



Effectiveness of forestry best management practices (BMPs) for reducing the risk of forest herbicide use to aquatic organisms in streams



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1. Introduction

The use of herbicides to control competing vegetation during stand establishment is a key component of intensive silviculture (McBroom et al., 2013). Herbicides reduce competition at stand establishment and thus help promote successful regeneration and compliance with legal reforestation standards (Wagner et al., 2004). Herbicides are an essential tool for increasing wood volume yields, with studies showing that control of competing vegetation using herbicides often results in 30–300% increases in wood volume yield for major commercial tree species in a wide range of site conditions (Wagner et al., 2004).

When silvicultural chemicals [fertilizers, pesticides (e.g. herbicides, insecticides)] are applied to forest land, they have the potential to impact stream water quality via inadvertent application to stream channels, transport by infiltration-excess or saturation-excess overland flow, spray drift, and leaching through the soil profile, although for herbicides, leaching and subsequent movement into streams through baseflow has typically not been observed in the field (Michael, 2004). The US Environmental Protection Agency (USEPA), under authority of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), specifies on pesticide labels various practices intended to prevent contamination of water bodies from pesticide application. Most pesticide labels contain standard language prohibiting mixing and loading of pesticides within a certain distance of water bodies, typically including those with intermittent flow. Labels also generally specify the use of various spray drift reduction techniques such as prohibiting application of pesticides within a certain distance of water bodies and specifying weather conditions under which applications may or may not be made, types of equipment that must be used for application (e.g. spray nozzle size), maximum application rates, application heights, and other factors that can reduce the potential for contamination of water bodies.

Since adoption of the Clean Water Act in the United States and the

Fisheries Act in Canada, forestry best management practices (BMPs) have been developed as the primary mechanism for achieving water quality protection from non-point source (NPS) pollutants that may result from forest management (Cristan et al., 2016, Pendly et al., 2015). Water quality protection is mandatory in all US states but the choice of BMPs to apply during forestry operations may be regulatory or non-regulatory, depending on the state. In Canada, forestry practices are regulated by the provincial governments. The Resource Management Act of 1991 is the principle statute in New Zealand underpinning the rules and regulations set by local unitary authorities for forestry activities, along with industry codes of practice. (The newly adopted National Environmental Standard for Plantation Forestry establishes national rules to ensure consistency across New Zealand, but does not take effect until May 2018). Silvicultural chemical BMPs have been developed to protect water quality when fertilizers and pesticides are applied. These BMPs are designed to minimize movement of silvicultural chemicals into bodies of water (primarily streams) and rely in part on the implementation of streamside management zones (SMZs) (Michael, 2004).

BMP implementation rates in the US have increased over time, in part due to increased compliance monitoring by states (Ice et al., 2010; NASF, 2015); the influence of voluntary forest certification schemes such as those developed by the Sustainable Forestry Initiative, Forest Stewardship Council, and American Tree Farm System, which require use of state-recommended BMPs and protection of riparian areas (Ice et al., 2010); and the influence of the SFI fiber sourcing standard which encourages use of trained logging professionals and support of logger training programs (MacDicken et al., 2015). As a result, BMP implementation rates in Florida have increased from 84% in 1985 to 99% in 2011 (Vowell et al., 2012). Similarly, overall BMP implementation rates in Texas increased from 79% in 1992 to 94% in 2011 (industrial site compliance rate in 2011 was 98%) (Simpson, 2007, Simpson et al.,

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2011). Across the southern US, the overall BMP compliance rate is reported to be 92%, while the compliance rate for silvicultural chemicals BMPs is 98.5% (SGSF, 2012). Pendlly et al. (2015) noted that in New Zealand, variation in environmental rules and BMPs between the 16 regional/unitary councils and 61 territorial authorities makes it difficult to assess compliance. However, according to the New Zealand Forest Owners Association, about 67% of all planted forests are FSC-certified (NZFOA, 2016) and the FSC requirement to reduce chemical use is influencing herbicide use in New Zealand's planted forests (Rolando et al., 2013).

The goal of the work described here was to assess the effectiveness of modern forestry BMPs for reducing the risk of forest herbicide use to aquatic organisms in streams. The initial step was to identify and summarize results from recent studies of operational forestry applications of herbicides in which data on herbicide concentrations in potentially impacted streams were collected. Then, we used those data to conduct a screening level risk assessment for non-target aquatic organisms that might reside in those streams.

2. Field studies

A number of previously published field studies have measured water concentrations of herbicides in streams, ponds, or wetlands following forestry applications (e.g. Feng et al., 1990; Michael, 2003; Michael and Boyer, 1986; Michael et al., 1999, 2006; Neary and Michael, 1989; Neary et al., 1984; Newton et al., 1984, 1994; Thompson et al., 1991, 2004; USEPA, 1998). However, many of these studies did not use modern BMPs. Many conducted during the early years of BMP development were “worst-case scenarios,” using treatments with herbicide application rates at or above label maximums, no or minimal SMZs, and sometimes direct application over water bodies. A literature search using Google Scholar (key words: forest, forestry, herbicide, water quality) identified five recent studies designed to evaluate the effectiveness of modern BMPs and application techniques for reducing movement of herbicides away from the site of application and into nearby streams. These studies were conducted in three distinct regions of the United States [Oregon's Coastal Range (Needle Branch watershed; Louch et al., 2017), East Texas (Neches River watershed; McBroom et al., 2013), and southwest Georgia (Dry Creek; Scarbrough et al., 2015)] and in New Zealand (Bay of Plenty region; Baillie et al., 2015; Baillie, 2016) and thus represent different climatological/geographic conditions and BMP guidelines/regulations.

2.1. Study sites and herbicide application

2.1.1. Needle Branch

This study is described in greater detail by Louch et al. (2017) and NCASI (2013). The study treatments were consistent with typical operational forestry activities. The Needle Branch watershed is a small (71 ha), steep, forested, headwater basin on the Tye Sandstone formation in Oregon's Coast Range. It receives approximately 2500 mm of precipitation annually, mostly as rain from October through May or June. The forest stand prior to harvest was mainly Douglas fir (*Pseudotsuga menziesii*) with red alder (*Alnus rubra*) in the riparian stands. The upper portion of the Needle Branch watershed, encompassing 49 ha, was harvested in 2009 using modern forest management practices as set out by the Oregon Forest Practices Act (FPA). At upper elevations, Needle Branch is not fish-bearing and no forested SMZ was required at the time. At middle elevations, Needle Branch is a small fish-bearing stream and an SMZ was maintained out to 15 m from the ordinary high water mark on both sides of the stream.

On August 22, 2010, the 2009 harvest site was treated with a herbicide mixture via single aerial application by helicopter. The mixture contained Accord® XRT (glyphosate), Chopper® Gen 2 (imazapyr), and Sulfomet® Extra (sulfometuron methyl and metsulfuron methyl). Application rates were 1.68 kg acid equivalent (a.e.)/ha (glyphosate),

0.21 kg a.e./ha (imazapyr), 0.16 kg active ingredient (a.i.)/ha (sulfometuron methyl), and 0.042 kg a.i./ha (metsulfuron methyl). As required by the Oregon FPA, the applicator maintained a no-spray buffer zone for herbicide application that extended 18 m from the stream on both sides along the fish-bearing portion of Needle Branch. Although no-spray zones were not required along non-fish-bearing streams, half-boom spraying (the spray boom on the stream side of the helicopter was turned off), which leaves a spray buffer of at least 3 m, was employed along the upper section of Needle Branch to minimize the potential for herbicides to directly impact the stream.

