5 h after application, but were not detectable in the next sample at 47 h after application (Fig. 5). At 1600-tributary, glyphosate concentra-

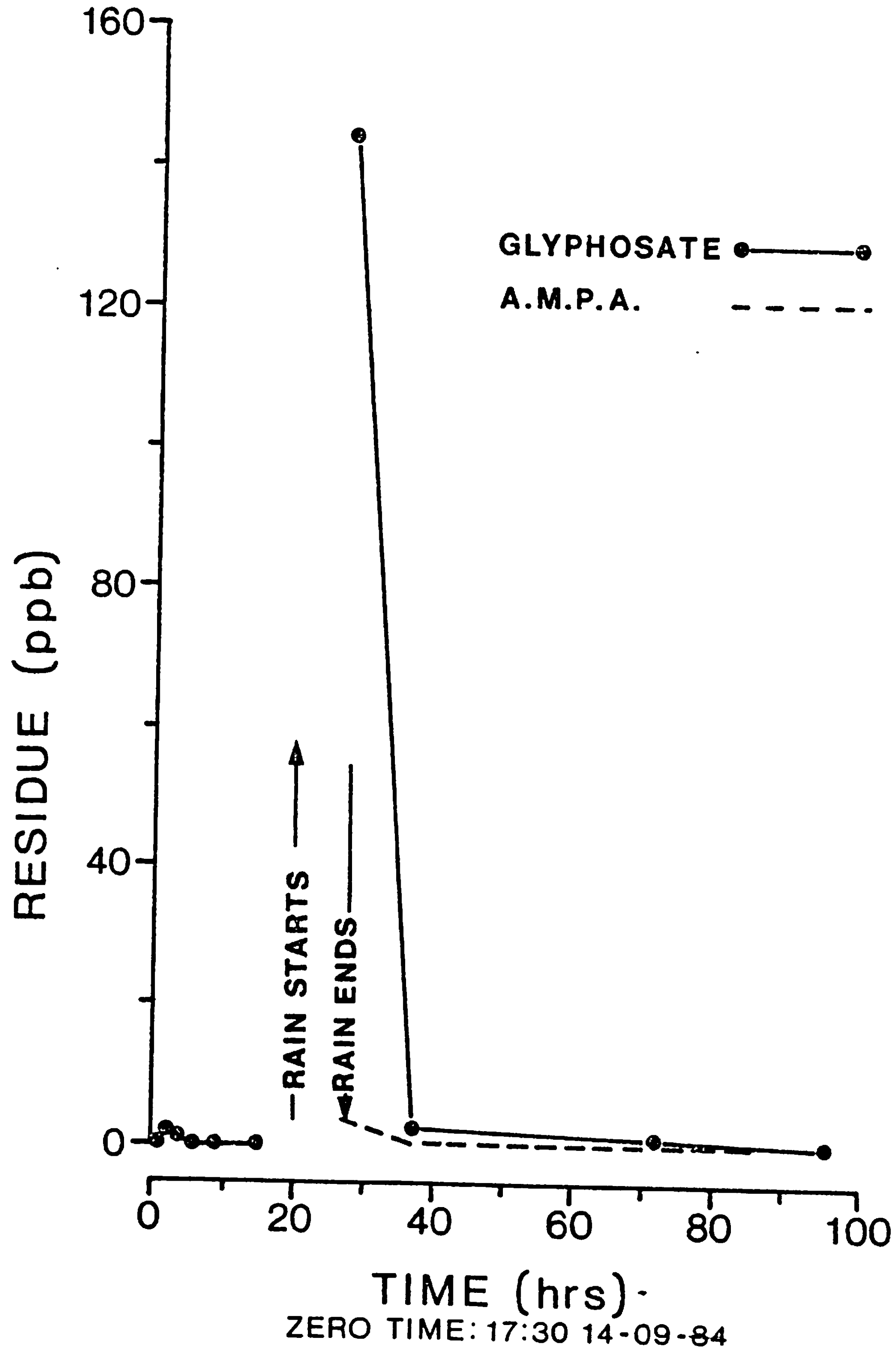

Figure 3. Short-term residue response to aerial overspray of glyphosate in streamwater from 750-tributary, Carnation Creek.

