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Potential Risks to Freshwater Aquatic Organisms Following a Silvicultural Application of Herbicides in Oregon's Coast Range

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ABSTRACT

Glyphosate, aminomethylphosphonic acid (AMPA), imazapyr, sulfometuron methyl (SMM), and metsulfuron methyl (MSM) were measured in streamwater collected during and after a routine application of herbicides to a forestry site in Oregon's Coast Range. Samples were collected at 3 stations: HIGH at the fish-no-fish interface in the middle of the harvest and spray unit, MID at the bottom of the unit, and LOW downstream of the unit. All herbicides were applied by helicopter in a single tank mix. AMPA, imazapyr, SMM, and MSM were not detected (ND) in any sample at 15, 600, 500, and 1000 ng/L, respectively. A pulse of glyphosate peaking at approximately equal to 62 ng/L manifested at HIGH during the application. Glyphosate pulses peaking at 115 ng/L (MID) and 42 ng/L (HIGH) were found during the first 2 postapplication storm events 8 and 10 days after treatment (DAT), respectively: glyphosate was less than 20 ng/L (ND) at all stations during all subsequent storm events. All glyphosate pulses were short-lived (4–12 h). Glyphosate in baseflow was approximately equal to 25 ng/L at all stations 3 DAT and was still approximately equal to 25 ng/L at HIGH, but ND at the other stations, 8 DAT: subsequently, glyphosate was ND in baseflow at all stations. Aquatic organisms were subjected to multiple short-duration, low-concentration glyphosate pulses corresponding to a cumulative time-weighted average (TWA) exposure of 6634 ng/L × h. Comparisons to TWA exposures associated with a range of toxicological endpoints for sensitive aquatic organisms suggests a margin of safety exceeding 100 at the experimental site, with the only potential exception resulting from the ability of fish to detect glyphosate via olfaction. For imazapyr, SMM, and MSM the NDs were at concentrations low enough to rule out effects on all organisms other than aquatic plants, and the low concentration and (assumed) pulsed nature of any exposure should mitigate this potential. *Integr Environ Assess Manag* 2017;13:396–409. © 2016 SETAC

Keywords: Forestry Glyphosate Herbicides Pulsed exposure Time-weighted average exposure

INTRODUCTION

The use of herbicides to control competing vegetation is a crucial component of modern forestry, and reliance on herbicides has increased as historical management practices have come under scrutiny (Kelpsas et al. 2015). For example, prescribed burning for vegetation control has declined during the past 2 decades, primarily due to concerns about fire escapes and smoke management. In addition, because the use of herbicides reduces the potential for both erosion and nutrient runoff (Neary and Michael 1996), concerns over both factors have led to increased use of herbicides over mechanical site preparation (Beasley 1979; Blackburn et al. 1986; McBroom et al. 2008).

Compared with agriculture, forestry herbicide applications are infrequent (typically 2 to 3 applications during the first 5 years of a 30- to 80-y rotation), use low application rates (generally less than the maximum allowed rate), and cover a small portion of the overall forest land base in any given year (Michael and Neary 1993; Neary and Michael 1996; Michael 2004; Shepard et al. 2004). In addition, the use of herbicides in forestry is subject to strict label restrictions and state-specific best management practices (BMPs) developed to minimize offsite movement of herbicides. Despite this, the use of herbicides in forestry remains controversial, with potential impacts to terrestrial and aquatic wildlife a primary concern.

When evaluating potential effects on aquatic organisms from use of pesticides in general, the US Environmental Protection Agency (USEPA) initially uses a screening model (GENEEC2) to estimate expected environmental concentrations (EECs) (USEPA 2004; NRC 2013). The default model

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scenario is a small farm pond (2 m deep with a surface area of 2.47 acres) in a 24.7-acre farm field assuming application at the maximum allowed rate without any spray buffer. The resulting EEC reflects spray drift and runoff from a 152 mm (6″) rain event lasting 24 h, with minimal accounting of chemical-specific fate and transport (USEPA 2004; NRC 2013). These assumptions are not a good model for flowing streams in forest lands, where herbicides are generally applied at rates well below the label maximum (Shepard et al. 2004) following modern BMPs that limit spray drift by controlling drop size, mandating spray and/or riparian buffers (RBs), restricting application heights, and specifying meteorological conditions (Felsot et al. 2010). Under these circumstances, delivery of herbicides to streamwater depends on many site-specific factors, including the physicochemical properties of the herbicides, the topography and hydrology of the application site, and soil type (SERA 2011a, 2011b). Despite this, both the US Fish and Wildlife Service and the National Marine Fisheries Service (NMFS) have used EECs from the standard farm pond scenario to support findings that specific pesticides pose risks to threatened and/or endangered aquatic species (NMFS 2010).

The US Department of Agriculture (USDA) also uses modeling to obtain herbicide EECs. However, USDA treats flowing streams as a unique case and addresses concentrations resulting from spray drift and runoff plus percolation separately (SERA 2011b). In addition, the model used by USDA (GLEAMS) incorporates chemical-specific fate and transport and allows for consideration of topography (slope) and soil type. Thus, USDA estimates concentrations due to spray drift in a 2 m-wide flowing stream draining a 10-acre area from a default aerial application scenario (454 g/acre) with variable spray buffers. Using the same model, USDA also estimates concentrations due to runoff plus percolation under variable conditions (soil type, precipitation, etc.). In the case of glyphosate and depending on the exact scenario, USDA estimates peak streamwater and annual average concentrations spanning the ranges from 0 to 83 000 ng/L and 0 to 2580 ng/L, respectively (SERA 2011b). Although estimates, these ranges suggest the impact site-specific conditions can have on instream herbicide concentrations resulting from aerial applications.

The approach to developing EECs taken by USDA provides a more realistic assessment than that taken by USEPA (2004) or NMFS (2010). Even so, USDA cautions that refinement to its concentration estimates based on site-specific considerations is warranted whenever aquatic organisms are potentially at risk (SERA 2011b). Ultimately, streamwater concentrations resulting from silvicultural applications of herbicides will be highly site and application specific, and accurate application-specific assessments of ecological risk require measured application-specific concentrations.

The literature provides a limited number of field studies reporting measured herbicide concentrations in streams during or after silvicultural applications made according to modern BMPs, and results show a wide range of concentrations (Rashin and Graber 1993; Dent and Robben 2000). More importantly, these studies often show herbicides manifesting in streamwater as pulses (Michael and Boyer 1986; Rashin and Graber 1993; Dent and Robben 2000; Michael 2003; McBroom et al. 2013; Scarbrough et al. 2014). The simplest approach to assessing risk to aquatic organisms from pulsed exposures is to compare the observed maximum (peak) concentration to chemical-specific toxicity metrics developed in laboratories (Giesy et al. 2000; SERA 2004a, 2004b, 2011a, 2011b). Example metrics include EC50, LC50, no observed effect concentration (NOEC), and no observed adverse effect concentration (NOAEC). However, these metrics generally reflect exposures to nominally constant concentrations for periods ranging from 48 h to 21 d, so this kind of comparison has the potential to overstate exposure, and thus risk, associated with pulsed exposures. An alternative approach potentially providing a more realistic assessment of exposure, and thus risk, is to base comparisons on time-weighted average (TWA) exposure concentrations (Reinert et al. 2002; Landrum et al. 2012).