2.1.2. Alto

This study site and experimental treatments are described in greater detail by McBroom et al. (2013). All treatments used in this study were consistent with typical operational forestry activities except for the combination of practices incorporated into the “Intensive Treatment,” which would typically not be applied to a single site. Thirteen watersheds within the larger Neches River watershed, in East Texas near the town of Alto, were selected for study. The topography of the area is dominated by rolling hills with flat floodplains associated with larger streams, and study watersheds have dendritic drainage systems formed by random headward erosion. All study watersheds were in loblolly pine (*Pinus taeda*) plantations.

Four of the experimental watersheds were large (70–135 ha); nine were small (2.5 ha). The watersheds were instrumented in 1999 and water samples were collected to establish that there were no background levels of herbicides. One large and three small watersheds were designated as controls and received no treatments. Unlike the other treatment watersheds, which contained mature trees, one large treatment watershed was a 5-year-old stand that was not harvested as a part of this study. The remaining experimental watersheds were clearcut harvested in March–May 2002.

SMZs in all treatment watersheds were retained as specified in the Texas BMP guidelines and were at least 15 m wide on both sides of the stream along all intermittent and well-defined ephemeral streams. SMZs were thinned following Texas BMPs, with retention of at least 11.5 m²/ha of basal area and 50% crown cover (McBroom et al., 2008). GPS data on spray lines were provided by the contractor and verified that no direct overspray of SMZs occurred. SMZs were also surveyed post-application and no death of sensitive hardwood tree species was observed.

On “Conventional Treatment” watersheds, a mixture of imazapyr (as Arsenal®) (0.28 kg a.e./ha) and glyphosate (as Accord®) (2.24 kg a.e./ha) was aerially broadcast by helicopter during site preparation (September 2002), which occurred 4–6 months post-harvest (3 months before replanting). A hand-applied (backpack sprayer) banded application (applied to a strip along/over each tree row) of Oustar® (0.55 kg a.i./ha hexazinone, 0.10 kg a.i./ha sulfometuron methyl) was made in April 2003 for herbaceous weed control (one year post-harvest, 4 months post-replanting).

“Intensive Treatment” watersheds received the same treatments as the “Conventional Treatment” watersheds plus subsoiling immediately prior to replanting, fertilization at the time of replanting, and an additional herbicide treatment in April 2004 (16 months post-replanting) for herbaceous weed control. The additional herbicide treatment was an aerial (helicopter) broadcast application of Oustar® (0.55 kg a.i./ha hexazinone, 0.10 kg a.i./ha sulfometuron methyl).

The “Competition Control” watershed held a 5-year-old loblolly pine plantation that received an aerial (helicopter) application of 0.17 kg a.e./ha of imazapyr (as Arsenal®) for woody competition release at the same time the other treatment watersheds received herbicide applications for site preparation.

2.1.3. Dry Creek

This study is described in greater detail by Scarbrough et al. (2015). Two adjacent first-order watersheds, in mature loblolly pine plantations

Table 1
Site characteristics, application data, and some BMPs used at each of the three study sites.

| Site characteristics | Watershed | Alto | Dry Creek | Bay of Plenty Pekepeke | Eastern Bay Of Plenty |
|-----------------------------|--|---|---|--|------------------------------------|
| Needle Branch | Steep sloped, V-shaped drainage, shallow soils over fractured and porous sandstones | Rolling hills with flat floodplains associated with larger streams | Stream 1: moderately incised in V-shaped valley; Stream 2: weakly defined within riparian wetland system | Gently rolling to steep | Steep |
| Watershed Number | 1 | 13 | 2 | 1 | 1 |
| Watershed Size | 70 ha | Small: 2.5 ha; Large: 70–135 ha | 33.3 ha (T1) 44.1 ha (T2) | 12.5 ha | 12 ha |
| Soil Types | Well-drained, loams & gravelly loams | Mostly fine-textured sand/sandy loams over clay | Mostly well-drained sands/loamy sands over clay/sandy loams | Well-drained sandy loam pumice | Well-drained loamy sand |
| Baseflow Typically Present? | Yes, but summer stream flows are low and can be discontinuously perennial | No on small watersheds, intermittent on large | Yes | Yes | Yes |
| BMP Type | Minimum of 15 m on each side of fish-bearing lower portion of stream, none along non-fish-bearing upper portion of stream | Minimum of 15 m on each side of perennial, intermittent, & well-defined ephemeral streams | 12 m on slopes less than 20%, 21 m on slopes of 21–40% | 10 m (Year 1) or 20 m (Year 2) either side of stream channel | 30 m either side of stream channel |
| SMZ Harvest | None | Partial harvest with retention of minimum of 11.5 m ² /ha of basal area | None in upstream half of watershed; partial harvest in downstream half with retention of minimum of 11.5 m ² /ha of basal area | Not reported | Not reported |
| Herbicide Application | No-spray buffer zone of 18 m on each side of fish-bearing lower portion of stream, half-boom spraying along non-fish-bearing upper portion of stream | No application in SMZs | No application in SMZs | No application in SMZs | No application in SMZs |

at the initiation of the study, drain into Dry Creek, a tributary to Lake Seminole that is located southwest of the City of Bainbridge, GA. The watersheds drain part of the Pelham Escarpment, a relatively steep landscape within the Upper Coastal Plain of southwest Georgia. The two streams in these watersheds are morphologically different. In one, the stream is moderately incised into a V-shaped valley. In the other, the stream is weakly defined within a riparian wetland system. Watershed T1 drains 33.3 ha and has an average stream channel width of 1.1 m. Watershed T2 drains 44.1 ha and has an average stream channel width of 1.7 m.

Between September and November 2003, 45% of T1 and 54% of T2 were clearcut following BMPs developed by the Georgia Forestry Commission (Terrell et al., 2012, Scarbrough et al., 2015). SMZs of 12 m on both sides of the stream were retained on slopes less than 20%, while 21 m-wide SMZs were retained on slopes of 21–40%. The stream in each watershed was divided into upstream and downstream reaches with each reach representing approximately half of the total stream length. SMZs along the upstream reach of each stream were not harvested, but along downstream reaches SMZs were partially harvested, leaving 11.5 m² of residual basal area per ha.

In preparation for replanting, imazapyr (as Chopper®) was applied to both watersheds on September 1, 2004 at the rate of 0.091 kg a.e./ha, using a skidder in the uplands and a backpack sprayer on slopes. Imazapyr was reapplied 30 days later at the same rate using a backpack sprayer to 12 ha of sloped areas adjacent to SMZs. On November 15–16, 2004, a controlled burn was conducted on both watersheds, which were then replanted with loblolly pine in December 2004.

On March 15, 2005, a mixture of hexazinone and sulfometuron methyl (as Oustar®) was applied to both watersheds for herbaceous weed control. Applications were made using a backpack sprayer at a rate of 0.531 kg a.i./ha hexazinone and 0.099 kg a.i./ha sulfometuron methyl. Scarbrough et al. (2015) noted that the landowner typically used a lower application rate for both Chopper® and Oustar®, but the higher label rates were used in the study to produce the herbicide runoff potential associated with label rates.

2.1.4. Bay of Plenty Pekepeke

This study is described in greater detail by Baillie et al. (2015). The 12.5 ha study site is located in the Pekepeke watershed, which drains the eastern slopes of the Kaingaroa Plateau. The terrain of the site is gently rolling to steep, and the site is dissected by several small first and second-order spring-fed perennial streams. Median annual rainfall in the area is 1300 mm. The watershed as a whole is in mixed age classes of *Pinus radiata*. The study site was harvested in 2011, received an aerial application of metsulfuron methyl and glyphosate for site preparation in March 2012, and was replanted with *P. radiata* in July 2012.