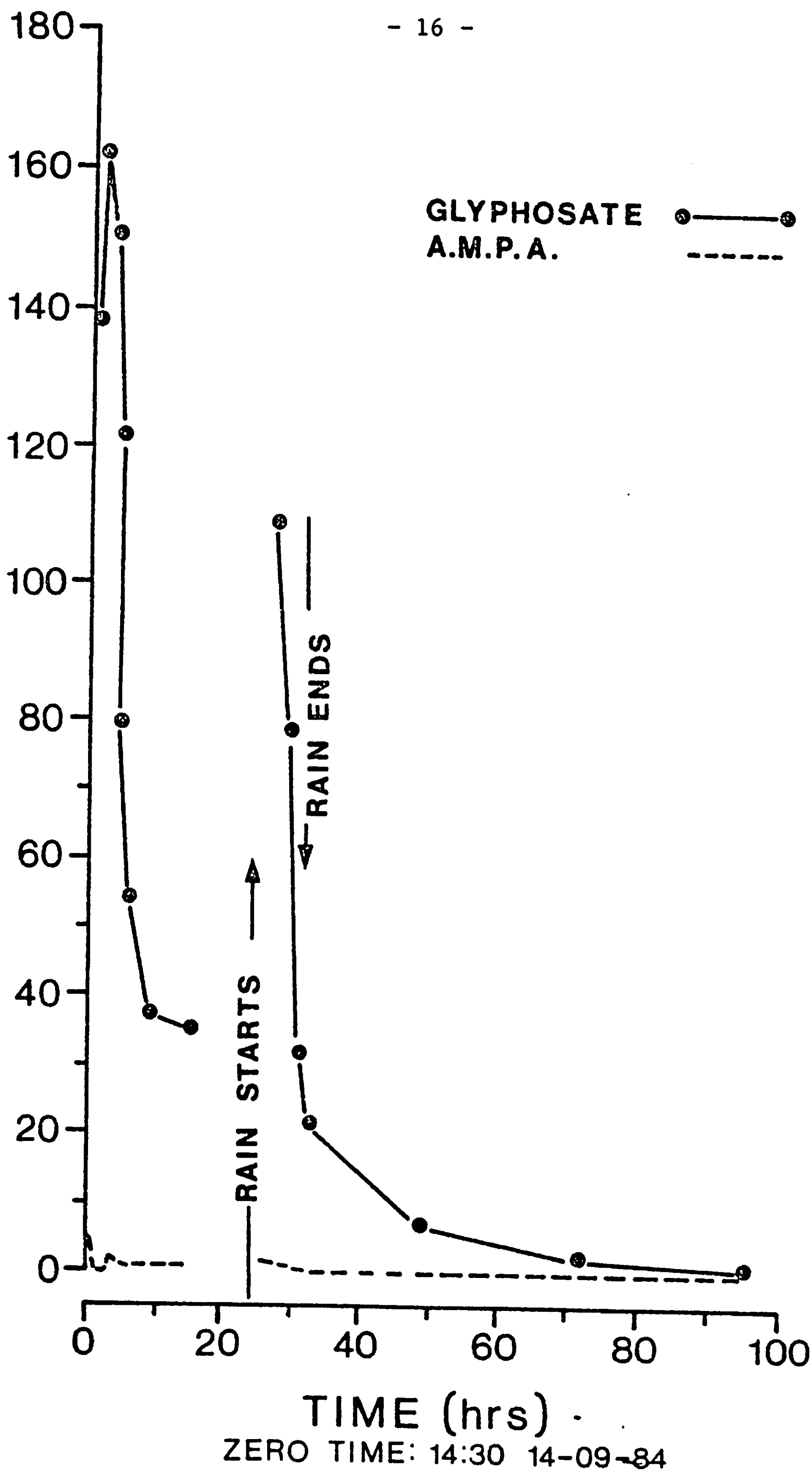

Figure 4. Short-term residue response to aerial overspray of glyphosate in streamwater from 1600-tributary, Carnation Creek.

