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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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Table I. Carnation Creek Watershed Flood Plain Soil Characteristics[a]

depth, cm	OM, %	CEC	N, %	P, ppm	K, %	pH	sand, %	silt, %	clay, %
				Stations 1–3					
0–5	30.39	45.85	0.60	17.05	0.03	4.94	55.85	23.70	20.46
5–15	19.47	51.33	0.50	15.18	0.02	4.55	55.79	23.73	20.48
15–35	9.28	26.37	0.21	1.47	0.01	5.28	62.01	17.50	20.49
				Stations 7–9					
0–5	30.90	50.47	0.12	54.04	0.03	4.49	62.02	24.99	12.99
5–15	14.88	48.13	0.84	10.55	0.02	4.20	54.68	24.90	20.42
15–35	10.21	27.44	0.07	1.03	0.01	4.65	65.80	16.23	17.97

[a] Key: OM = organic matter; CEC = cation-exchange capacity.

underlain by coarse-textured mineral soils, low in organic matter. Given that climatic, hydrological, and physical characteristics of coastal forest ecosystems are unique, that residue mobility and persistence may be affected by such factors, and that no information was available on the behavior of glyphosate in a coastal rainforest ecosystem, a research program was initiated to provide data relevant to the fate of the herbicide glyphosate (ROUNDUP) in a coastal British Columbia watershed.

The specific objectives of this portion of the study were (a) to assess the uniformity of glyphosate deposition following a rotary-wing, aerial application of ROUNDUP with a MICROFOIL (Union Carbide Inc., Ambler, PA) boom, in a coastal British Columbia watershed, (b) to determine foliar residue levels in the major target species and subsequently monitor the persistence of associated litter residues, (c) to monitor the persistence of glyphosate and its major degradation product, AMPA, in both well-drained and seasonally flooded soils over a 1-year period following aerial application, and (d) to determine the leaching potential of glyphosate and AMPA in soil systems typical of a coastal British Columbia watershed.

MATERIALS AND METHODS

Site Description. A general description of the Carnation Creek watershed study site is given in part 1 (Feng et al., 1990). The 10-km^2 study site is typical of coastal watersheds in British Columbia and is characterized by a narrow valley bottom with steep slopes rising to 700 m in elevation. Vegetation in the valley bottom is dominated by salmonberry (*Rubus spectabilis*) and red alder (*Alnus rubra* Bong.) (King and Oswald, 1982).

Soils on the slopes are shallow, coarse-textured, and highly organic (Oswald, 1973). Soils of the alluvial flood plain are highly stratified into organic surface layers underlain by gravel, bedrock, or silty clay deposits depending on location within the watershed. Characteristics of soils from sampling sites used in this study are presented in Table I.

Annual precipitation in the watershed ranges from 210 to 480 cm, falling predominantly as rain in October and March. A detailed description of the watershed hydrology is available in a previous publication (Hetherington, 1989).

Site Preparation. Three soil sampling sites were chosen within the watershed as indicated in Figure 1. Sites in the upper (stations 1–3) and lower (stations 7–9) reaches of the watershed were selected to monitor persistence and leaching in well-drained soils. The middle watershed soil site (stations 4–6) was established in a low-lying area known to be seasonally flooded. Water table levels and degree of soil satration for the various sampling locations and dates are presented elsewhere (Hetherington, 1989). At each site, three 5 × 5 m areas were cleared by removing the plant canopy, large debris, and slash. The area was then subdivided to provide three replicate sampling areas or stations.

At each of the soil sampling sites, a total of eight deposit collectors constructed of aluminum foil supported on corrugated cardboard squares (surface area 400 cm^2) were placed around the periphery of the cleared area. The deposit collectors (approximately 10 cm above ground level) were used to estimate the initial residue deposited on the soil surface at each site and allow assessment of the deposit uniformity throughout the watershed.

Foliage and leaf litter sampling stations were established in areas dominated by salmonberry and red alder, respectively (Figure 1).

Herbicide Application. ROUNDUP (isopropylamine salt of glyphosate) was applied at a nominal rate of 2 kg/ha AI and spray volume of 252 L/ha. Applications were made over a 10-day period to 11 individual spray blocks (Figure 1), with use of a Bell-47 helicopter and a MICROFOIL boom equipped with 1.5-mm-i.d. hayrake nozzles. Details of the herbicide applications, including meteorological conditions at time of spraying, have been reported by Reynolds et al. (1989).