To assess the risks to aquatic organisms resulting from the use of herbicides as part of forestry in Oregon's Coast Range, we conducted a nominal 70-d study to characterize concentrations of glyphosate, imazapyr, sulfometuron methyl (SMM), and metsulfuron methyl (MSM) in streamwater during and after an aerial site preparation application of herbicides. Maximum (peak) measured concentrations were then compared to traditional toxicity metrics (NOECs and NOAECs) from a range of laboratory and mesocosm studies to assess the potential for effects on the site-specific aquatic community. As an alternative, TWA exposure concentrations were also calculated when results allowed and compared to TWA concentrations from the same laboratory and mesocosm studies.

MATERIALS AND METHODS

Site description and herbicide application

The study site was the Needle Branch watershed in Oregon's Coast Range (Figure 1), approximately 16 km from Toledo, Oregon. This is 1 of 3 watersheds studied as part of the historic (1959–1973) Alsea Watershed Study (Stednick 2008) and is part of the current Alsea Watershed Study Revisited (begun in 2006), which is allowing comparison of watershed responses to logging and reforestation before and after adoption of the Oregon Forest Practices Act (OFPA) and rules. The Needle Branch watershed is a small (175 acre), steep, forested, headwater basin on the Tyee Sandstone formation (Corliss and Dyrness 1965) receiving approximately 250 cm of precipitation annually, mostly as rain from October through May or June. The forest stand before the 2009 harvest was mainly Douglas fir (*Pseudotsuga menziesii*) with red alder (*Alnus rubra*) in the riparian stands.

Three gauging stations were established in the Needle Branch drainage (Figure 1). The highest elevation station (HIGH) was located in the harvest unit at the fish-no-fish interface, above which no RB was left (the OFPA does not require RBs around no fish reaches). The mid-elevation

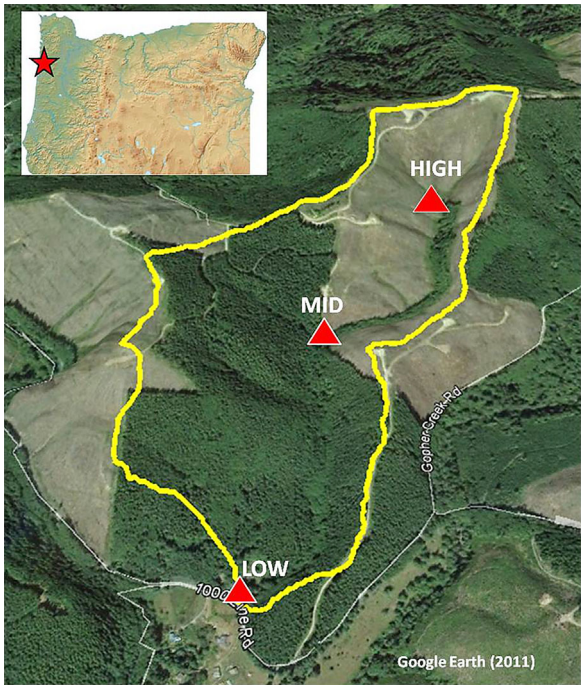

Figure 1. Herbicide monitoring stations established in the Needle Branch watershed (HIGH = bottom of no-fish stream reach; MID = bottom of harvest and spray unit; LOW = main gauge near mouth of watershed).

station (MID) was located at the bottom of the harvest unit, and an approximately equal to 15 m lateral RB on both sides of the stream was left between MID and HIGH. The lowest elevation station (LOW) was near the confluence of Needle Branch and Drift Creek, approximately 1 km downstream of the lower boundary of the harvest (spray) unit. Pressure transducers mounted in stilling wells connected to a compound weir at LOW and a trapezoidal flume at MID were used to monitor stream stage.

The upper portion of the Needle Branch drainage was harvested in August to September 2009. On August 22, 2010, the harvest unit (91 acre) was sprayed (helicopter) with a mixture of Accord® XRT II (glyphosate), Chopper® Gen II (imazapyr), and Sulfomet® Extra (SMM and MSM) corresponding to 681 g/acre glyphosate (acid equivalents or a.e.), 85 g/acre imazapyr (a.e.), 64 g/acre SMM (active ingredient or a.i.), and 17 g/acre MSM (a.i.), rates consistent with recommendations for site preparation before replanting of Douglas fir in Oregon's Coast Range (Kelpsas et al. 2015). As required by the OFPA, an 18 m (horizontal distance) spray buffer was respected on each side of the stream between MID and HIGH (fish-bearing reach). Above HIGH, herbicides were applied parallel to the stream with the spray boom on the stream side turned off (half-boom spraying), leaving a spray buffer of at least 3 m.

Sample collection and handling

Two automatic samplers (ISCO® 3700, Teledyne Technologies, Lincoln, Nebraska, USA) were installed at each of the 3 gauging stations (Figure 1). Bottles in 1 sampler contained pH 7 buffer as a means of preserving samples for determinations of imazapyr, SMM, and MSM at collection (NCASI 2007; Fischer et al. 2008). The second sampler collected unpreserved samples for determinations of glyphosate and aminomethylphosphonic acid (AMPA), a byproduct of the degradation of glyphosate.

The site preparation application was initiated at 11:38 AM and was completed at 1:18 PM. All samplers were programmed to collect a sample every hour starting at 9 AM and ending at 8:00 AM the next day (August 23). Subsequently, samplers were manually triggered whenever a storm event was predicted. All samplers were programmed to initiate collection at the same time using the same sampling frequency, which varied from 1 per h to 1 every 6 h. Manual grab samples were collected nominally once per week during baseflow conditions.

Storm event samples were retrieved as soon as possible after collection (always within 72 h) and delivered to the National Council for Air and Stream Improvement (NCASI) laboratory in Corvallis, Oregon (≈1 h drive time). On receipt, approximately equal to 800 mL of each pH preserved sample was transferred to a 1 L high density polyethylene (HDPE) bottle and frozen (no filtration). For a subset of these samples, 2 approximately equal to 400 mL splits were generated and 1 was spiked with imazapyr, SMM, and MSM before freezing. Nominally, 180 mL of the unbuffered samples was filtered (0.7 μm glass fiber filter) into 250 mL HDPE bottles and frozen. For a subset of these samples, an additional 180 mL volume was spiked with glyphosate and AMPA before filtration and freezing.

Sample analysis

On thawing, extracts for determination of glyphosate and AMPA were prepared as described by Hanke et al. (2008). Briefly, 80 mL of sample filtrate (filtered before freezing) was derivatized using 9-fluorenylmethylchloroformate (FMOC) and then subjected to postderivatization cleanup on a solid phase extraction (SPE) cartridge. The eluate from the cleanup was brought to an exact 1 mL final volume with 80:20 water: methanol, and 25 μL was analyzed by high performance liquid chromatography (HPLC) using an amino column for separation coupled with fluorescence (FLUOR) detection ($\lambda_{ex} = 264$ nm, $\lambda_{em} = 315$ nm). All quantifications were versus multipoint external calibrations prepared using purchased prederivatized glyphosate-FMOC and AMPA-FMOC (Crescent Chemicals, Islandia, NY) spanning the range from 15 to 15 000 ng/L. In addition to analysis of the sample spikes described above, every analytical batch included a calibration standard (calibration verification), method blank, blank spike (ongoing precision and recovery or OPR), and matrix spike (thawed sample spiked immediately before analysis). Additional details of this HPLC/FLUOR (henceforth LC/F) analysis as implemented by NCASI are available (NCASI 2013). A small subset of samples was also submitted to AXYS Analytical Services (Sidney, British Columbia, Canada) for confirmation of LC/F results using nominally the same sample preparation coupled with a liquid chromatography-tandem mass spectrometry (LC/MS-MS) instrumental finish.