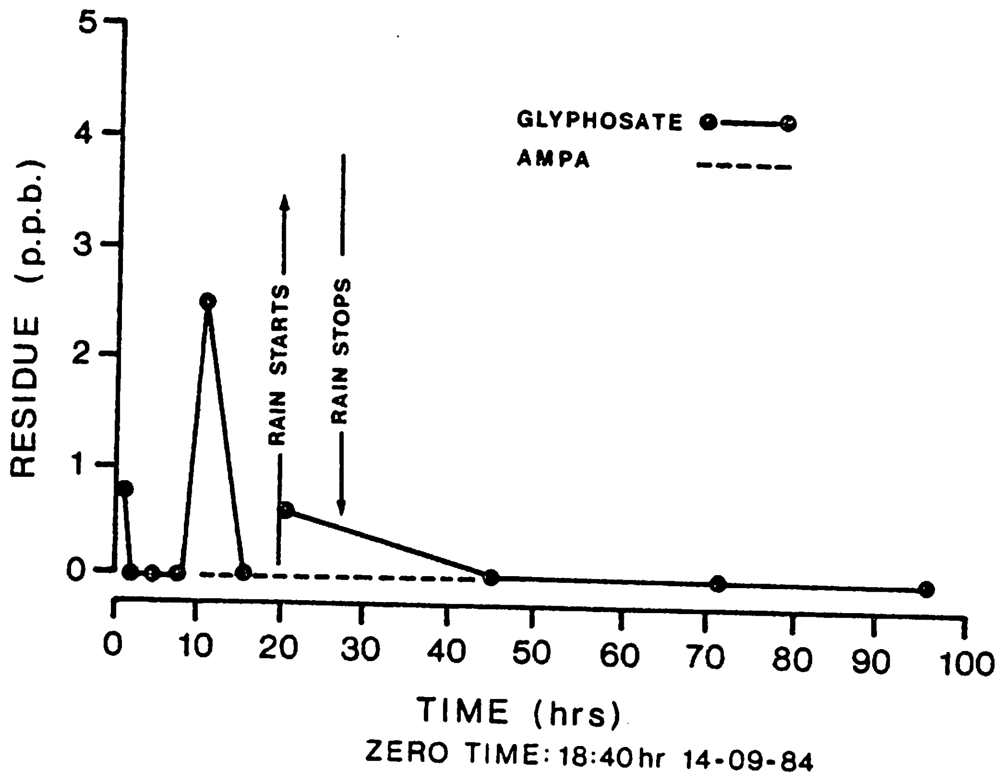

Figure 5. Short-term residue response to aerial overspray of glyphosate in streamwater from 1450-tributary, Carnation Creek.