In November 2012 and again in October 2013, aerial applications (helicopter) of Release KT® (7.4 kg/ha terbuthylazine, 1.1 kg/ha hexazinone) were made. In 2012, the entire 12.5 ha were sprayed; in 2013, only 10.6 ha were sprayed. Operational BMPs that required 10-meter no-spray buffers around any visible flowing water were followed the first year. In the second year, the width of no-spray buffers was expanded to approximately 20 m. Several spray drift reduction techniques were used, including spray booms within 80% of rotor length, application heights of 8–10 m above ground level, turning spray off before traversing streams, and “extremely coarse” (as defined by ASABE, 2009) spray droplets.

2.1.5. Eastern Bay of Plenty

This study site is described in greater detail by Baillie (2016). The study area is located in steep hill country where the mean annual rainfall is 1504 mm. The site is located within a 193-ha watershed covered by young (≤2-year-old) second-rotation or mature (28–29-year-old) first-rotation *P. radiata*. In November 2014, herbicides were applied to 30 ha of one-year-old trees. The study site received an aerial (helicopter) application of 6 kg/ha terbuthylazine and 1.5 kg/ha

hexazinone, as AGPRO Valzine Extra. These application rates are typical for this type of operation in this area. During herbicide application, a no-spray buffer of approximately 30 m was maintained around the stream. Spray nozzles delivered “ultracoarse” (as defined by ASABE, 2009) spray droplets and the application height was 12–21 m above ground level.

Water monitoring point one (W1) was set up at the downstream end of a headwater stream draining a 12-ha watershed, 57% of which was treated with herbicides. Water monitoring point two (W2) was located in a larger stream, immediately downstream of the outflow from the headwater stream. W2 was also impacted by runoff from another sub-watershed draining a portion of the treated area. The author included information about and data collected at one other monitoring points, but it was in a location that received water from watersheds that were impacted by herbicide treatments in other locations and so is not included in this summary and risk assessment.

2.1.6. Summary

Table 1 presents site characteristics, application data, and some BMPs used at each of the six study sites. In all six studies, SMZs were maintained along streams, although at Needle Branch, SMZs were found only along the fish-bearing segment of the stream. In all cases, care was taken to avoid direct application of herbicides to stream water, primarily by using no-spray buffer zones, but at a minimum, by using half-boom spraying. However, as Baillie et al. (2015) pointed out, on some sites, there is a possibility that ephemeral channels or channels screened by logging slash may inadvertently receive direct overspray. Other BMPs employed in these studies to reduce the likelihood of off-site movement of herbicides included preparing tank mixes at locations distant from streams, applying herbicides only under favorable weather conditions, using spray nozzles that produce large spray droplets, spraying as close to ground level as possible, and using global positioning system (GPS) to delineate spray lines. Table 2 shows herbicide application rates used at the study sites.

2.2. Water sample collection, sample processing and analysis

Methods for water sample collection, processing, and analysis in the US studies are described in greater detail by Louch et al. (2017) and NCASI (2013) (Needle Branch); McBroom et al. (2013) and NCASI (2007) (Alto); and Scarbrough et al. (2015) (Dry Creek). At each study site, prior to herbicide application, each watershed/sampling point was fully instrumented to record/gage stream flow and each water sampling

Table 2
Herbicide application rates used at study sites.

| Herbicide | Herbicide Application Rate (kg/ha) | | | | |
|---------------------|------------------------------------|--|----------------------|------------------------|-----------------------|
| | Needle Branch | Alto | Dry Creek | Bay of Plenty Pekepeke | Eastern Bay of Plenty |
| Glyphosate | 1.68 ^a | 2.24 ^a | Not applied | Not applied | Not applied |
| Hexazinone | Not applied | 0.55 ^a –0.28 ^c | 0.531 ^b | 1.1 ^a | 1.5 ^a |
| Imazapyr | 0.21 ^a | 0.28 ^a 0.17 ^a | 0.091 ^{b,d} | Not applied | Not applied |
| Metsulfuron Methyl | 0.042 ^a | Not applied | Not applied | Not applied | Not applied |
| Sulfometuron Methyl | 0.16 ^a | 0.10 ^a 0.05 ^c | 0.099 ^b | Not applied | Not applied |
| Terbuthylazine | Not applied | Not applied | Not applied | 7.4 ^a | 6.0 ^a |

^a Aerial application (helicopter).

^b Ground application (backpack sprayer).

^c Banded ground application (backpack sprayer).

^d Ground application (skidder-mounted sprayer).

point was equipped with autosamplers for collecting analytical samples during storm events.

At Needle Branch, three water sampling stations were set up with two autosamplers at each. The lowest elevation station (NBL) was near the mouth of Needle Branch. The middle elevation (NBM) station was located immediately below the 2009 harvest area where Needle Branch is a small, fish-bearing stream. The highest elevation station (NBH) was located within the harvest site at the fish/no-fish interface of the stream. During herbicide application, samplers were programmed to collect a sample every hour for 24 h, starting prior to application and finishing approximately 19 h post-application. Subsequently, samplers were manually started whenever a storm event was predicted. All samplers were programmed to initiate sampling at the same time and follow the same sampling frequency, which varied from 1 per hour to 1 every 6 h. Manual grab samples were collected about once per week during baseflow conditions.

At the Alto site, two autosamplers were placed at the single sampling point for each watershed. The autosamplers were configured to initiate sample collection based on an initial rise in stream flow (stage) and samples were collected on either a default time base or triggered by continuing increases in stream flow. A limited number of baseflow grab samples were collected manually during the study.

At the Dry Creek site, each watershed was equipped with a single autosampler programmed to collect samples during storm events. Grab samples were collected manually prior to herbicide application, immediately following application, and intermittently between storm events throughout the study.

Methods for water sample collection, processing, and analysis in the New Zealand studies are described in greater detail in Baillie et al. (2015) and Baillie (2016). At both locations, water samples were collected manually. At the Bay of Plenty Pekepeke site, one water monitoring point (W1) was established at the base of the study watershed, a second (W2) was established not far downstream of that. Baseflow stream water samples were collected twice prior to spraying, every 15 min for the first two hours post-application, on days 1, 2, 5, 8, 12, and 20 post-application (year 2 only), and monthly for 7 (year 1) or 6 (year 2) months post-application. Stormflow samples were collected during two rain events (34 and 167 DAT) post-application in year one and during three rain events (7, 36, and 170 DAT) post-application in year two.

At the eastern Bay of Plenty site, one water monitoring point (W1) was established at the base of the study watershed, a second (W2) was established about 100 m downstream of W1, and a third (W3) 1.43 km downstream of W2. Water samples were collected twice prior to herbicide application at W1 and W2 and once at W3. At W1, samples were collected at 15-min intervals during the first five hours post-application then composited into hourly samples. At W2 and W3, single samples were collected during that five-hour period. Subsequently, water samples were collected from all three sites at days 1, 2, 7, 30, 34, 59, 94, and 154 DAT. The remoteness and steepness of the site limited the ability to monitor storm events.