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Imazapyr, SMM, and MSM were determined in thawed, pH 7 preserved samples using the basic approach described by multiple researchers (Wells and Michael 1987; Powely and deBernard 1998) and previously applied by NCASI (NCASI 2007; McBroom et al. 2013). Briefly, thawed samples were filtered (0.45 μm nylon membrane) and 200 mL of the filtrate was adjusted to pH less than or equal to 2.5 and pulled through a conditioned reverse-phase SPE cartridge. After washing and drying, it was eluted through a strong anion exchange SPE cartridge using 50 mL methanol. This volume was reduced to exactly 1 mL and 25 μL was analyzed by HPLC (phenyl-hexyl column) with ultraviolet detection (235 nm). All quantifications were versus multipoint external calibrations prepared using pure standards (Chem Service, West Chester, Pennsylvania). These calibrations spanned the range of 600 to 50 000 ng/L.

RESULTS

Sample collection

Figure 2 shows stage data (water height at the flume) for LOW covering the period over which most samples were collected. The figure also shows when storm event and baseflow samples were collected and that sample collection effectively captured all storm events out to 70 days after treatment (DAT).

Quality assurance

Detection limits, background interference, and data censoring. Method detection limits (MDLs) were determined in an unspiked pretreatment baseflow sample (blank control sample) collected at LOW. The resulting MDLs were 4 ng/L for AMPA, 18 ng/L for glyphosate (a.e.), 200 ng/L for imazapyr (a.e.), 500 ng/L for SMM (a.i.), and 1000 ng/L for MSM (a.i.). In all cases, the experimental MDLs reflected the presence of chromatographic interferences equivalent, on average, to 2.4 ng/L AMPA, 13 ng/L glyphosate, 95 ng/L imazapyr, 231 ng/L SMM, and 382 ng/L MSM in the blank control sample.

In all cases, the retention times of the interfering peaks were shifted slightly relative to the respective herbicide, meaning that these peaks were not due to presence of the herbicides in the blank control sample. More importantly, all measured concentrations in postapplication field samples for all herbicides except glyphosate were at levels nominally equivalent (i.e., within a factor of 2) to the pre-application background, and were in all cases below the lower calibration levels (LCL). In addition, multiple lines of evidence showed the analyte-specific interferences varying on a sample-specific basis (NCASI 2013) (Table S1). Overall, these factors led to the decision to censor imazapyr and AMPA results at the corresponding LCLs (600 and 15 ng/L, respectively), SMM and MSM results at the corresponding MDLs (500 and 1000 ng/L, respectively), and glyphosate results at the nominal reporting limit of the LC/MS-MS analysis (20 ng/L). Although these censoring levels are somewhat subjective, they were considered a reasonable compromise between reporting false-positives versus false-negatives.

Storage stability, spike recovery, and analytical bias. Table 1 summarizes herbicide recoveries from unfiltered samples

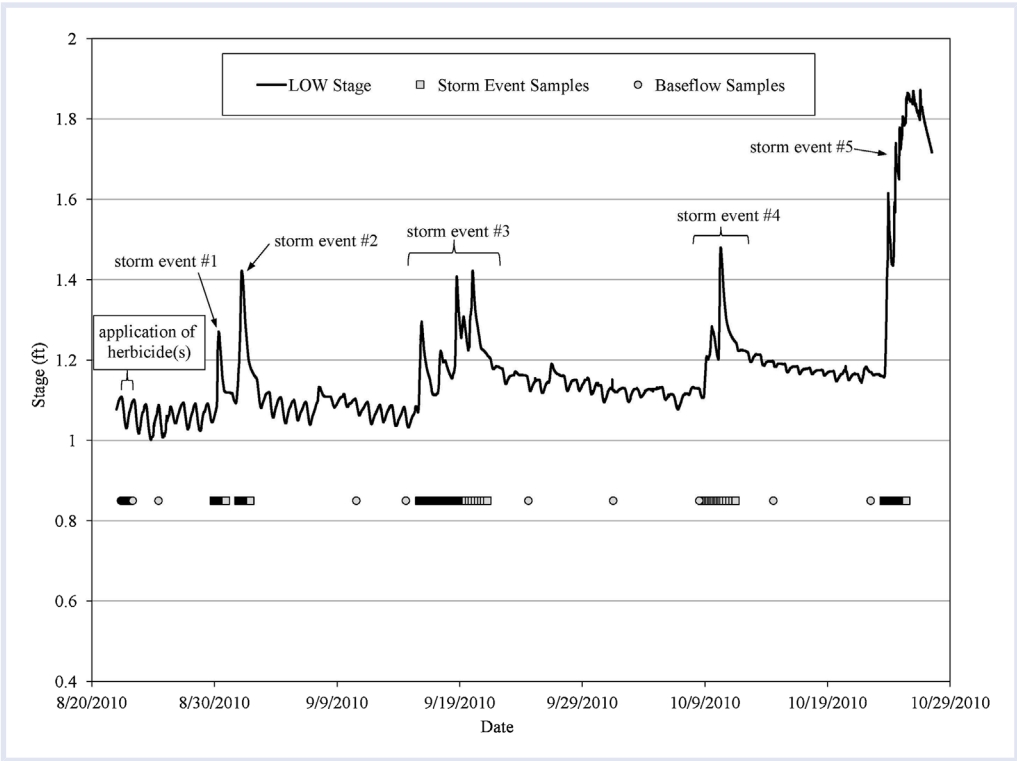

Figure 2. Stage level at LOW from 8/22/2010 through 10/27/2010 with all samples identified.

Table 1. Recovery of herbicide spikes added to samples immediately before freezing

	Spike level (ng/L)	Percent recovery		
		Mean	SD	*n*
Imazapyr[a]	4800–11 900	94	2.7	8
SMM[a]	4800–11 900	73	3.4	8
MSM[a]	4800–11 900	92	3.8	8
Glyphosate[b]	2000–10 000	97	2.8	9
Glyphosate[b]	500–900	94	5.0	6
AMPA[b]	2000–10 000	80	5.9	9
AMPA[b]	500–900	81	5.5	6

AMPA = aminomethylphosphonic acid; MSM = metsulfuron methyl; SD = standard deviation; SMM = sulfometuron methyl.
[a]Whole samples spiked before freezing (filtration carried out on thawed samples). All samples thawed and analyzed within 770 days of freezing.
[b]Samples spiked before filtration and freezing. All samples thawed and analyzed within 300 days of freezing.

spiked before freezing. For imazapyr, SMM, and MSM, these recoveries reflect losses incurred during storage, the freeze thaw cycle, filtration of thawed samples, sample preparation, and sample analysis. For these herbicides, recovery was unaffected by storage to 770 days in a freezer (NCASI 2013), and results from Fischer et al. (2008) support little to no loss of imazapyr, SMM, or MSM during the time between sample collection and freezing (≈72 h maximum). Table 1 results are therefore considered good measures of overall recovery at concentrations greater than approximately equal to 5000 ng/L. However, all samples were less than 1000 ng/L, and overall recovery at these lower concentrations can only be estimated by combining recoveries from low-level (laboratory) matrix spikes (not presented) with Table 1 results. Thus, considering concentrations less than 1000 ng/L only, overall recovery was estimated at approximately equal to 78%, approximately equal to 73%, and approximately equal to 68% for imazapyr, SMM, and MSM, respectively.