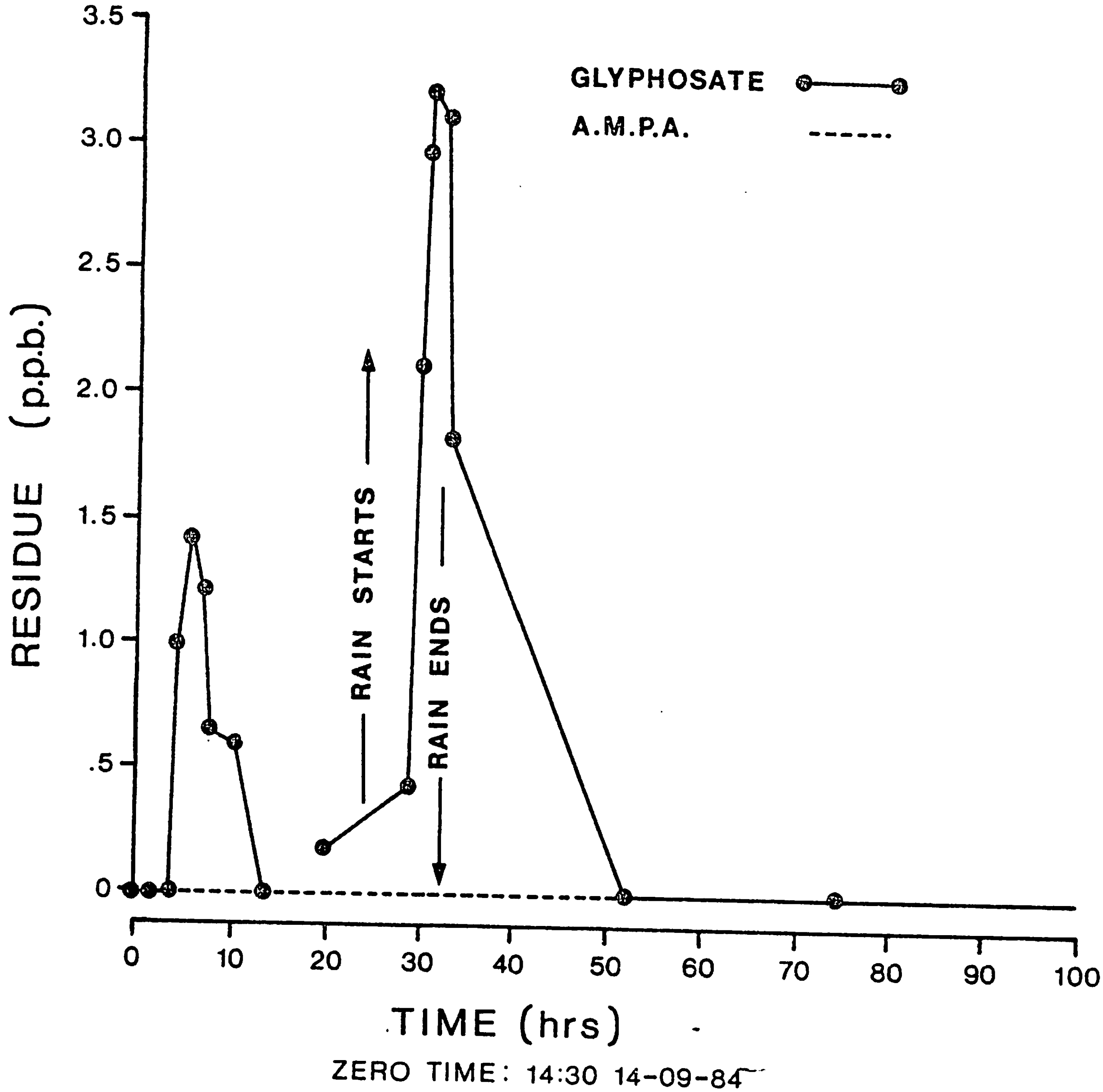

Figure 6. Short-term residue response to aerial overspray of glyphosate in streamwater from Carnation Creek at B-weir.

tions increased to 109 ppb during the first rainfall at 27.5 h, and decreased from there to 1.3 ppb at 96 h after application (Fig. 4). AMPA concentrations also rose to 1.8 ppb during the rainfall, but decreased to non-detectable levels at 49 h after application.