2.3. Results

2.3.1. Needle Branch

A pulse of dissolved glyphosate manifested at NBH during application under baseflow conditions. This pulse maximized at 0.062 µg/L [three times the method detection limit (MDL)], with a pulse width-at-half-height of less than 4 h. Concentrations returned to pre-application background levels within about 9 h. An associated pulse was not detected (< 0.020 µg/L) at the farthest downstream sampling site (NBL), while no glyphosate samples were collected during application at the mid-elevation site (NBM) due to malfunctioning sampling equipment. Subsequent baseflow samples collected three days after treatment (DAT) showed 0.030, 0.021, and 0.033 µg/L dissolved glyphosate at NBH, NBM, and NBL, respectively, and < 0.020 µg/L glyphosate at all

sites at 19 DAT.

Samples collected during the first storm event (8 DAT) showed a clear pulse of dissolved glyphosate at NBM, with a maximum concentration of 0.149 µg/L. The pulse persisted above the MDL for about ten hours, and concentrations rose and fell during the pulse with no samples near the single observed peak concentration. There was also a glyphosate pulse, peaking at 0.058 µg/L, at NBL during the first storm event. Glyphosate was detected (0.045 µg/L) only in the first sample collected during the first storm event at NBH.

During the second storm event (10 DAT), a clear pulse of dissolved glyphosate manifested at NBH, but not at NBM or NBL. The maximum concentration observed was 0.084 µg/L (4x MDL), and the pulse persisted for approximately 11–12 h. Results from all subsequent storm events showed dissolved glyphosate at < 0.020 µg/L in all samples.

Sulfometuron methyl and metsulfuron methyl were not detected (ND) in any samples with method detection limits (MDLs) of 0.5 µg/L and 1 µg/L, respectively. Because of sample-to-sample variability in background interference, dissolved imazapyr could not be reliably quantified at concentrations < 0.6 µg/L, a threshold that was not exceeded in any sample. Thus, imazapyr was also ND in all samples, including samples collected during application of herbicides.

2.3.2. Alto

All herbicide concentrations on control watersheds were below the MDL (< 0.3 µg/L) (NCASI, 2007). During the study, there were no significant ($p > 0.05$) differences in stream water herbicide concentrations between large and small watersheds nor, when the same herbicide treatments were applied, were there any differences between conventional and intensive treatment watersheds.

2.3.2.1. Glyphosate (Site Preparation Application, Conventional and Intensive Treatments). Screening analyses of composite samples for glyphosate indicated that the maximum potential concentration of glyphosate in any one sample was about 10 µg/L and concentrations dropped to 1–2 µg/L 3 months after treatment. These estimates assume that all the glyphosate found in a composite was associated with only one of the samples. This is a conservative assumption, and the true maximum concentration in any individual sample was probably lower. No additional analyses of samples for glyphosate were conducted.

2.3.2.2. Imazapyr (Site Preparation Application, Conventional and Intensive Treatments). All streams were dry at the time of application. In all watersheds, the highest stream water concentrations of imazapyr were measured in the first post-application runoff events (24 or 30 DAT), which were also the first runoff events after the summer dry season. Maximum individual (single sample) concentrations ranged from 1.3 µg/L to 39.3 µg/L. By 5 months post-application, average imazapyr concentrations in runoff event samples on all treatment watersheds ranged from below the limit of quantification (LOQ) (< 1.0 µg/L) to just above (all averages < 2 µg/L). Subsequent measurements were all near or below the LOQ. In the “Competition Control” watershed, concentrations fell below the LOQ within 2 months post-application.

Baseflow samples were collected at some sites on the day after the first post-application runoff event (25 DAT). Imazapyr concentrations ranged from 15.2 µg/L to below the LOQ (< 1 µg/L). Due to a long period of drought, baseflow samples were next collected from all watersheds 4–5 months post-application and the imazapyr concentration was below the LOQ in all samples.

2.3.2.3. Oustar® (Banded release application, Conventional and Intensive Treatments). The first runoff events resulted in the highest hexazinone concentrations, with 9.4 µg/L as the highest single sample hexazinone concentration reported. For most watersheds, concentrations fell below the LOQ by the third to fifth post-application runoff event, which, depending on the watershed, ranged from 226 to 296 DAT.

Sulfometuron methyl concentrations in all samples collected on all watersheds following the banded application were below the LOQ (< 1 µg/L).

2.3.2.4. Oustar® (Aerial release application, Intensive treatment only). The highest single sample hexazinone concentration was 29.9 µg/L, in a sample collected in the first runoff event (24 DAT). Hexazinone levels on all watersheds declined to below the LOQ (< 1 µg/L) within 5 months and 6 post-treatment rainfall events, although most watersheds fell below the LOQ sooner, in one case by the third post-application rainfall event (67 DAT). Baseflow samples were collected in some watersheds 25 DAT; all sample concentrations were below the LOQ.

Sulfometuron methyl was present at concentrations above the LOQ in samples collected during the first two post-application rainfall events (24 and 30 DAT). Concentrations ranged from 1.0 to 2.5 µg/L. By the third rainfall event (67 DAT), sulfometuron methyl concentrations in all samples were below the LOQ.

2.3.3. Dry Creek

2.3.3.1. Imazapyr (Site preparation). Imazapyr was below the MDL (< 0.30 µg/L) in all baseflow samples collected from both watersheds on the 2nd through 5th DAT following the initial application (prior to the first storm event). Imazapyr remained below the MDL in all subsequent baseflow samples except for samples collected from T1 on the day after the first post-application storm event (7 DAT) and in samples collected 1 and 4 days after the second application of imazapyr to the watershed’s sloped areas. In those samples, imazapyr concentrations were between the LOQ (0.97 µg/L) and the MDL (0.3 µg/L).

The first storm event after initial imazapyr application occurred Day 6 post-application. The maximum concentration of imazapyr found in any sample, 7.3 µg/L, was in a sample from watershed T1 during this storm event. During the same storm event, the maximum imazapyr concentration found at T2 was 2.0 µg/L. During the second post-application storm event (15 DAT), the maximum concentrations detected in watersheds T1 and T2 were 5.7 µg/L and 2.6 µg/L, respectively. During the third post-application storm event (44 DAT), which was 15 days after the second application to slopes, imazapyr concentrations in all storm flow samples from both watersheds were below the LOQ (< 0.97 µg/L). During the fourth post-application storm event (73 DAT), which was 44 days after the second application to slopes, no samples were collected from T1, but all samples collected at T2 were below the MDL (< 0.3 µg/L). Imazapyr concentrations remained below the MDL (< 0.3 µg/L) at both T1 and T2 in all subsequent storm event samples.

2.3.3.2. Oustar® (Herbaceous weed control). Hexazinone was present in baseflow samples at concentrations greater than the LOQ (0.97 µg/L) only in samples collected following the first (1 DAT) and second (7 DAT) post-application storm events. Samples collected from watershed T2 one day after the first post-application storm event contained 1.3 µg/L hexazinone while those from watershed T1 were below the LOQ. Over the three days following the second post-application storm event, baseflow samples from watershed T1 contained up to 1.7 µg/L hexazinone and those from watershed T2 contained as much as 2.3 µg/L. Hexazinone levels in subsequent baseflow samples were all below the LOQ. Sulfometuron methyl was below the MDL of 0.17 µg/L in all baseflow samples.

The maximum hexazinone concentration found in any storm water sample was 7.7 µg/L, which was collected on watershed T2 during the first storm event (1 DAT) post-application. The maximum concentration found in samples from watershed T1 during this storm event was 7.5 µg/L. Over the second (7 DAT), third (12 DAT), and fourth (17 DAT) storm events, measured hexazinone concentrations at both watersheds were similar. Maximum concentrations for each storm event were

4.1 µg/L at T1, 2.0 µg/L at T2, and 3.3 µg/L at T1 for the second, third, and fourth storm events, respectively. In the final storm flow samples collected during the fourth storm event, hexazinone concentrations at both watersheds were about 1 µg/L, just above the LOQ.