Glyphosate and AMPA spikes were made to samples before filtration and freezing, and Table 1 shows nominally 80% recovery of AMPA and 95% recovery of glyphosate regardless of spike level. Recovery of both analytes was unaffected by storage out to 300 days in a freezer, and a separate study (not presented; NCASI 2013) showed no loss of a 500 ng/L AMPA spike over 7 days at 22 °C (in the dark) in Needle Branch water holding 36 mg/L suspended sediment. Corresponding results for glyphosate suggested 5% loss of a 500 ng/L spike over 7 days (NCASI 2013). Based on these results, overall recovery of dissolved glyphosate is estimated to be approximately equal to 90%. The corresponding estimate for AMPA is approximately equal to 80%.

As discussed, bias is approximated as spike recovery and results indicated sample concentrations were biased low by anywhere from 10% to 40% depending on the herbicide. However, this does not account for the impact of background interference, which can add high bias to concentrations measured in unspiked samples using either HPLC analysis. For glyphosate, comparing results from the LC/F and LC/MS-MS analyses (Supplemental Data Table S1) shows bias in the LC/F results ranging from approximately equal to 7 to 42 ng/L.

Overall, LC/F results for glyphosate were subject to high bias due to variable background interference and low bias due to losses over sample processing and storage. Thus, the absolute bias in the LC/F result for any given sample is unknown. Ultimately, the weight of evidence suggests that most glyphosate concentrations from LC/F analyses were high biased, and for this reason none of the glyphosate results were recovery corrected. Regardless, when available, LC/MS-MS results were taken as the best measures of glyphosate, and these concentrations are considered to be low biased by no more than 10% (and were not recovery corrected).

Measured herbicide concentrations

Streamwater concentrations during herbicide application. Results for glyphosate showed a clear pulse at HIGH (Figure 3) peaking at 62 ng/L in the sample collected at 12:00 AM and returning to pre-application background (≈20 ng/L) by 8:00 PM. Although it took approximately 9 h for the glyphosate signal at HIGH to dissipate, the pulse width-at-half-height was less than 4 h (Figure 3). Glyphosate was not detected (<20 ng/L) at LOW during the nominal 20-h monitoring period following the application (Figure 3), and no samples were collected at MID due to autosampler malfunction. AMPA was not detected (ND) in any samples (<15 ng/L).

The autosampler collecting buffered samples at HIGH malfunctioned during this sampling episode, whereas all samples collected at MID were ND for imazapyr (<600 ng/L), SMM (<500 ng/L), and MSM (<1000 ng/L). Because of the NDs at MID, samples collected at LOW were not analyzed for imazapyr, SMM, or MSM.

Streamwater concentrations during postapplication storm events. A distinct pulse of glyphosate was observed at MID during the first postapplication storm event 8 DAT (Figure 4). Results from the LC/F analysis show this pulse maximizing at 149 ng/L, whereas the LC/MS-MS analysis returned 115 ng/L. LC/F results (Figure 4) show this pulse persisting for approximately equal to 10 h, with a width-at-half-height of approximately equal to 4 h.

LC/F results also suggest a glyphosate pulse at LOW maximizing at 58 ng/L during this first storm event (Figure 4). However, the LC/MS-MS confirmation performed on the sample collected 2 h earlier and showing the second highest concentration at LOW during this storm (51 ng/L from LC/F analysis) returned ND at 19 ng/L (Figure 4), suggesting that this pulse was due in large part to the background interferent known to be present in samples. Based on this, it was concluded that glyphosate was less than 20 ng/L in all samples collected at LOW during the first storm event.

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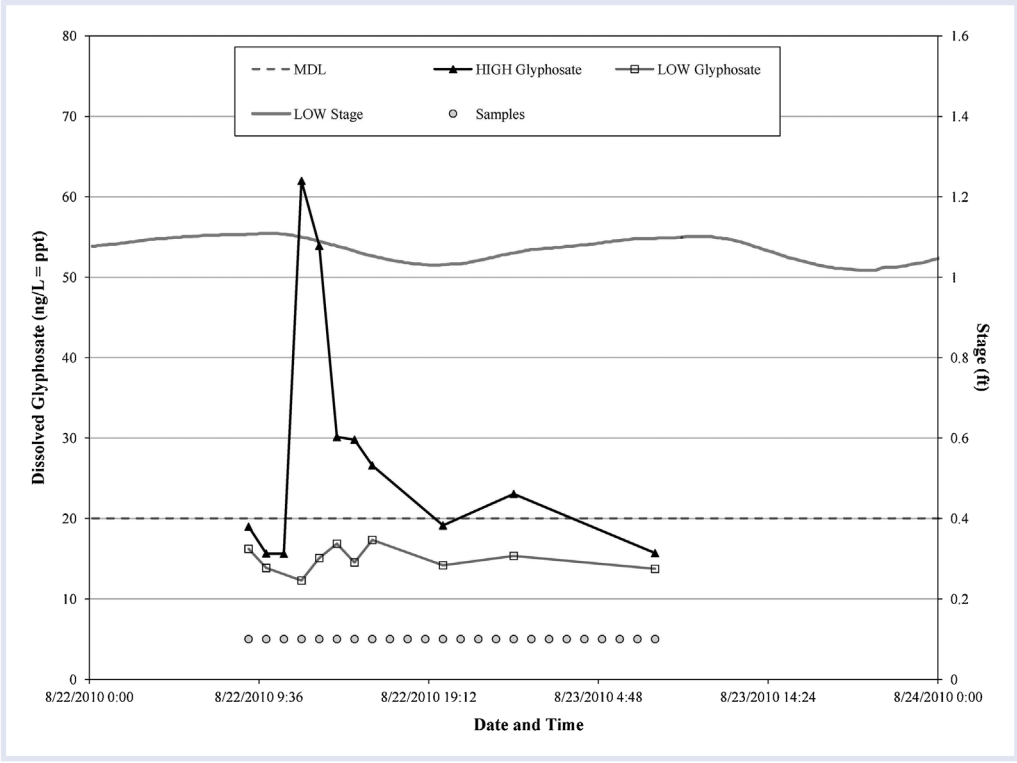

Figure 3. Dissolved glyphosate in streamwater (baseflow) during and immediately following application of herbicides (all concentrations plotted regardless of detection limit).