Sampling Methodology. Deposit sampling sheets were collected immediately following chemical application, packaged, stored, and shipped for analyses.

Fresh foliage was collected immediately following treatment by felling a representative tree (red alder) or by clipping brush (salmonberry). Individual leaves were then harvested to provide a composite sample for determination of initial foliar residues in each species.

A total of 20 m^2 of nylon mesh was placed under individual trees at approximately 0.5 m above the ground surface to trap leaf litter. Leaf senescence and defoliation began in mid-September 1984. Leaf litter samples were collected from nylon mesh traps between 1 Oct and 30 Nov. Samples of leaf litter were collected biweekly generally and on a weekly schedule during the peak leaf fall period.

Soil samples were obtained from each sampling station with use of a Campbell soil coring device. Soil cores of 10-cm diameter and 30-cm depth were obtained and subsequently divided into three sections corresponding to 0–5, 5–15, and 15–30 cm soil layers, respectively, with each layer independently analyzed for chemical residue. For samples taken after 150 days, a fourth layer corresponding to a depth of 30–35 cm was obtained. Soil samples were collected on a temporal schedule as shown in Figure 3. Details of sampling methodologies for all substrates are reported by Feng and Klassen (1986).

Residue Analysis. Samples of the ROUNDUP formulation (356 g of AI/L), tank mixes, and deposit collectors were obtained and analyzed as described in part 1 (Feng et al., 1990). Whole samples of foliage and leaf litter were air-dried and macerated by passage through a Hobart chopper. Finely chopped particles were mixed in large, inflated, plastic bags to provide a homogeneous sample. From the homogenized samples, two subsamples (5 g) were taken and used for determination of oven-dry weight and residue content, respectively. Results were corrected for recovery efficiency of the analytical method (Table II) and reported as micrograms per gram of oven-dried leaf tissue.

Soil samples obtained from the Carnation Creek study site were immediately frozen, shipped, and stored under cold (−10 °C), dark conditions until analysis. Subsamples (5 g) of air-dried and homogenized soils were extracted. Results were corrected for recovery efficiency of the analytical method (Table II) and reported as micrograms per gram of air-dry mass. The analytical procedures, including HPLC specifications utilized