The response of glyphosate concentrations in runoff observed in 1600-tributary were in agreement with findings from other studies that direct application and spray drift were the major source of herbicide entry into a stream (Brown 1980; Newton et al. 1984). Although the runoff results from 750-tributary of a 100-fold increase over a initial prerainfall response to overspray (Fig. 3) was in contrast with these findings, the similarity of maximum detected glyphosate concentrations during this first rainfall at 750- and 1600-tributaries (144 and 109 ppb, respectively) suggested that the increase was from relatively low initial response values rather than from high runoff values. However, the longer duration that residues were observed at 750-tributary in runoff (>45 h) compared to the initial response (<5 h; Fig. 3) were in agreement with Norris et al. (1983) that mobilization in runoff may yield longer lasting effects than direct application. The runoff response generated at 750-tributary may have been from several residue sources, including mobilization in ephemeral stream channels (Norris et al. 1983) and residue washed off leaves of overhanging riparian vegetation. In a study of agricultural watersheds, residue input through overland flow during runoff was greater than input from groundflow (Edwards et al. 1980), probably from the strong adsorption properties of glyphosate to basic soil types (Sprankle et al. 1977) resisting residue leaching into groundflow. Glyphosate in runoff at B-weir (3.2 ppb) from the first rainfall was also twice as high as the initial response (1.4 ppb) to application (Fig. 6). The additional residue input from several charged ephemeral streams draining the spray blocks, such as 750-tributary, may have generated this increase in response at B-weir.

Long-term Residue Response

Residues in major storm events

Eight major storm events occurred between 10 October, 1984 and 11 February, 1985 (Table 2). Numerous smaller storm events that did not achieve threshold discharge also occurred during the sampling program (Fig. 7). The only quantifiable glyphosate concentrations found at 750- and 1600-tributaries in the storm event sample program were during the first storm event 23 days after application, with measured values of 0.52 and 0.53 ppb (Table 3). This response was less than 0.5 % that of the first runoff in the short-term sample program. All residue values from samples beyond 23 days after application were in unquantifiable trace quantities between the LOQ and LOD. AMPA was only found in trace quantities in the long-term sample program. At 750-tributary, detectable glyphosate and AMPA concentrations were only found in the first major storm event at 23 and 24 days after application, with samples from another six major storm events yielding no dectectable residues (Table 3).

At 1600-tributary, detectable residues were found in five major storm events (numbers 1, 2, 3, 4 and 8) at 23-27, 49, 59 and 150 days after application (Table 3). AMPA was also detected during the first four storm events at 23-30, 49 and 59 days after application (Table 3). Glyphosate persistence to 150 days at 1600-tributary was similar to the reported persistence in runoff (to 122 days), but not to the higher glyphosate residue concentrations found in agricultural watersheds (Edwards et al. 1980).

Glyphosate and AMPA residues were detected at B-weir as a pooling of runoff from all spray blocks only in storm event number 6 at 84 days after application (Table 3). These results on glyphosate persistence are in agreement with other studies that found the first rainfalls after treatment generated the highest residue concentrations (Kimmins 1975; Brown 1980; Edwards et al. 1980).

Ten of the eleven samples containing detectable residues were collected while discharge was greater than the storm event threshold, with the exception being a sample from 1600-tributary containing AMPA at 30 days after application (Table 3). The probable source of residues in the ten samples was overland flow. Overland flow was prevalent in the Carnation Creek alluvial floodplain where the spray blocks were located. During stormflows, water levels often rose 0.5 m and swollen ephemeral stream channels extended well beyond stream banks into riparian vegetation. The high solubility of glyphosate (12,000 mg/L at 25°C) probably facilitated some residue mobilization within these extended stream channels (Norris et al. 1983).

Buffered C-tributary was monitored during and after the major storm events following application. Trace glyphosate residue quantities were found in only one sample, during major storm number 3, 49 days after application (Table 3). The probable source of this residue was mobilization from overland flow and swollen ephemeral stream channels that extended into the treated areas. As Carnation Creek watershed was

Table 2. Summary of storm event data at Carnation Creek, 1984-1985

Major Storm Number	Date	Days After Application (14.09.1984)	Peak Discharge (m^3/sec)	Rainfall (mm) 24 h Total* Preceeding	Rainfall (mm) Cumulative** from Application
a***	15.09.84	1	2	39	39
1	7.10.84	23	22	69	168
2	9.10.84	25	28	42	325
3	2.11.84	49	12	43	630
4	12.11.84	59	8.0	43	816
5	19.11.84	66	7.9	47	939
6	7.12.84	84	9.5	66	1145
7	14.12.84	91	11	94	1299
8	11.02.85	150	8.5	52	1488

*For the 24 h preceeding the time that threshold discharge was attained.
**Up to 0800 hours on the day threshold was attained.
***First rainfall after application; discharge did not attain threshold 7.0 m3/sec to designate as a major storm.