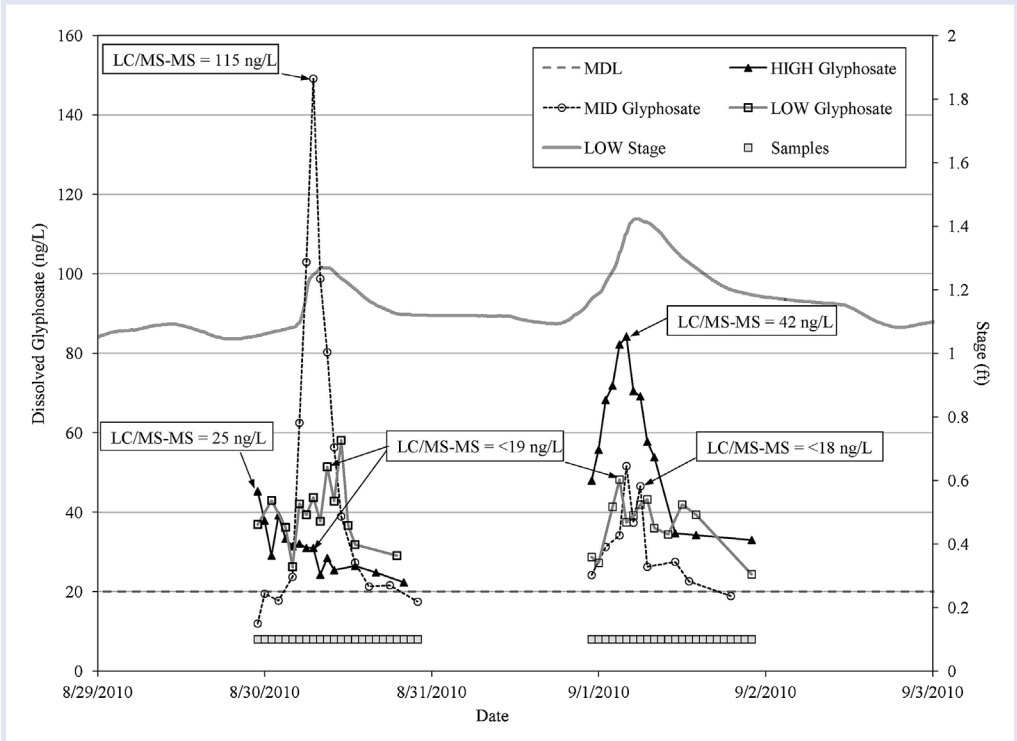

Figure 4. Dissolved glyphosate in streamwater during first 2 postapplication storm events with results from LC/MS-MS confirmations (all concentrations plotted regardless of detection limit).

Results from HIGH show the presence of glyphosate in the first sample during the first storm event (8 DAT), which was collected before the pulse observed at MID manifested (Figure 4). This sample gave 45 ng/L by the LC/F analysis, whereas the LC/MS-MS analysis returned 25 ng/L. Results from the LC/F analysis (Figure 4) show concentrations at HIGH dropping in all subsequent samples, and the LC/MS-MS analysis of the ninth sample collected at HIGH during this storm showed glyphosate was less than 19 ng/L versus 31 ng/L from the LC/F analysis (Figure 4). All this is consistent with glyphosate concentrations decreasing at HIGH during this storm from a maximum of approximately equal to 25 ng/L in baseflow immediately before onset to less than 20 ng/L over the first 9 h of the event.

During the second storm event 10 DAT, a distinct pulse of glyphosate was observed at HIGH (Figure 4). The highest concentration found at HIGH by LC/F during this storm was 84 ng/L. The corresponding LC/MS-MS result was 42 ng/L (Figure 4). Overall, results at HIGH show a nominal 11- to 12-h pulse maximizing at approximately equal to 40 ng/L with a width-at-half-height of approximately 8 to 9 h. Although LC/F results also suggest lower concentration glyphosate pulses at MID and LOW during this storm, LC/MS-MS results (Figure 4) are consistent with glyphosate being less than 20 ng/L in all these samples.

Figure 5 shows glyphosate in all 3 sampling stations during the third postapplication storm event, which started 24 DAT and continued through 30 DAT. These results show no evidence of any sustained glyphosate pulse as observed during the first 2 storm events (Figure 4). In addition, the 2 samples submitted for confirmation by LC/MS-MS returned less than 20 ng/L. Considering that one of these samples had the highest concentration found by the LC/F analysis (62 ng/L; Figure 5), these results support concluding that glyphosate was less than 20 ng/L in all samples collected at all 3 stations during the third storm event.

AMPA, imazapyr, SMM, and MSM were not detected in any sample collected during this study, and glyphosate was effectively ND in all samples from the third storm event. These factors led to the decision to not analyze samples from later storm events.

Glyphosate in baseflow. The first set of baseflow grab samples was collected on 8/25/2010 (3 DAT). LC/F analysis of these samples returned glyphosate concentrations of 30, 21, and 33 ng/L at HIGH, MID, and LOW, respectively: results from LC/MS-MS confirmation analyses on the HIGH and LOW samples were 23 and 26 ng/L, respectively (Table S1). The next set of baseflow samples was collected 19 DAT after 2 storm events, and glyphosate by LC/F was less than 20 ng/L at all 3 sampling stations. On September 14, 2010 (23 DAT) baseflow at LOW measured 34 ng/L glyphosate by LC/F but, consistent with LC/F results from HIGH and MID, the LC/MS-MS analysis returned less than 19 ng/L. LC/F results from the next 2 baseflow samplings (33 and 40 DAT) were less than 20 ng/L at all 3 stations.

Overall, results show that glyphosate was present at approximately equal to 25 ng/L in baseflow at all 3 stations

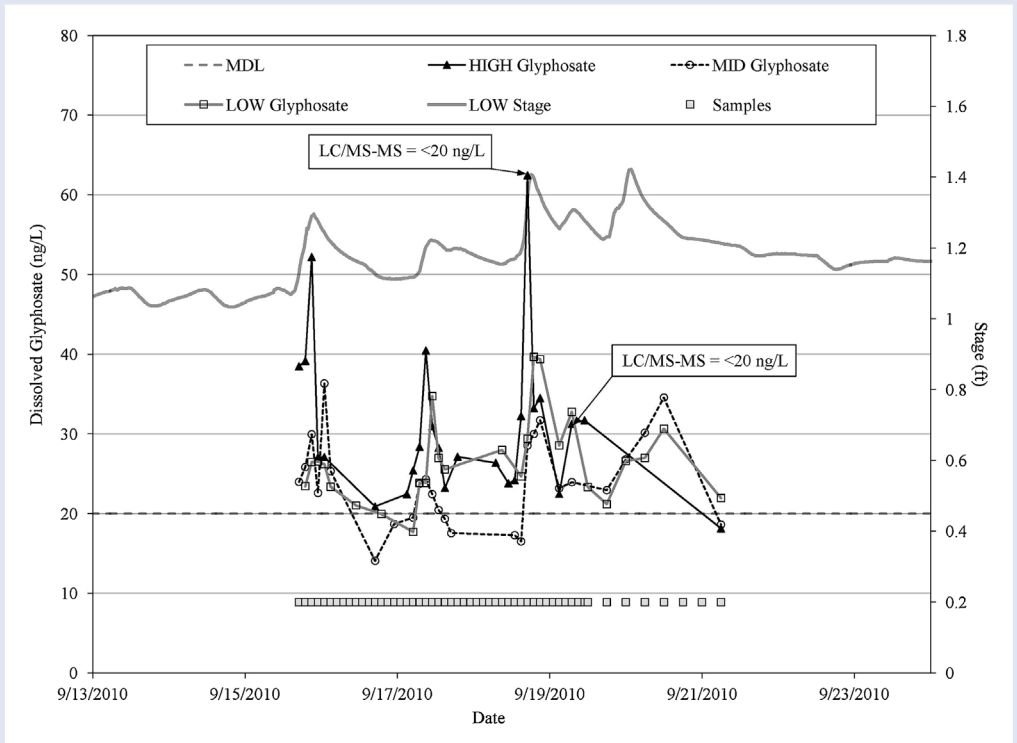

Figure 5. Dissolved glyphosate in streamwater during third postapplication storm event with results from LC/MS-MS confirmations (all concentrations plotted regardless of detection limit).