The maximum sulfometuron methyl concentration found in any storm water sample was 1.24 µg/L in a sample collected at watershed T2 during the first storm event (1 DAT) after Oustar® application. The maximum concentration found in samples from watershed T1 during this storm was 0.99 µg/L. In all samples collected during subsequent storm events, the concentration of sulfometuron methyl was below the LOQ (< 0.55 µg/L).

2.3.4. Bay of Plenty Pekepeke

During year one, no herbicide residues were detected prior to herbicide application at W1. On the day of application, at W1, terbuthylazine concentrations peaked at 1160 µg/L at the start of the monitoring period and declined from there to 12 µg/L after 8 h of monitoring. Concentrations were < 0.4 µg/L in baseflow for the rest of the study period. Hexazinone concentrations followed a similar pattern, with the peak of 230 µg/L detected at the start of the monitoring period and a decline to 1 µg/L at the end of the monitoring period that day. Concentrations were ≤ 1 µg/L in baseflow for the rest of the study period. At W2 on the day of application, concentrations of terbuthylazine and hexazinone peaked at 32 and 7 µg/L, respectively and for the remainder of the year, concentrations in baseflow for both remained < 1.5 µg/L. During two small rainfall events in year one (34 and 167 DAT), concentrations for both herbicides at W1 were in the range of 0.24–1.05 µg/L.

During year two, no terbuthylazine was detected at W1 prior to herbicide application, but hexazinone was detected at < 0.2 µg/L. On the day of herbicide application, terbuthylazine and hexazinone concentrations at W1 peaked at 4 and 3 µg/L, respectively. Higher concentrations were detected at W1 during the first rainfall event (7 DAT), with terbuthylazine and hexazinone concentrations peaking at 210 and 7 µg/L, respectively, declining to 7.5 and < 3 µg/L, respectively, 24 h later. During the second rainfall event (36 DAT), peak concentrations of terbuthylazine at W1 reached 5 µg/L, while those of hexazinone remained below 3 µg/L. At W2, traces (≤ 2 µg/L) of hexazinone were detected prior to and on the day of herbicide application. On the day of application, W2 terbuthylazine concentrations measured 0.2 µg/L. During the first post-application rainfall event (7 DAT), terbuthylazine concentrations reached 7 µg/L then declined to < 1.5 µg/L, where they remained for the rest of the monitoring period. During the same rainfall event, hexazinone concentrations measured 4 µg/L then declined to < 1.3 µg/L, where they remained for the rest of the monitoring period. At W3, the highest terbuthylazine and hexazinone concentrations were recorded during this rainfall event (0.9 and 0.4 µg/L, respectively).

2.3.5. Eastern Bay of Plenty

At W1, concentrations of terbuthylazine peaked at 9.6 µg/L on the day of herbicide application, declined to < 3 µg/L by the end of the day, and remained below that concentration for the remaining 5 months of the study. Concentrations also declined moving downstream, with a peak of 2.5 µg/L at W2 on the day of application and concentrations never exceeding 0.3 µg/L at W3 for the duration of the study. A similar picture was found for hexazinone. At W1, the concentration peaked at 5.3 µg/L on the day of herbicide application, declined to 2.9 µg/L by the end of the day, and remained in the range of 3.7 to < 1 µg/L for the rest of the study. Concentrations also declined moving downstream, with a peak of 2.1 µg/L at W2 on the day of application and concentrations remaining below 0.5 µg/L at W3 for the duration of the study.

2.3.6. Summary

Peak herbicide concentrations were generally low, but they did vary substantially among sites (Table 3). The Bay of Plenty Pekepeke site

reported the highest peak concentrations of hexazinone and terbuthylazine while the Alto watershed featured the highest peak concentrations of glyphosate, imazapyr, and sulfometuron methyl. The Needle Branch and Eastern Bay of Plenty sites featured the lowest peak concentrations.

In each of the studies described above, the length of time that elevated concentrations of herbicides were present in stream water was very short. The Needle Branch report described two pulses of dissolved glyphosate, one persisting for about 10 h during the first post-application storm event and a second that lasted for about 12 h during the second post application storm event (NCASI, 2013). In both cases, the peak concentrations were present for only a portion of these periods. At Alto, peak concentrations of herbicides persisted in storm flow for a relatively short time, appearing as pulses that dissipated in less than 24 h (McBroom et al., 2013). Similarly, measurable concentrations of herbicides at Dry Creek were short-lived, lasting only 12–24 h during storms (Scarborough et al., 2015). The peak concentrations at the two Bay of Plenty sites occurred during herbicide application and lasted less than 8 h.

The shapes of herbicide concentration peaks were variable among and within studies. For example, during the first post-application runoff event at Needle Branch, the glyphosate concentration peak at the Needle Branch NBM sampler was a single symmetrical, sharp pulse. In contrast, the peak at NBH started high, then tailed off throughout the runoff event, while at NBL, the peak was broad and irregular throughout. Peak shapes could potentially be affected by, among other things, duration and intensity of rainfall events, time between rainfall events, and size of the stream at the sampler location.

All sites reported detectable levels of herbicide in baseflow samples at some point. At Needle Branch and the two Bay of Plenty sites, herbicides were detected in baseflow on the day of application, which likely represented inadvertent overspray or spray drift, and also in some subsequent samples. At Dry Creek, herbicides were detected in baseflow samples collected in the first few days following herbicide application and immediately after initial post-application rainfall events.

3. Potential risk to non-target aquatic organisms

Pesticide exposure risks are often characterized by the ratios of observed concentrations to concentrations of concern. One such ratio, the Risk Quotient (RQ), is used by the USEPA (2004) during screening level risk assessments in the pesticide registration and registration review processes. The RQ is the ratio of a model-predicted expected environmental concentration (EEC) to acute and chronic toxicity values for the most sensitive organisms that have been identified in toxicity testing. RQs are then compared to a series of defined “Levels of Concern” (LOC) to analyze potential risk and guide possible regulatory action (USEPA, 2004). Calculation of RQs is a screening activity using conservative input values and RQs do not have specific meanings with respect to degree or probability of adverse effect. If an RQ achieves the LOC, it is an indication that additional refinement of the risk picture is necessary.

We applied this screening assessment to the peak herbicide concentrations observed at the five sites. For acute exposures to aquatic animals, the LOC is achieved when the RQ value exceeds 0.5 (0.05 for endangered species). For acute exposures to plants and for chronic exposures to both animals and plants (endangered or not), the LOC is achieved when the RQ exceeds 1.

Additional information on toxicity testing and the toxicity values used in the RQ calculations for this section may be found in the Supplemental Material.

Glyphosate RQs were calculated using toxicity values for the most sensitive species identified by Durkin (2011a) and the peak glyphosate concentration reported in the Alto study (Table 4). None of the calculated RQs reach a value associated with a LOC, indicating low risk to non-target aquatic organisms, even at peak glyphosate concentrations

Table 3
Maximum single-sample concentrations of herbicides in stream water at each of the three study sites.

| Herbicide | Herbicide Concentration (µg/L) | | | | |
|---------------------|--------------------------------|-------------------|-------------|-------------------------|-----------------------|
| | Needle Branch | Alto | Dry Creek | Bay of Plenty- Pekepeke | Eastern Bay of Plenty |
| Glyphosate | 0.149 | 10.0 ^a | Not applied | Not applied | Not applied |
| Hexazinone | Not applied | 29.9 | 7.7 | 230.0 | 5.3 |
| Imazapyr | < 0.6 ^b | 39.3 | 7.3 | Not applied | Not applied |
| Metsulfuron Methyl | < 1.0 ^b | Not applied | Not applied | Not applied | Not applied |
| Sulfometuron Methyl | < 0.5 ^b | 2.5 | 1.24 | Not applied | Not applied |
| Terbutylazine | Not applied | Not applied | Not applied | 1160.0 | 9.6 |

^a Maximum potential concentration in a single sample based on analysis of composite samples reflecting 2 to 5 individual samples.