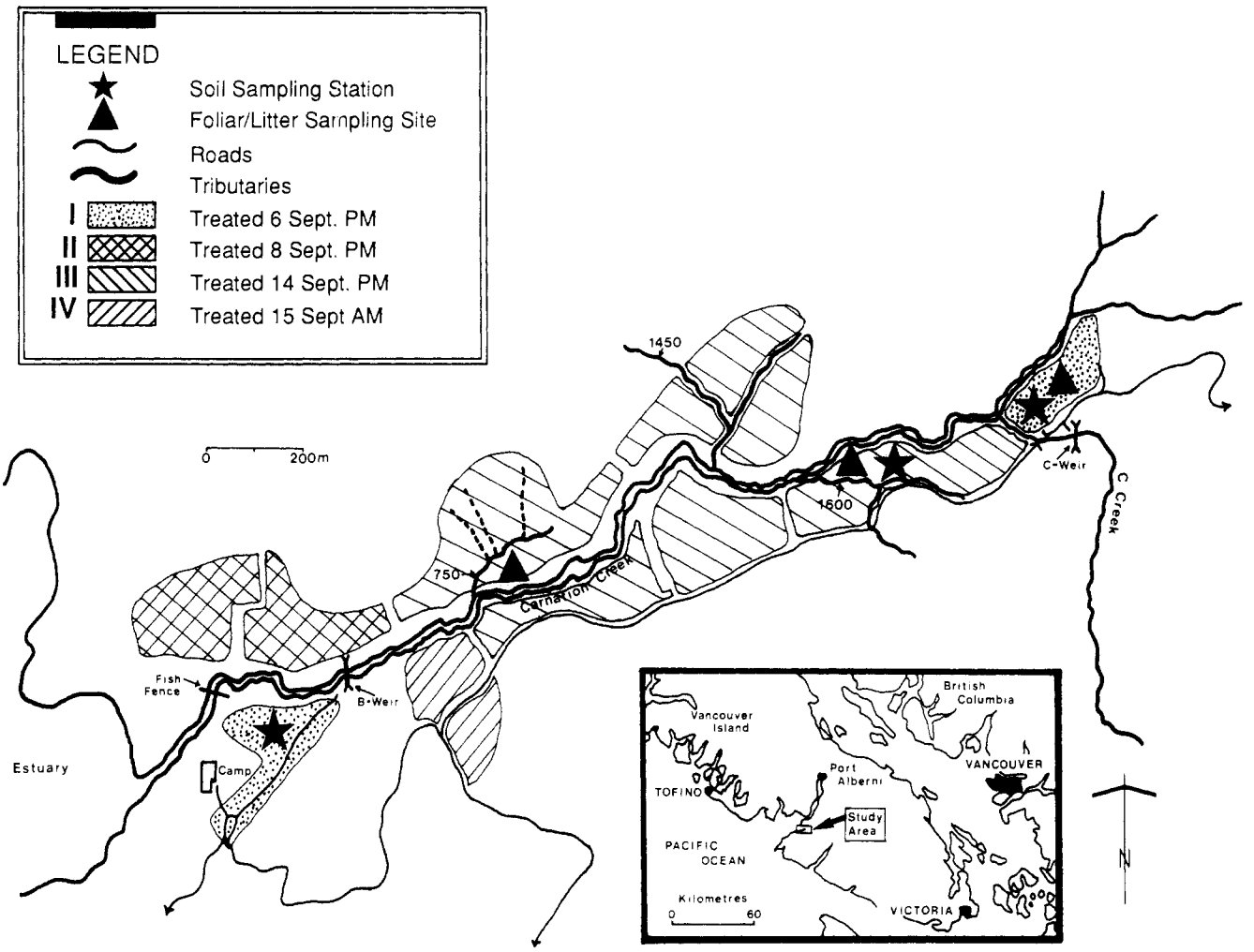

Figure 1. Location of the Carnation Creek watershed study area and terrestrial sampling locations.

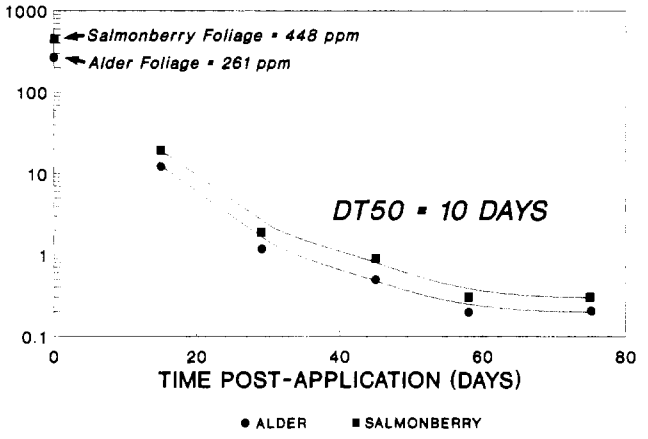

Figure 2. Dissipation of glyphosate residues in leaf litter of the Carnation Creek watershed.

for leaf litter, foliage, and soil sample analyses are detailed in Thompson et al. (1989).

Throughout the course of analytical determinations 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 II). The QC data were subsequently used to correct the field sample data for recovery efficiency of the analytical method.

Statistical Analysis. Glyphosate residues recovered from artificial deposit collectors or initial soil samples were used to estimate initial deposit rates. Application rate estimates (kg/ha) were calculated by multiplying residues ($\mu g/cm^2$) on deposit collectors by a conversion factor of 0.10. Mean deposit rates calculated for each of the three sampling locations were subjected to a one-way analysis of variance (ANOVA), with 2 degrees of freedom. The Bonferroni (BON) multiple comparison procedure was used to elucidate which deposit rates were significantly different in the case of the ANOVA F value being significant at $P < 0.05$.

Leaf litter residues (micrograms per gram dry mass) were regressed against the log transform of time postapplication by simple linear regression analyses. A significant F value ($P < 0.10$) from the regression ANOVA was interpreted as evidence of a significant decline of litter residues with time, and a coefficient of determination (R^2) greater than 0.75 was considered acceptable in terms of using the regression equation to estimate time to 50% and 90% dissipation (DT_{50} and DT_{90}, respectively). These values were also estimated by graphical interpolation of untransformed data for comparative purposes.

Soil residues (micrograms per gram dry mass) as determined from subsamples in each individual layer were multiplied by the dry mass of the corresponding individual layer and totaled to yield soil residue data in terms of micrograms per layer. Total soil residues (total micrograms per 30-cm core) were then calculated for each sampling station and time and grouped according to location to derive mean soil residues for each watershed location at each sampling time. Mean total soil residue data were subjected to ANOVA and regression analyses similar to that described for litter residues.