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3 DAT and was still present at approximately equal to 25 ng/L at HIGH but less than 20 ng/L at MID and LOW immediately before the first storm event 8 DAT (Figure 4). Subsequently, glyphosate was less than 20 ng/L in baseflow at all 3 stations.

DISCUSSION

In-stream concentrations

In this study, imazapyr, SMM, and MSM were not detected in any sample, including those collected during the aerial application. Using the maximum glyphosate concentration found during application (62 ng/L at HIGH) and an assumption that spray drift for the other herbicides was proportional to application rates suggests the maximum concentrations of imazapyr, SMM, and MSM that might have manifested at HIGH during the application would be less than 10 ng/L in all cases. This indicates that measurement of these herbicides at Needle Branch would have required an analytical method capable of quantifications to less than 10 ng/L.

The limited amount of relevant field work in the literature means that there are limited concentration data useful for comparison to the Needle Branch results. In the case of glyphosate, many field studies purposely involved applications directly to streams (Newton et al. 1984; Kreutzweiser et al. 1989) or ponds (Goldsborough and Beck 1989; Goldsborough and Brown 1993) and so are not comparable to Needle Branch results. In addition, it is our contention that streamwater concentrations from aerial applications are highly application-specific, meaning that comparisons based on concentrations absent some accounting for site-specific factors (topography, geology, etc.) have limited utility: comparison of the Needle Branch results for all 4 herbicides to results from relevant field studies and USDA estimates (Tables S2 and S3) are generally supportive of this assessment.

Ecological significance

Imazapyr, sulfometuron methyl, and metsulfuron methyl. Imazapyr, SMM, and MSM were less than 600 ng/L (a.e.), less than 500 ng/L (a.i.), and less than 1000 ng/L (a.i.), respectively, in all samples collected during this study. Thus, the worst-case exposure scenarios for Needle Branch would be chronic exposure at these concentrations, which are well below levels shown to have adverse effects on fish, amphibians, and aquatic invertebrates based on traditional toxicity testing using nominally continuous (chronic) exposure regimes (SERA 2004a, 2004b, 2011a). For imazapyr, concentrations less than 600 ng/L are also below levels shown to impact macroinvertebrate community structure (Fowlkes et al. 2003) or aquatic plants in general (SERA 2011a). Thus, consistent with USEPA's conclusion that the use of imazapyr in forestry will "most likely result in 'no effect'" on endangered anadromous salmonids (Turner 2003), our results suggest no direct or indirect impacts on the Needle Branch aquatic community attributable to imazapyr.

For SMM and MSM, the Needle Branch NDs are high enough that effects on aquatic plants and/or algae cannot be ruled out, meaning that indirect effects on higher level organisms or overall community structure also cannot be ruled out. However, at Needle Branch the glyphosate results indicate that the aquatic community would have been subjected to a series of short-lived (<24 h), low-concentration pulsed exposures to SMM and MSM separated by variable recovery periods spanning a few days to weeks. This type of exposure regimen has been shown to reduce the effects of MSM on aquatic plants relative to continuous exposures at equivalent TWA concentrations (Cedergreen et al. 2005), although contrary results have also been presented (Boxall et al. 2013). Regardless, the potential for direct effects on aquatic plants, and thus indirect effects on higher level organisms or the aquatic community as a whole, depends on the exact exposure regimen, including the length of any recovery period and/or periods. Thus, actual measured concentrations would be required to conclude that the aquatic community at Needle Branch was impacted as a result of application of SMM and MSM.

Glyphosate. The maximum confirmed concentration of glyphosate at Needle Branch was 115 ng/L (a.e.) in a storm event sample at MID, and this concentration persisted for only approximately equal to 3 to 4 h. On the other hand, dissolved glyphosate in baseflow at HIGH was nominally 25 ng/L for up to 8 days. Thus, worst-case exposure scenarios for Needle Branch might be an acute (≤96 h) exposure at approximately equal to 100 ng/L or a chronic (>96 h) exposure at approximately equal to 25 ng/L. However, our results show that exposure at Needle Branch consisted of a series of short-term (acute or pulsed) exposures on top of a longer-term (chronic) background. This kind of exposure regime is not generally modeled by laboratory bioassays from which the various metrics (e.g., NOECs) used to characterize toxicity are obtained, so these metrics are not directly comparable to the glyphosate exposure regime at Needle Branch.

One approach to assessing risk under these conditions would be to compare TWA exposure concentrations associated with the various NOECs and NOAECs to the TWA exposure concentration documented at Needle Branch. Although exposure-response reciprocity between the 2 (TWA) exposure scenarios will be endpoint- and organism-specific and will vary depending on multiple factors including the exposure-specific concentration dynamics (e.g., pulse-specific half-life, inter-pulse recovery periods) and scenario-specific toxicokinetics (Reinert et al. 2002; Landrum et al. 2012), comparisons based on TWA exposure would provide some first approximation of margin of safety for glyphosate as "margin of exposure." Thus, Table 2 gives calculated TWA exposures to technical glyphosate (i.e., glyphosate absent any of the adjuvants found in commercial formulations) associated with some of the lowest reported NOECs and NOAECs and compares these values to the TWA exposure at Needle Branch calculated by multiplying the highest concentration observed during a storm event by the associated (nominal) pulse-specific width-at-half-height and summing across all events.

Table 2. Comparison of TWA exposures to technical glyphosate associated with multiple scenarios [a]

Scenario and species	Exposure		TWA exposure		Experimental endpoint	Reference
	Conc. (ng/L) [b]	Duration (h)	Absolute(ng/L × h)	Relative		
Needle Branch:						
Application pulse	62	4	248	0.04		This study
Storm pulse #1 (8 DAT)	115	10	1150	0.17		
Storm pulse #2 (10 DAT)	42	12	504	0.08		
Baseflow (to 8 DAT)	25	192	4800	0.72		
Cumulative exposure			6702	1		
NOECs and NOAECs for technical glyphosate based on "traditional" endpoints						
Myriophyllum sibiricum (watermilfoil)	80 000	336	2.69E+07	4011	Root length	Perkins 1997
Skeletonema costatum (diatom/algae)	280 000	168	4.70E+07	7019	Survival, growth	Giesy et al. 2000
Scenedesmus quadricauda (algae)	770 000	96	7.39E+07	11 030	Survival, growth	Saenz et al. 1997
Scenedesmus acutus (algae)	2 000 000	96	1.92E+08	28 648	Survival, growth	Saenz et al. 1997
Navicula pelliculosa (diatom/algae)	1 700 000	120	2.04E+08	30 439	Survival, growth	SERA 2011b
Lemna gibba (duckweed sp.)	1 300 000	336	4.37E+08	65 175	Survival, growth	SERA 2011b
Selenastrum capricornutum (diatom/algae)	9 600 000	120	1.15E+09	171 889	Survival, growth	SERA 2011b
Anabaena flos-aquae (cyanobacteria)	11 500 000	120	1.38E+09	205 909	Survival, growth	SERA 2011b
Rana clamitans (green frog)	1 790 000	1008	1.80E+09	269 221	Survival	Howe et al. 2004
Crinia insignifera (adult sign-bearing froglet)	45 000 000	96	4.32E+09	644 584	Survival	Giesy et al. 2000
Daphnia magna (invertebrate)	95 600 000	48	4.59E+09	684 691	survival	SERA 2011b
Daphnia magna (invertebrate)	50 000 000	504	2.52E+10	3 760 072	Survival, growth, reproduction	ABC Inc. 1982
Hyalella azteca (invertebrate)	265 000 000	240	6.36E+10	9 489 705	Survival	Giesy et al. 2000
Chrionomus tentans (invertebrate)	265 000 000	240	6.36E+10	9 489 705	Survival	Giesy et al. 2000
Effects concentrations from studies examining community level effects [d]						
"Microbial community" (microcosm study)	10 000	336	1.44E+6 [e]	215	"Community composition"	Pesce et al. 2009
NOECs and NOAECs for technical glyphosate based on biochemical or "nontraditional" endpoints						
Oncorhynchus kisutch (coho salmon)	100 000	0.5	50,000	7	Olfaction	Tierney et al. 2006
Oncorhynchus mykiss (rainbow trout)	10 000 000	1	1.00E+07	1492	Avoidance	Folmar 1976
Oncorhynchus mykiss (rainbow trout)	110 000	168	1.85E+07	2757	Plasma vitellogenin	Xie et al. 2005