^b Analytical detection limit.

reported at Needle Branch or Alto.

Imazapyr RQs were calculated using toxicity values for the most sensitive species identified by Durkin (2011b) and Yahnke et al. (2013) and the peak imazapyr concentration reported in the Alto study (Table 4). Only one calculated RQ, that associated with macrophyte toxicity at the Alto peak concentration, reaches a value associated with a LOC.

Hexazinone RQs were calculated using the toxicity values for the most sensitive species identified by Berrill et al. (1994), Durkin et al. (2005) and USEPA (2010) and the peak hexazinone concentration reported in the Bay of Plenty Pekepeke study (Table 4). Two calculated RQs, those associated with algae and macrophyte toxicity, reach values associated with a LOC. In addition, an RQ for algae, which also reached a value associated with a LOC, was calculated using the peak concentration reported in the Alto study (Table 4).

No RQs could be calculated for metsulfuron methyl. The only study in which metsulfuron methyl was applied was the Needle Branch study. Metsulfuron methyl concentrations in stream water were below the detection limit of 1.0 µg a.i./L in all samples. Klotzbach and Durkin

(2004a) reviewed and summarized available data (including unpublished studies submitted to EPA in support of pesticide registration) on aquatic toxicity of metsulfuron methyl. Aquatic macrophytes appear to be the organisms most sensitive to metsulfuron methyl, with reported EC₅₀ values of 0.22 µg a.i./L (*Myriophyllum sibiricum*) and 0.36 µg a.i./L (*Lemna minor*), which are below the detection limit for the Needle Branch study. However, because the actual concentration of metsulfuron methyl is uncertain, no assessment of risk can be made in this circumstance.

Sulfometuron methyl RQs were calculated using toxicity values for the most sensitive species identified by Klotzbach and Durkin (2004b), Roshon et al. (1999), and USEPA (2012) and the peak sulfometuron methyl concentration reported in the Alto study (Table 4). In addition, RQs for aquatic plants were also calculated using the peak concentration reported in the Dry Creek study (Table 4). Only the calculated RQs associated with macrophyte toxicity reach values associated with a LOC.

Terbutylazine RQs were calculated using toxicity values for the most sensitive species identified by the European Chemicals Agency

Table 4
Herbicide Risk Quotients (RQs) calculated using toxicity values for the most sensitive species and peak herbicide concentrations reported in Table 3.

| RQ Type | RQ | | | | | RQ value that reaches a LOC |
|---|-------------------------|-----------------------------|-------------------------|----------------------------------|---|-----------------------------|
| | Glyphosate ^a | Imazapyr ^b | Hexazinone ^c | Sulfometuron Methyl ^d | Terbutylazine ^e | |
| Acute – aquatic animals | | | | | | > 0.5 |
| Fish | 0.010 | 0.0019 | 0.0010 | 0.00034 | 0.5 | |
| Amphibian | 0.013 | 0.0051 | 0.0023 | 0.0027 | - ^f | |
| Aquatic Invertebrate | 0.0067 | 0.0006 | 0.0024 | 0.0000042 | 0.11 | |
| Acute endangered species – aquatic animals | | | | | | > 0.05 |
| Fish | 0.010 | 0.0019 | 0.0010 | 0.00034 | 0.5 (BoP-P ^g)0.1 (EBoP ^h) | |
| Amphibian | 0.013 | 0.0051 | 0.0023 | 0.0027 | - ^f | |
| Aquatic Invertebrate | 0.0067 | 0.0006 | 0.0024 | 0.0000042 | 0.11 | |
| Chronic – all animals | | | | | | > 1 |
| Fish | 0.00039 | 0.00033 | 0.014 | 0.0021 | 12.9 | |
| Aquatic Invertebrate | 0.0002 | 0.00040 | 0.012 | 0.000026 | 61.1 | |
| Acute/Chronic Non-endangered or Endangered Plants | | | | | | > 1 |
| Algae | 0.083 | 0.0034 | 33.8 (BoP-P)4.4 (Alto) | 0.54 (Alto)0.27 (Dry Creek) | 1054.5(BoP-P)8.7(EBoP) | |
| Macrophyte | 0.012 | 0.74 (Dry Creek)3.97 (Alto) | 3.3 | 20.83 (Alto)10.33 (Dry Creek) | 90.6 | |

^a Glyphosate RQs calculated using toxicity values for the most sensitive species identified by Durkin (2011a) and the peak glyphosate concentration reported in the Alto study.

^b Imazapyr RQs calculated using toxicity values for the most sensitive species identified by Durkin (2011b) and the peak imazapyr concentration reported in the Alto study.

^c Hexazinone RQs calculated using toxicity values for the most sensitive species identified by Berrill et al. (1994), Durkin et al. (2005) and USEPA (2010) and the peak hexazinone concentration reported in the Bay of Plenty-Pekepeke Watershed study. In addition, an RQ for algae was calculated using the peak hexazinone concentration reported in the Alto study.

^d Sulfometuron Methyl RQs calculated using the toxicity values for the most sensitive species identified by Klotzbach and Durkin (2004b) and USEPA (2012) and the peak sulfometuron methyl concentration reported in the Alto study, and, for aquatic plants, the peak concentration reported in the Dry Creek study.

^e Terbutylazine RQs calculated using the toxicity values for the most sensitive species identified by the European Chemicals Agency (ECHA, 2015) and the peak terbutylazine concentration reported in the Bay of Plenty-Pekepeke Watershed study. In addition, RQs for acute endangered fish and for algae were calculated using the peak terbutylazine concentration reported in the Eastern bay of Plenty study.

^f No applicable toxicity data available.

^g Bay of Plenty-Pekepeke Watershed.

^h Eastern Bay of Plenty.

(ECHA, 2015) and the peak concentrations at both Bay of Plenty sites (Table 4). Calculated RQs reached values associated with a LOC for “Acute Endangered Species - Aquatic Animals,” “Chronic – All Animals” (Bay of Plenty Pekepeke only), and for acute and chronic exposures to algae (both sites) and macrophytes (Bay of Plenty Pekepeke only).

4. Discussion

4.1. Variation in herbicide concentrations across sites

Although the reported stream water herbicide concentrations varied among the sites, terbuthylazine and hexazinone concentrations on the day of application at the Bay of Plenty Pekepeke site in Year One were considerably higher than peak herbicide concentrations reported at the other sites, a result that is clearly reflected in the screening risk assessment. However, at that site, Baillie et al. (2015) also placed tracer plates alongside the stream channel in order to measure spray deposition in the stream during application. On the day of application, 14–36% of the full application rate of Release KT® reached the stream, potentially because no-spray buffers around the stream were narrower than those used in Year Two of the same study and in the other studies.

The differences in reported peak stream water concentrations among the sites are likely a function of a many different factors, including site characteristics, rainfall patterns and amount, and specific herbicides applied, and cannot be attributed to any particular characteristic. The soil types at the sites are similar, all are described as well-drained and as loamy, sandy loam, and sandy. Topography, on the other hand, encompasses the full range from mostly level (a riparian wetland system) to steep hills.