RESULTS AND DISCUSSION

Formulation and Tank-Mix Analyses. Results of the ROUNDUP formulation and tank-mix analyses are presented in part 1 of this series (Feng et al., 1990).

Initial Deposit at Soil Sampling Sites. Deposit estimates calculated from artificial deposit collector resi-

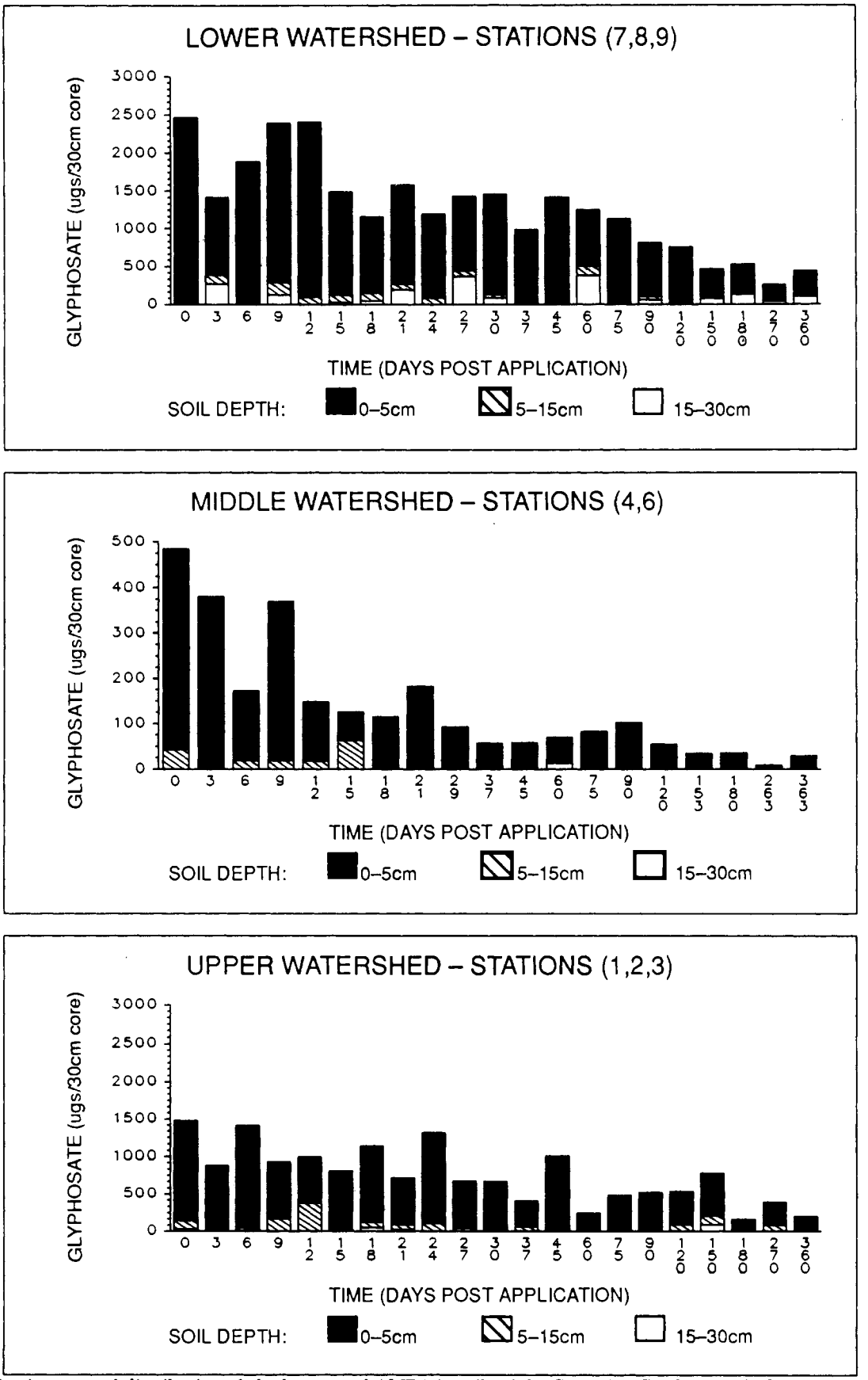

Figure 3. Persistence and distribution of glyphosate and AMPA in soils of the Carnation Creek watershed.