Conc. = concentration; TWA = time-weighted average.
[a]Results reflecting exposure to various glyphosate formulations (e.g., Roundup® or Vision®) not included.
[b]Concentrations as ng/L acid equivalent (a.e.).
[c]Relative to cumulative exposure at Needle Branch.
[d]Exposure conditions associated with observed effects.
[e]TWA exposure calculated assuming concentration remained stable at 10 000 ng/L for the first 6 d of the 14-d exposure period (per measured concentrations reported by Pesce et al. [2009]).

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Considering "traditional" endpoints only, the lowest reported NOECs and NOAECs for technical glyphosate are all associated with TWA exposures orders of magnitude higher than observed at Needle Branch (Table 2), suggesting that the use of glyphosate had no impact on site-specific aquatic organisms. However, the results listed in Table 2 reflect exposure to technical glyphosate, so do not account for the toxicity of the adjuvants (e.g., surfactants) present in commercial glyphosate formulations (e.g., Accord; XRT II, Roundup®, Vision®) or site-specific tank mixes. Because many of these adjuvants have their own toxicity profiles (Edington et al. 2004) any margin of safety based on glyphosate alone may be biased high. Thus, Table 3 gives calculated TWA exposures associated with the lowest reported NOECs and NOAECs for Roundup and/or Vision formulations.

Again, considering traditional endpoints only, the lowest NOEC and NOAECs for Roundup and Vision are (again) associated with TWA exposures orders of magnitude higher than observed at Needle Branch (Table 3). In this case, direct comparison of the TWA exposures assumes that all adjuvants are present in all Needle Branch samples at the same proportion (relative to glyphosate a.e.) found in Roundup and Vision. Thus, the relative exposures listed in Table 3 suggest no impact on aquatic organisms at Needle Branch even allowing for the presence of adjuvants.

As discussed, assessment of potential impacts on the aquatic community at Needle Branch is based on direct effects acting on single species, and the comparisons summarized in Tables 2 and 3 suggest there was a large margin of safety at Needle Branch even allowing for the potential impact of adjuvants. This, in turn, suggests limited potential for long-term indirect or community level effects. TWA exposures associated with the few studies examining the impact of glyphosate on microbial communities are also listed in Tables 2 and 3, and all exceed the TWA exposures documented at Needle Branch by a minimum factor of 200, suggesting that adverse effects on microbial communities did not occur at Needle Branch.

Another factor to consider is the potential for effects associated with nontraditional or biochemical endpoints, and Tables 2 and 3 list TWA exposures associated with some of these endpoints. The apparent margin of safety at Needle Branch is greater than 100 for most endpoints, and greater than 10 for all endpoints except olfaction by salmon and/or rainbow trout.

Regarding olfaction by salmonids, experimental results (Tierney et al. 2006, 2007) indicate that these fish are orders of magnitude more sensitive to unidentified constituents in commercial formulations (e.g., Roundup) than to glyphosate itself. Thus, identification of these chemicals followed by measurements in streamwater will be necessary to fully evaluate the potential for olfactory-mediated effects resulting from real world applications. Regardless, at Needle Branch specifically, olfactory-mediated effects would have impacted only those fish present above MID from late August through late September, 2010. Because adult coho are not expected in Needle Branch until early October-November (D. Bateman, Oregon State University, personal communication), 2010 prespawn adult coho were subjected to much lower concentrations (<20 ng/L) than documented in September, whereas juvenile coho from the 2010 spawn were exposed to even lower concentrations.

AMPA and glyphosate on suspended sediment. Glyphosate on solids (suspended sediment [SS]) can also affect aquatic organisms, and the study plan called for extraction and analysis of SS for AMPA and glyphosate (NCASI 2013). However, inspection suggested very low SS concentrations in all samples (most samples had "clarity" equivalent to baseflow) so only a small number of whole (unfiltered) samples, those judged as having the highest SS in a sampling episode, were frozen for analysis. AMPA and glyphosate were not detected at levels exceeding blank levels in any sample SS (8 ng/L AMPA and 13 ng/L glyphosate equivalents: unknown sample mass). This outcome indicates little risk to the Needle Branch aquatic community posed by AMPA or glyphosate on SS, given the generally low SS concentrations during our experiment.

Cumulative risk. The large margins separating the TWA concentration of glyphosate at Needle Branch and the TWA concentrations associated with the lowest reported NOECs and NOAECs for glyphosate (Tables 2 and 3) combined with the very low concentrations of the other herbicides suggests the potential for cumulative effects at Needle Branch was negligible. This conclusion is supported by work reported by Tatum et al. (2012), which showed the herbicide mixtures used in forestry generally manifesting additive or antagonistic effects, not synergistic effects, on the survival of *Ceriodaphnia dubia* and fathead minnow. Ultimately, however, we have no in-stream concentration data for most components (herbicides and adjuvants) of the site-specific tank mix used at Needle Branch, so our results do not fully address the question of cumulative risk.

CONCLUSIONS

In this study AMPA, imazapyr, SMM, and MSM were not detected in any sample at concentrations exceeding 15 ng/L, 600 ng/L, 500 ng/L, and 1000 ng/L, respectively. However, a clear pulse of glyphosate was observed at the highest elevation station (HIGH, at the fish-no-fish interface in the middle of the spray unit above which there was no RB) during the application. This pulse maximized at approximately equal to 62 ng/L and persisted for approximately 3 to 4 h, with a lower concentration "tail" persisting for perhaps an additional 9 h (Figure 3). Glyphosate was not detected (<20 ng/L) at the lowest elevation station (LOW, ~1 km below the harvest/spray unit) during the application. Glyphosate was present at approximately equal to 25 ng/L in baseflow at all 3 stations 3 DAT and was still approximately equal to 25 ng/L at HIGH 8 DAT, but less than 20 ng/L at the 2 lower elevation stations. All subsequent baseflow samples were less than 20 ng/L glyphosate. In addition, discrete pulses of glyphosate were observed at the 2 sampling stations located within

Table 3. Comparison of time-weighted average exposures to Roundup® or Vision® formulations associated with multiple scenarios[a]