Table 3. Occurrence of herbicide residues in storm event sampling at Carnation Creek

Major Storm Event Number	Number of Samples per Site*		Days After Application (14.09.1985)	Residue Concentrations (ppb)							
				750-trib		1600-trib		B-weir		C-trib	
	During	After		Gly	AMPA	Gly	AMPA	Gly	AMPA	Gly	AMPA
1	1		23	0.52	Tr	0.53	Tr	ND	ND	ND	ND
	1		24	Tr	Tr	Tr	Tr	ND	ND	ND	ND
2	1		25	ND	ND	Tr	Tr	ND	ND	ND	ND
		1	27	ND	ND	Tr	Tr	ND	ND	ND	ND
		1	30	ND	ND	ND	Tr	ND	ND	ND	ND
		3	33, 40, 47	ND	ND	ND	ND	ND	ND	ND	ND
3	1		49	ND	ND	Tr	Tr	ND	ND	Tr	ND
		3	51, 53, 57	ND	ND	ND	ND	ND	ND	ND	ND
4	1		59	ND	ND	Tr	Tr	ND	ND	ND	ND
		2	60, 62	ND	ND	ND	ND	ND	ND	ND	ND
5	1		66	ND	ND	ND	ND	ND	ND	ND	ND
		4	67,69,73,80	ND	ND	ND	ND	ND	ND	ND	ND
6	1		84	ND	ND	ND	ND	Tr	Tr	ND	ND
		2	85, 87	ND	ND	ND	ND	ND	ND	ND	ND
7	0	0	91								
8	1		150	ND	ND	Tr	ND	ND	ND	ND	ND
		5	151,153,157 164,171	ND	ND	ND	ND	ND	ND	ND	ND

Tr = Trace quantity between LOD and LOQ ; ND = Not Detectable
* Samples collected either during or after the defined storm event.

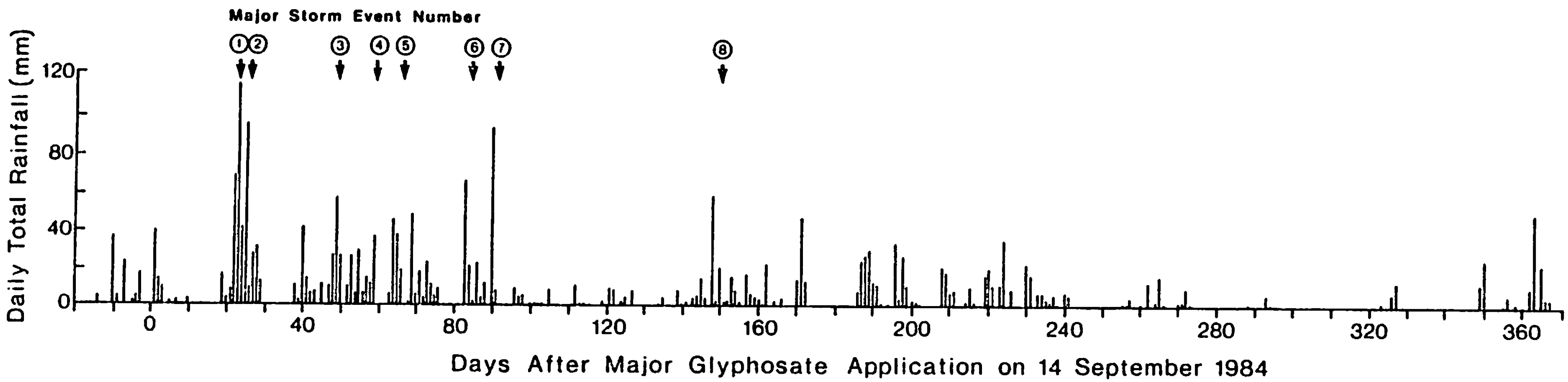

Figure 7. Carnation Creek discharge and rainfall at B-weir during the streamwater sample program.

selected for being typical of areas requiring glyphosate treatment for conifer release in the coastal regions of British Columbia, similar results may also be expected in buffered streams along operational treatments in other areas.