dues were consistently higher than those resulting from initial soil residues (Table III). Mean deposit rates derived from artificial collectors at the upper, middle, and lower watershed locations were statistically different from one another as determined by ANOVA and the BON multiple comparison procedure ($P < 0.05$). The lack of statistical differences in similar comparisons based on initial soil residues is an artifact of the high variability in these residue samples and the lower number of replicates used. High variability in initial soil residues result-

Table II. Validation Data for Analytical Methods[a]

substrate level	fortificn	N	analyte	% recovery mean ± sd (CV, %)	LOD	LOQ
humus	0.1–6.0	132	GLYPH	77.7 ± 8.9 (11.56)	0.05	0.10
soils	0.025–1.5	132	AMPA	67.7 ± 10.9 (16.09)	0.01	0.03
mineral	0.1–6.0	30	GLYPH	73.5 ± 7.7 (10.53)	0.02	0.05
soils	0.025–1.5	30	AMPA	58.2 ± 10.9 (12.77)	0.02	0.05
leaf	0.5–5.0	4	GLYPH	84.4 ± 5.3 (6.25)	0.10	0.30
litter (s)	0.1–1.0	4	AMPA	54.7 ± 1.7 (3.21)	0.03	0.08
leaf	0.5–5.0	4	GLYPH	81.3 ± 7.7 (9.47)	0.10	0.30
litter (a)	0.1–1.0	4	AMPA	60.9 ± 12.2 (20.03)	0.03	0.08

[a] All values presented in tersm of ppm = μg/g dry mass (for solids). LOD = limits of detection = detector response equivalent to 2 × S:N ratio. LOD and LOQ values for deposit collectors equate to 2.5×10^{-5} and 1.25×10^{-4} kg/ha, respectively.

Table III. Comparison of Nominal and Empirical Estimates of Initial Glyphosate Deposition at Carnation Creek Watershed

sampling location	treatment area	nom rate[a]	init deposition rate est, kg/ha [mean ± SD (% CV)] deposit collector	soil residue
stations 1–3 (upper watershed)	I	2.0	2.54 ± 0.32 (13) A	1.72 ± 0.31 (18)
stations 4–6 (midwatershed)	III	2.1	1.62 ± 0.24 (15) B	0.60 ± 0.09 (16)
stations 7–9 (lower watershed)	I	2.0	3.42 ± 0.46 (14) C	3.23 ± 2.30 (71)
overall av		2.0	2.52 ± 0.90 (36)	1.85 ± 1.32 (71)

[a] Nominal rates as reported by Reynolds (1988)9 Values based on total residue (glyphosate plus AMPA) with $n = 8$ for deposit collectors and $n = 3$ for soil residues. Deposit collector values followed by different letters are significantly different ($P < 0.05$) as determined by LSD and Bonferroni multiple comparison procedures.

ing from aerial applications is commonly observed (Newton et al., 1984) and may be related to a number of variables. Potential factors affecting ground deposit variability include site variables (air turbulence within microsites, differential interception of the spray cloud by surrounding vegetation), application variables (differences in release height, dispersal system function, orientation as related to wind direction, degree of overlap, swath displacement and/or drift), and meteorological variables (windspeed, wind direction, air temperature, boundary layer stability). One anomalous data value in the initial soil residue data (station 8, 5.67 kg/ha) resulted in an extremely high mean deposit estimate for the lower watershed location. The artificial deposit collector data also showed unusually high residues, indicating that the high deposit rate may be attributed to application error (i.e., swath overlap or nozzle malfunction).

Initial levels of AMPA were less than 2% of corresponding glyphosate residues for all deposit collector samples but varied between 4 and 13% for initial deposit as determined from soil sample residues. The higher levels of AMPA in 0-time soil samples as compared with deposit collector samples may be indicative of slight degradation of glyphosate during the 2-year storage period for soil samples.

Overall average deposit within the watershed ranged from a high estimate of 2.52 based on artificial deposit collector data and 1.85 kg/ha based on initial soil residue data (Table III), indicating an overall application rate close to the nominal rate of 2.0–2.1 kg/ha AI.

Foliar and Leaf Litter Residues. Results of the foliage sample analyses indicated that an effective impingement of glyphosate occurred on both target species, resulting in initial foliar residues of glyphosate ranging from 261 μg/g for red alder to 448 μg/g for salmonberry. Initial foliar residues observed in this study are in agreement with those of Newton et al. (1984), who observed residues ranging from 89 to 489 μg/g in various target foliage samples including red alder and salmonberry, but contrast with results of Freedman et al. (1988) who reported glyphosate residues in red maple foliage of 5.1 mg/g. The apparent discrepancy in these results may be related to differences in mean leaf area and corresponding impingement of glyphosate on the leaf surface and/or differences in methods of sampling. Residues of AMPA were less than 2% of coincident glyphosate residues for both foliage types.