Scenario and Species	Exposure		TWA exposure		Experimental endpoint	Reference
	Conc. (ng/L)[b]	Duration(h)	Absolute(ng/L × h)	Relative[c]		
Needle Branch						
Application pulse	62	4	248	0.04		This study
Storm pulse #1 (8 DAT)	115	10	1150	0.17		
Storm pulse #2 (10 DAT)	42	12	504	0.08		
Baseflow (to 8 DAT)	25	192	4800	0.72		
Cumulative exposure			6702	1		
NOECs and NOAECs for Roundup or Vision based on "traditional" endpoints						
Selanastrum capricornutum (algae)	226 300	72	1.63E+07	2431	Growth (biomass)	LiSEC 1989
Litoria moorei (motorbike frog tadpole)	496 000	48	2.38E+07	3552	Survival	Mann and Bidwell 1999
Oncorhynchus mykiss (fingerling rainbow trout)	260 000	96	2.50E+07	3724	Survival	Folmar et al. 1979
Daphnia magna (invertebrate)	589 000	48	2.83E+07	4218	Survival, growth	Folmar et al. 1979
Chlorella sorokiniana (algae)	620 000	48	2.98E+07	4440	Survival, growth	Christy et al. 1981
Oreochromis niloticus (tilapia)	310 000	96	2.98E+07	4440	Survival	SERA 2011b
Lepomis macrochirus (bluegill sunfish)	700 000	96	6.72E+07	10 027	Survival	Forbis et al. 1982
Myriophyllum sibiricum (watermilfoil)	242 000	336	8.13E+07	12 132	Root length	Perkins 1997
Daphnia magna (invertebrate)	992 000	504	5.00E+08	74 600	Survival, growth, reproduction	Giesy et al. 2000
Gammarus pseudolimnaeus (invertebrate)	14 000 000	48	6.72E+08	100 269	Survival	ABC Inc. 1982
Lemna minor (duckweed sp.)	16 910 000	48	8.12E+08	121 110	?	Lockhart et al. 1989
Potamogeton pectinatus (pondweed)	7 440 000	336	2.50E+09	372 999	Growth	Hartman and Martin 1985
Effects concentrations from studies examining community level effects[d]						
"Microbial community" (mesocosm study)	210 000	2160	6.51E+6[e]	971	"Community composition"	Baker et al. 2014
"Microbial community" (mesocosm study)	6 000 000	192	4.57E+8[f]	68 189	"Community composition"	Vera et al. 2010
"Microbial community" (mesocosm study)	4 500 000	264	4.70E+8[f]	70 128	"Community composition"	Perez et al. 2007
NOECs and NOAECs for Roundup or Vision based on biochemical or "nontraditional" endpoints						
Oncorhynchus mykiss (rainbow trout)	7400	0.0333	246	0.04	Neurophysiological olfaction	Tierney et al. 2007
Oncorhynchus mykiss (rainbow trout)	7400	0.5	3700	0.6	"Behavioral olfaction"	Tierney et al. 2007
Oncorhynchus mykiss (rainbow trout)	742 000	0.167	1.24E+05	18	Avoidance	Tierney et al. 2007
Ephemeralla walkeri (mayfly)	1 000 000	1	1.00E+06	149	Avoidance	Folmar 1978
Oncorhynchus mykiss (rainbow trout)	6 750 000	96	6.48E+08	96 688	"Erratic swimming and rapid respiration"	Morgan et al. 1991
Oncorhynchus kisutch (coho salmon)	2 880 000	240	6.91E+08	103 133	"Several sublethal parameters"	Mitchell et al. 1987
Oncorhynchus mykiss (rainbow trout)	8 000 000	1440	1.15E+10	1 718 890	"Aggressive behavior"	Morgan and Kiceniuk 1992

Conc. = concentration; TWA = time-weighted average.
[a]Results reflecting exposure to Roundup or Vision formulations only.
[b]Concentrations as ng/L acid equivalent (a.e.). Roundup and Vision concentrations converted to glyphosate a.e. assuming 1 mg of formulation is equivalent to 0.31 mg glyphosate acid (Giesy et al. 2000).
[c]Relative to cumulative exposure at Needle Branch.
[d]Exposure conditions associated with observed effects.
[e]Two applications at 210 000 ng/L on day 0 and ≈day 21 of a nominal 3-month experimental period; concentrations following each application calculated at intervals equivalent to reported half-lives, so TWA exposure is less than the product of initial exposure concentration and time. No effects observed using 2 separate applications at 2 880 000 ng/L (TWA exposure 8.91E+7 ppt-h).
[f]Concentrations calculated at intervals equivalent to reported half-life, so TWA exposure is less than the product of initial exposure concentration and time.

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or at the boundary of the harvest (spray) unit during the first 2 postapplication storm events. During the first event (8 DAT), a nominal 10-h pulse maximizing at 115 ng/L was found at the middle elevation site (MID, at the lower boundary of the harvest or spray unit), whereas a nominal 12-h pulse maximizing at 42 ng/L was observed at HIGH during the second event (10 DAT). Glyphosate was less than 20 ng/L in all storm event samples collected at LOW.

The observation that glyphosate manifested as discrete pulses associated with the first few postapplication storm events is generally consistent with observations from other field studies reflecting aerial applications according to modern forestry practices (Michael 2004; McBroom et al. 2013; Scarbrough et al. 2014). Thus, it is to be anticipated that the other herbicides monitored at Needle Branch also manifested as fairly narrow pulses (<24 h), in this case at concentrations much less than 1000 ng/L. Based on these results, it appears that analytical tools with detection limits in the low ng/L range (e.g., 1–10 ng/L) will be required to fully characterize delivery of imazapyr, SMS, and MSM to streamwater following aerial applications according to modern silvicultural BMPs. In any case, the concentrations documented at Needle Branch are some of the lowest from any field study.

Given that the concentrations of imazapyr, SMM, and MSM in Needle Branch following application of herbicides are unknown, it is difficult to make any statements regarding potential effects on the aquatic community. However, in the case of imazapyr the analytical results are sufficient to suggest that there was no direct or indirect impact, as even effects on aquatic plants are expected to occur only at concentrations greater than 600 ng/L. Likewise, the analytical results are sufficient to document SMM and MSM concentrations well below the levels shown to have adverse effects on fish, amphibians, or invertebrates but leave the potential for direct effects on aquatic plants and algae, and thus indirect effects on higher level organisms. This potential would be mitigated assuming short-term episodic exposures to SMM and MSM as documented for glyphosate.

Although the TWA glyphosate exposure at Needle Branch was of the same magnitude associated with olfaction in salmon and trout, coho salmon were not present in Needle Branch during the study period. Thus, coho salmon specifically were not subjected to any quantifiable insult resulting from this specific application of glyphosate. Beyond this, the TWA glyphosate exposures documented at Needle Branch were well below levels shown to have effects on fish, amphibians, invertebrates, aquatic plants, or the aquatic community as a whole. This outcome supports an overall absence of effects due to exposure to glyphosate, the issue of exposure–response reciprocity when comparing TWA exposures notwithstanding.

Regarding the issue of cumulative risk, the margins of safety documented at Needle Branch combined with an assumption of additivity suggests negligible cumulative risk to aquatic organisms at Needle Branch. However, our results do not fully address cumulative risk, and this may be an issue warranting additional study supported by the ability to measure all components (herbicides and adjuvants) of a site-specific tank mix in streamwater.

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SUPPLEMENTAL DATA

Table S1. Comparison of dissolved AMPA and glyphosate concentrations measured by LC/F and LC/MS-MS in select samples.

Table S2. Streamwater concentrations of imazapyr, sulfometuron methyl, and metsulfuron methyl following nominally routine herbicide applications as part of forestry.

Table S3. Streamwater concentrations of glyphosate following nominally routine herbicide applications as part of forestry.

Supplemental Word File. Detailed descriptions of Tables S1-3.

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