The presence or absence of ephemeral streams and the visibility of small streams may impact herbicide concentrations, especially on the day of application, when, for example, inadvertent application to small streams hidden by vegetation could occur. On the other hand, inadvertent application isn't a concern when streams are dry (e.g. the first Alto application) at the time of application.

Rainfall pattern and timing may affect herbicide transport into streams. The longer an applied herbicide remains in surface organic matter and the top layers of soil, the more degradation will occur and the less herbicide will be available for transport into streams during a storm event. The reverse is also true. For example, at Dry Creek, the highest hexazinone concentration detected was produced during a storm event that occurred the day after herbicide application (Scarborough et al., 2015). McBroom et al. (2013) looked at the impact of rainfall timing and suggested that, in cases where a second rainfall event follows closely behind the preceding event, herbicide that was mobilized in the initial event may be stored in runoff source areas and thus be immediately available for transport.

4.2. Significance of exposure duration to herbicide effects

In the screening level assessments of potential risk to non-target aquatic organisms of herbicide use, some of the calculated RQs exceeded the LOC. (Table 4). However, RQ calculations are based solely on exposure concentration, while the potential for adverse effects following herbicide application is a function of both exposure concentration and exposure duration. At the most basic level, the relationship between concentration (C), duration (T), and effect (E) is characterized by the equation $C \times T = E$ (Haber's Law) (Witschi, 1999, Rozman, 2000). The precise quantitative relationship between C, T, and E is a function of chemical and organism-specific factors, but the concept that exposures to higher concentrations for shorter times produce the same effects as exposures to lower concentrations for longer times generally holds true (Rozman, 2000, Miller et al., 2000).

At each of the study sites, the durations of peak herbicide concentrations were much shorter than the exposure duration for the toxicity tests used to derive the toxicity values used in the screening risk

assessment. Toxicity values for aquatic animals are typically based on exposures of 48 or 96 h and those for aquatic plants are typically based on exposures of 14 or 21 days. Peak stream water concentrations reported in the field studies summarized here lasted less than 24 h. Understanding the relationships between exposure duration, exposure concentration, and adverse effects is particularly important when estimating the potential risk to aquatic plants from forestry applications of herbicides, which are designed to target plants rather than animals.

Bowmer (1986), in a review of bioassays and macrophyte ecotoxicology, reports that when macrophytes are exposed to herbicides that inhibit photosynthesis, there is a consistent pattern of recovery following exposure to high concentrations for short periods, with photosynthetic function rapidly recovered once exposures are terminated. Bowmer et al. (1985) and Bowmer (1986) reported that several species of “submerged weeds” (macrophytes) could be controlled with long-term exposures to < 0.2 mg/L of the herbicide terbuthyryne, but in short-term (2 h) exposures, concentrations greater than 11.2 mg/L were required to produce long-term depression of photosynthesis in shoot cuttings from *Elodea canadensis* and exposures of up to 44.8 mg/L had no effect on growth or survival of cuttings or rooted plants. Bowmer (1986) reported similar results in tests when *E. canadensis* was exposed to hexazinone for 24 h or 6 days.

Cedergreen et al. (2005) compared the effects of 3-h, 4-day, and 7-day exposures of *L. minor* to six different herbicides representing 3 different modes of herbicidal action. One of the herbicides tested, metsulfuron methyl, may be used in forestry. The authors reported that, based on 4-day EC₅₀ and EC₁₀ values, it took a 10-fold higher exposure to metsulfuron methyl in the 3-h pulse exposure to produce the same effect on growth as a 4-day continuous exposure.

Belgers et al. (2011) exposed the macrophyte *Myriophyllum spicatum* to a series of concentrations of metsulfuron methyl for 1, 3, 7, 14, or 21 days, and then determined EC₅₀ and EC₁₀ values for growth of all of the exposure groups at day 42. The results indicated that considerably higher concentrations could be tolerated for shorter exposure periods. For example, the EC₅₀ value for new tissues (as determined by dry weight of new shoots + new roots) for a one-day exposure was 2.07 µg/L while those for 7-day and 14-day exposures were 0.571 µg/L and 0.168 µg/L, respectively. The authors suggested that use of a time-weighted average (TWA) approach may be more appropriate for assessing risk to aquatic plants than simply comparing an EC₅₀ value to a maximum exposure concentration.

Boxall et al. (2013) compared continuous exposures of *L. minor* to metsulfuron methyl with 2-day and 4-day pulse exposures over a total treatment time of 42 days. In the pulsed exposures, plants were exposed to the herbicide for 2 or 4 days/week and to plain growth media for the remainder of the week. Boxall et al. (2013) chose to use higher exposure concentrations for the pulsed exposures so that the time-averaged (42 day) total exposure (time-weighted average) would be the same for each test group. Thus, exposure concentrations for the 2-day and 4-day groups were 3.5 and 1.75 times higher, respectively, than that for the continuous group. They found that the degree of growth inhibition at the end of 42 days was similar for each treatment group; some differences were statistically significant, but not likely biologically significant. So, for example, looking at the lowest exposure treatment groups, continuous exposure to 0.1 µg/L metsulfuron methyl produces the same degree of growth inhibition as 2-day/week exposures to 0.35 µg/L.

Another factor to consider when evaluating the toxicity of herbicides to aquatic plants is the capacity of plants to recover from the growth inhibition induced by herbicide exposure. For example, Cedergreen et al. (2005) found that after 3-h exposures to metsulfuron methyl at “near lethal” concentrations that “almost terminated” growth of *L. minor* for 4 days, plant growth resumed at a rate similar to that of controls. Similarly, Teodorovic et al. (2012), when comparing effects of atrazine on *L. minor* and *Myriophyllum aquaticum*, concluded that, while the two species of macrophyte responded differently, both showed “a

good indication of plant recovery potential.” Finally, Belgers et al. (2011) noted that, while metsulfuron methyl inhibited new tissue formation in *M. spicatum*, it was not lethal to the main shoots over the 42 days of the study.

4.3. Comparison to other forestry field studies

There have been a number of previously published field studies that measured stream water concentrations of herbicides following forestry applications. However, few of those studies employed modern BMPs. Indeed, many were designed as “worst-case scenarios,” using application rates at or above label maximums, no SMZs, and even direct application over waterbodies. Others used application methods that are not directly comparable to current operational herbicide applications, e.g. the study described by Neary et al. (1986) in which pellets impregnated with hexazinone were placed by hand in a grid across the study watershed.

A review of the results of studies in which the herbicide active ingredients used at Needle Branch, Alto, and Dry Creek were applied using application methods and formulations relevant to current operations confirms that, as might be expected, higher application rates and a lack of BMP implementation generally lead to higher herbicide concentrations in impacted waterbodies (Table 5). The highest herbicide concentrations were in bodies of water that were directly oversprayed (Newton et al., 1984, 1994, Feng et al., 1990, Thompson et al., 2004), had no buffer (Michael and Boyer, 1986, Thompson et al., 2004), and/or used the highest application rates (Newton et al., 1994, Michael et al., 1999). Compared to previous studies, application rates used at Needle Branch, Alto, and Dry Creek tended to be lower and no-spray buffer zones tended to be wider. Maximum water concentrations of herbicides also tended to be lower, in some cases by one or more orders of magnitude.

Michael (2004) reviewed studies of environmental fate of forestry herbicides. He identified a pattern of herbicide movement into streams that seemed to be consistent among studies, in which baseflow is characterized by herbicide concentrations that are near or below analytical limits and maximum herbicide concentrations in stream water occur immediately following application or during the first storm event, with concentrations decreasing with each subsequent storm event until the fourth or fifth post-application event, at which time herbicide concentrations fall below detectable limits. This pattern was generally true in the three U.S. studies summarized here.