Leaf senescence and defoliation began in mid-September 1984, and the first leaf litter samples were collected 15 days postapplication. Initial leaf litter residues (12.5 and 19.2 μg/g dry mass) were approximately 10-fold lower than initial foliar residues (261 and 448 μg/g dry mass) observed in fresh foliage of alder and salmonberry, respectively, on the day of application. Such a disparity in foliar and leaf litter residues may result from a variety of dissipation mechanisms acting on the foliar residues including uptake, translocation, and metabolism within the plant, washoff resulting from the rainfall event (39 mm), which occurred 23 h postapplication, and/or microbial degradation on the leaf surface. Lund-Hoie (1985b) reported that only 20% of the glyphosate initially applied was absorbed in ash and birch foliage and that decomposition of the absorbed chemical was slow (35% in 2 months). Newton et al. (1984) observed a similar rapid dissipation of glyphosate residues in hardwood foliage following a rainfall of 12 h after application. In combination, these results lend support to the hypothesis that washoff with rainfall is a major mechanism of dissipation for foliar residues where rainfall occurs shortly after application. Further research is required on binding and subsequent washoff of glyphosate from treated leaf surfaces.

Glyphosate residues in leaf litter declined as a logarithmic function of time postapplication in both alder ($F = 8.97$, $P = 0.06$; $R^2 = 0.75$) and salmonberry ($F = 9.2$, $P = 0.06$; $R^2 = 0.76$). Based on regression analysis, DT_{50} and DT_{90} values for both alder and salmonberry litter residues were 10 and 32–35 days, respectively. Similarly, time to 50% dissipation based on graphical interpolation was estimated as 8 days for alder and 9 days for salmonberry (Figure 2). AMPA residues in leaf litter also declined with time and were at or below limits of detection within 29 days postapplication. The estimated DT_{50} value for glyphosate residue in leaf litter is comparable to the value of 14 days determined by Newton et al. (1984).

Leaching Potential. Soil core samples were divided into separate layers according to depth [0–5 cm (organic), 5–15 cm (organic), 15–30 cm (organic and mineral)], and each layer was analyzed separately to allow determination of the distribution of glyphosate and AMPA residues within the soil profile. At sampling dates beyond 150 days postapplication, a fourth layer [30–35 cm (mineral)] was obtained and analyzed. Results of these analyses are presented as histograms of mean glyphosate concentration from replicate sample stations according to location within the watershed (Figure 3). Quantifiable residues of glyphosate were found in only 1 of the 32 samples from the 30–35-cm layer; the residue level in this layer (0.46 ppm) was equivalent to 11.5% of the total found in the core. Analysis of residue distribution data indicated that in general (156/168 core samples) >90%

of glyphosate residue occurred in the 0–15-cm organic layer. Two anomalous values (glyphosate residue levels in the 15–30-cm layer exceeding 10% of the core total) were observed in the soil residue distribution data, both occurring in the lower watershed location (day 60, 30.28%, day 360, 27.6%). No differences in leaching potential between the seasonally flooded and well-drained soil sites were apparent. AMPA residue distribution was similar to that of glyphosate, being retained primarily in the upper 0–15-cm layer.

Distribution of glyphosate and AMPA within the soil cores indicates that neither chemical is susceptible to leaching. These findings are consistent with the general literature (Helling, 1971; Sprankle et al., 1975; Rueppel et al., 1977; Damanakis, 1976; Edwards et al., 1980; Roy et al., 1989) and support the conclusion of Torstensson (1985), who stated that glyphosate is practically immobile in soil. Research conducted on the absorption of glyphosate to soils or soil fractions (i.e., mineral components) suggests that glyphosate is bound to soils through the phosphonic acid moiety and that sorption is positively correlated with clay content, cation-exchange capacity, and unoccupied phosphate sorption capacity (Sprankle et al., 1975; Hance, 1976; Glass, 1986). Carnation Creek soils are characterized by a relatively high cation-exchange capacity, clay content, and organic matter content, especially in the upper 15-cm layers (Table I). Thus, we conclude that the lack of vertical mobility exhibited by glyphosate in these soils is due to strong adsorption to cation saturated clays and/or organic matter in the upper soil horizons.