Residues in Bi-Weekly Samples to 1 Year After Application

No detectable residues were found in any of the 13 scheduled bi-weekly samples from 196 - 339 days after application. Rainfall was infrequent during this period (Fig. 7) and overland flow was absent during sample collection. Ephemeral 750- and C-tributaries were completely dry at times beyond 263 days after application (Appendix 2), precluding collection of four samples from each station.

Implications of Glyphosate in Streamwater

The glyphosate concentrations observed in Carnation Creek and its tributaries remained below the 96 hour LC_{50} values for trout (86 ppm; WSSA 1983) and rainbow trout (140 ppm; Folmar et al. 1979). The margin of safety maintained for these species at oversprayed 750- and 1600-tributaries ($< 1/530 \times LC_{50}$) was greater than the recommended 'rule of thumb' of $1/100 \times LC_{50}$ for non-bioaccumulating chemicals (Brown 1980). Residue concentrations at 1600- and C-tributaries and at B-weir also induced a minimum to no-significant response in aquatic invertebrates (Kreutzweiser et al. in prep.)[6]. Other studies on fish utilization of oversprayed sidechannels and habitat changes (water temperature, changes in riparian vegetation, erosion, sediment inputs, stream chemis-

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[6]D. Kreutzweiser, P. Kingsbury and J.C. Feng. Drift response of stream invertebrates to aerial applications of glyphosate. Can. For. Serv., For. Pest Manage. Inst., Sault Ste. Marie, Ont. P6A 5M7, Submitted to Bull. Environ. Contam. Toxicol.

try, algal populations, food supply and litter inputs) underway at Carnation Creek (Reynolds 1985)[1] may help illuminate tolerance levels of aquatic systems to Roundup application.

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Appendix 1. Short-term streamwater sample collection schedule

Date	750-tributary	1450-tributary	1600-tributary	B-Weir
	Sample Collection Times			
6.09.1984				1954-2054
				2104-2154
8.09.1984				1420-1510
				1520-1610
				1620-1710
				2020
				2320
9.09.1984				0520
				1720
10.09.1984				1720
11.09.1984				1720
12.09.1984				1720
14.09.1984	1736-1836	1843-1943	1440-1530	1440-1530
	1840-1940	1953-2053	1540-1630	1540-1630
	1945-2045	2103-2053	1740-1830	1640-1730
	2345	2213-2313	1840-1930	1740-1830
			1940-2030	1840-1930
			2040-2130	1940-2030
				2040-2130
				2140-2230
15.09.1984	0245	0213	0001	0130
	0845	0513	0600	0430
	2045	1113	1800	1030
		1509	2000	1900
			2200	2000
			2325	2100
				2200
				2300
				2345
16.09.1984	1830	1900	1600	1930
17.09.1984	1830	1900	1600	1930
18.09.1984	1830	1900	1600	1930

Appendix 2. Long-term bi-weekly streamwater sample collection schedule.

Bi-Weekly Sample Number	Days After Application (14.09.1984)	750-trib	1600-trib	C-trib	B-weir
1	196	x	x	x	x
2	210	x	x	x	x
3	224	x	x	x	x
4	238	x	x	x	x
5	252	x	x	x	x
6	263	dry	x	x	x
7	280	x	x	x	x
8	297	dry	x	dry	x
9	311	x	x	dry	x
10	326	dry	x	dry	x
11	339	dry	x	dry	x
12	355	x	x	dry	x
13	364	x	x	x	x