Table 5

Peak herbicide concentrations, application rates, and BMPs employed in studies in which the herbicide active ingredients used at study sites were applied using application methods and formulations relevant to current forestry operations.

| Herbicide | Application Rate (kg/ha) | BMPs Employed | Type of Waterbody | Peak Water Concentration (µg/L) | References |
|---------------------|--------------------------|---|------------------------------------|--|--------------------------|
| Glyphosate | 3.3 | None, application swaths crossed stream | Small stream, shallow beaver ponds | 300 | Newton et al. (1984) |
| Glyphosate | 2 | 10-m SMZ or no SMZ + intentional overspray | Creek + tributaries | 162 (no SMZ), < 1.0 (with SMZ) | Feng et al. (1990) |
| Glyphosate | 4.12 | None, intentional overspray | Streams, ponds (multiple sites) | 1200 | Newton et al. (1994) |
| Glyphosate | 1.07–2.14 (1.95 average) | 3 zones: direct overspray; adjacent to overspray; 30–60 m buffer from overspray | Wetlands | 310 ^a (buffer)1 80 ^b (adjacent)1950 (overspray) | Thompson et al. (2004) |
| Hexazinone | 1.7 | Not stated | Stream | < 1.0 | Neary et al. (1984) |
| Hexazinone | 6.72 | 10-m buffer on perennial streams | Stream | 472 | Michael et al. (1999) |
| Imazapyr | 2.24 | 15-m no-spray buffer or no buffer | Streams | 30 (buffer)169 (no buffer) | Michael and Boyer (1986) |
| Sulfometuron methyl | 0.42 | 5-m buffer | Watershed perimeter ditches | 7 | Neary and Michael (1989) |
| Sulfometuron methyl | 0.42 | 15-m SMZ where water visible | Streams | 44 | Michael (2003) |
| Sulfometuron methyl | 0.053 | 3-m buffer | Drainage ditch | 24 | Michael et al. (2006) |

^a 14 of 16 samples were below the detection level (< 10 µg/L).

^b Mean of 11 wetlands, individual sample maximum not provided.

4.4. Application rates

An examination of application rates reported in the Needle Branch, Alto, and Dry Creek studies shows that herbicides were typically applied at rates well below the maximum label rates. For example, at Dry Creek, Chopper® was applied at the rate of 0.38 L/ha, which is less than 7% of the label maximum recommended rate (5.9 L/ha) for site preparation in loblolly pine. At Alto, Accord® was applied at the rate of 4.7 L/ha, which is about 27% of the label maximum recommended rate (17.5 L/ha) for site preparation in loblolly pine. The exception to this pattern was the Oustar® application at Dry Creek, which was made at a recommended label rate of 0.84 kg/ha (Scarborough et al., 2015). The authors noted that the landowner typically used a lower application rate, but the higher label rate was used in the study to produce the herbicide runoff potential associated with label rates (Scarborough et al., 2015). In the two Bay of Plenty sites, both Release KT® and AGPRO Valzine Extra were applied within label recommendations. However, both these herbicide products were developed specifically for use in New Zealand's *P. radiata* forests.

According to a recent survey of herbicide use in forestry in the U.S., the practice of using less than maximum label rates of herbicides is widespread (NCASI, 2015). NCASI (2015) reported a national trend of application rates lower, and sometimes significantly lower, than the rates recommended on herbicide labels. For example, according to the survey, the area-weighted average application rate for sulfometuron methyl in the southern US is only about 30% of the maximum label rate. Similarly, the area-weighted average application rates across the United States for glyphosate, hexazinone, imazapyr, and metsulfuron methyl fall in the range of about 24–35% of their respective label maximum rates (NCASI, 2015). An earlier survey, conducted in 1999, also reported the same trend to use lower than maximum label rates (Shepard et al., 2004). The reductions reported were greater in the 2011 survey, however, and NCASI (2015) noted that the average volume of herbicides applied per hectare declined between 1999 and 2011, with reductions of 13.7%, 55%, and 9.1% in applications made for site preparation, herbaceous weed control, and release, respectively.

Under terms of FIFRA and the Food Quality Protection Act (FQPA), USEPA is responsible for registration and periodic review of herbicides and other pesticides used in the United States. As part of both the registration and review processes, USEPA conducts ecological risk assessments using a variety of default assumptions, one of which is that the herbicide will be applied at the maximum rate allowed on the

product's label, or, in the case of new registrations, the maximum rate proposed by the manufacturer (USEPA, 2009). Based on the outcome, EPA identifies specific mitigation measures and application rates that are intended to ensure that non-target organisms will not be placed at risk from use of the product (USEPA, 2016). A similar procedure is followed by the New Zealand EPA when assessing applications for product registration. The forest industry practice of using herbicide application rates lower than label maximums adds another level of protection and increases the margin between expected environmental concentrations and exposure levels that pose little to no risk to non-target organisms. In addition, NCASI (2015) reported the wide-scale adoption of spray drift control technologies by the forest products industry, which further reduces the potential for movement of applied herbicides into waterbodies.

5. Conclusion

Operational forestry herbicide applications using modern BMPs were made at five distinctly different sites in the US [Coastal Range of Oregon (Needle Branch), East Texas (Alto), and southwest Georgia (Dry Creek)] and New Zealand (Bay of Plenty region; Baillie et al., 2015, Baillie, 2016). SMZs, ranging from 12 m to 21 m, were installed as specified in each US state's BMP guidelines. No-spray zones equivalent to the SMZs were observed at Alto and Dry Creek. No-spray zones at Bay of Plenty Pekepeke were 10 m (Year One) or 20 m (Year Two) and those at the Eastern Bay of Plenty site were 30 m. At Needle Branch, an 18-m no-spray zone was observed, as specified in the Oregon FPA guidelines, for the fish-bearing portion of the stream. In addition, half-boom spraying, while not required, was employed along the upper non-fish-bearing portion of the stream. At most study sites, maximum herbicide concentrations in stream water were in the low ppb range and occurred as brief (< 24 h) pulses associated with storm water runoff from just the first few post-application storm events. At the Bay of Plenty Pekepeke site, peak concentrations were higher and occurred on the day of application, presumably due to direct deposition into the stream from inadvertent overspray or drift. However, the peaks were brief, lasting less than 8 h.

The herbicides used in these studies have low acute toxicity to fish, amphibians, or aquatic invertebrates (see, e.g. Tatum, 2004). At all sites, maximum stream water concentrations of herbicides were lower than the concentrations associated with acute toxicity in these organisms. Aquatic plants, on the other hand, show more sensitivity to these forestry herbicides. The lowest reported toxicity values for some species of algae and macrophytes are below the peak concentrations reported for imazapyr, hexazinone, sulfometuron methyl, and terbutylazine at one or more sites. However, the exposure durations, especially to peak concentrations, reported in these field studies are much shorter than those used in the laboratory toxicity testing upon which the EC₅₀ values are based and there is ample evidence that aquatic plants can tolerate much higher exposures if exposure times are short.

Overall, the low exposure levels and short exposure durations reported in the five studies described here suggest that use of herbicides in forestry while following modern BMPs poses minimal risk to non-target aquatic animals. A greater potential of risk to non-target plants exists due to the greater sensitivity of plants to herbicides, however, this potential for risk may be mitigated by the very brief exposures to peak concentrations and the pattern of pulsed, rather than continuous, exposures.

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