Persistence. The mean total residue of glyphosate (total micrograms per 30-cm core) at each sampling date is represented by the height of the histogram bars in Figure 3. Although total residues of glyphosate clearly declined with time in all locations and ANOVA F values for regression of linear and semilog-transformed data were significant ($P < 0.05$), poor regression coefficients ($0.17 < r^2 > 0.46$) prohibited the use of these models for estimating DT_{50} and DT_{90} values or establishing confidence limits for these endpoints. In addition, no statistically valid comparisons could be made with respect to persistence of glyphosate or AMPA in seasonally flooded soils and well-drained soils.

Graphical analysis of glyphosate residue data indicated that glyphosate residues were consistently less than 50% of initial residues 45–60 days postapplication at all locations, and thus a conservative estimate of DT_{50} for glyphosate was established as 45–60 days. Although quantifiable residues of glyphosate remained after 360 days, residue levels were low, equating to 6–18% of initial glyphosate residue in terms of total micrograms in the 30-cm core. Residues in the organic 0–5-cm layer declined from high levels of 8.16–39.80 ppm initially to 0.25–2.89 ppm after 360 days. AMPA residues levels were low at time 0 (4–13% of glyphosate residues) and followed a pattern of transient increase and decline at all sampling locations. The maximum AMPA residue was observed in the upper organic layer of samples from the upper watershed location on day 18 (mean (n = 3) 9.185 ppm) and equated to less than 40% of initial glyphosate residues. After 360 days AMPA residue levels had declined to 6–27% of initial glyphosate residues. Torstensson (1985) summarizes a number of investigations providing conclusive proof that the degradation of glyphosate in soils occurs primarily via cometabolism by soil microbes. The general decline in glyphosate residues over time at all three sampling locations, coupled with a transient increase in AMPA residues, suggests that microbial degradation is also the major mechanism of dissipation for glyphosate in these soils.

The middle watershed sampling location is low-lying and seasonally flooded. At the time of application and for some time thereafter, surface water was actually moving over portions of the lower lying stations at this location (Hetherington, 1989). In fact, no samples were taken from station 5 due to complete flooding of this sampling location. As a result, initial soil residues of glyphosate in the middle watershed location were very low compared to the upper and lower watershed locations (note differences of scale in Figure 3), probably owing to interception and off-site movement of the chemical with runoff water.

The persistence estimate of 45–60 days resulting from this study is well within the range of 50% degradation times determined for various forest soils studied in the laboratory (Torstensson and Stark, 1981). The DT_{50} estimate is also in good agreement with that of Newton et al. (1984), who reported a value of 40.2 days for glyphosate in a western coastal soil of Oregon, but somewhat longer than that of Roy et al. (1989) who reported a 50% dissipation time of 24 days in a boreal forest soil of Ontario, Canada. Torstensson (1985) noted that the variable rate of degradation of glyphosate cannot be correlated to a single soil factor but reflects the general microbial activity of the soils, which in turn is affected by a multiplicity of environmental factors. The agreement of our data with previously published data indicates that none of the environmental factors in existence at Carnation Creek resulted in excessive persistence of glyphosate.

CONCLUSIONS

Although the overall chemical application to the watershed, empirically estimated as 1.85–2.52 kg/ha, was close to the nominal rate of 2.0–2.1 kg/ha, both methods of deposit estimation (artificial collectors and initial soil residues) indicated highly variable deposit between sampling locations and suggest that aerial applications, as conducted in this study, may result in nonuniform chemical deposit on target. Such differences in chemical deposition are of questionable practical importance in terms of efficacy and may be attributed to day to day meteorological and/or operational variability.

Although initial impingement of the active ingredient on target foliage was high, resultant leaf litter residues were 10-fold lower and dissipated rapidly, thus representing an insignificant, transient source of residue input to other ecosystem compartments. Initial soil residues of glyphosate in well-drained sites were high 31.42–39.80 μg/g, while in a seasonally flooded location initial soil residues were lower (8.16 μg/g) owing to interception of the chemical by surface water present on-site at the time of application. Little evidence of leaching was observed in either well-drained or seasonally flooded soils. Glyphosate soil residues were nonpersistent, dissipating to 13–18% of initial levels within 360 days postapplication, with an estimated time to 50% dissipation of 45–60 days. The behavior of glyphosate soil residues, as observed in this study, is in agreement with the general literature indicating that glyphosate is nonmobile in and relatively nonpersistent in soils.

Given the low acute toxicity to terrestrial organisms ranging from microorganisms to mammalian species (Eijsackers, 1985; Grossbard, 1985; Atkinson, 1985; Sullivan, 1985; Fletcher and Freedman, 1986; Torstensson and Stark, 1978; Muller et al., 1981), its lack of potential to bioaccumulate (Newton et al., 1984), and its environmen-

tal behavior as observed in this and other studies (Newton et al., 1984; Roy et al., 1989), a significant toxic impact resulting from soil or leaf litter residues would be highly unlikely.

In combination, the aquatic and terrestrial environmental fate research programs conducted at the Carnation Creek watershed support the continued registration and use of the glyphosate as a biodegradable, nonpersistent, and nonmobile chemical herbicide for silvicultural management.

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Reaction of Reducing Sugars with Sulfathiazole and Importance of This Reaction to Sulfonamide Residue Analysis Using Chromatographic, Colorimetric, Microbiological, or ELISA Methods

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Studies with sulfathiazole (ST) as a representative sulfonamide demonstrated that the N^4 aromatic amino group of sulfonamides can react with reducing sugars to form a variety of different sugar-bound compounds. ST was not destroyed in this reaction, and free ST could be produced from some of these sugar-bound compounds by aqueous dilution and, especially, by acidification. Different effects of these sugar-bound ST compounds, especially the N^4-linked ST Amadori compound, were noted on various methods of sulfonamide residue analysis. The sugar-bound ST compounds exhibited chromatographic behavior different from that of free ST, did not visualize with a common TLC Bratton–Marshall spray specific for sulfonamides, did not inhibit the growth of *Escherichia coli* and *Staphylococcus aureus* strains susceptible to free ST, but did inhibit binding of antisera in an indirect competitive enzyme-linked immunosorbent assay (ELISA) as much as 33 times greater, on a molar basis, than free ST.

The widespread use of antibiotics for animal husbandry and as feed additives has led to concern that foods derived from animals could be contaminated with antibiotics (Moates, 1986). Antibiotics in food could result in allergic or toxic reactions in sensitive consumers. Also, there are general concerns that the widespread use of antibiotics could contribute to antibiotic resistance in pathogenic organisms. A variety of sensitive methods have been developed to detect, quantitate, and therefore control antibiotic residues in food.

The sulfonamides (Anand, 1975) are a group of synthetic antibiotics widely used in agriculture and human therapy. Using a colorimetric method to detect sulfathiazole (ST) in honey, Low et al. (1989) noted that this sulfonamide disappeared by reaction with reducing-sugar solutions at elevated temperatures. This apparent loss of ST was surprising, since ST was reported to be remarkably stable in heated acidic aqueous solutions (Pawelczyk and Zajac, 1976).

The formation of a sugar–sulfonamide reaction product, N^4-glucopyranosylsulfamethazine, has been reported by Paulson et al. (1981), Giera et al. (1982), and Parks (1984) for sulfamethazine (also known as sulphadimidine in the literature) residue analysis of swine tissue. Parks suggested that analytical procedures for sulfonamides should account for this type of derivative; however, this suggestion has been ignored in some more recent analytical procedures for sulfonamide residues.

The following study was undertaken to investigate further the reaction between ST and reducing sugars and the effect that this reaction would have on various analytical procedures commonly used for sulfonamide analysis.

EXPERIMENTAL SECTION

Instrumentation and Materials. UV absorbances were recorded with a Hewlett-Packard Model 8451A diode array spectrophotometer (Hewlett-Packard (Canada) Ltd., Mississauga, ON). Absorbance values in microtiter plates were measured with a Model EL 309 ELISA reader (Bio-Tek Instruments, Inc., Burlington, VT). Solvents were removed from samples with a Büchi Rotavapor-R (Fisher Scientific, Edmonton, AB) with a bath temperature maintained ≤40 °C. Thin-layer chromatography (TLC) plates were 20 × 20 cm PE SIL G/UV with polyester backing purchased from Whatman Ltd., Maidstone, England. A Master-Mite Model 10008 heat gun (Master Appliance Corp., Racine, WI) was used to evaporate solvent and for charring of TLC plates. A Model UVS-54 lamp (254-nm light emission produced by Ultra Violet Products, Inc., San Gabriel, CA) was used to check for TLC UV absorbance. Centrifuga-

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