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Abiotic Factors Influence Surface Water Herbicide Concentrations Following Silvicultural Aerial Application in Oregon's North Coast Range

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ABSTRACT

Nontarget impacts of routine aerial silvicultural practices on surface water quality are not well documented. Thus, uncertainty remains regarding herbicide treatment effects on ecological and human health. To investigate factors that influence silvicultural herbicide concentrations in surface water and identify any potential risks, we conducted a 2-year study that monitored multiple streams for herbicide residues following aerial application of glyphosate, clopyralid, sulfometuron methyl (SMM), and metsulfuron methyl (MSM). The monitored streams drain recently harvested forest lands that also serve as municipal water sources for nearby communities in western Oregon's north coast range. A paired watershed design targeted predicted episodic pulses with water samples collected before, during, and after herbicide application, and during the first posttreatment storm events. We report no relic herbicide detections in control or test streams. Aerial application of glyphosate, clopyralid, SMM, and MSM resulted in no detections in control streams and only trace, episodic concentrations in test streams. Across all test streams from both study years, maximum SMM and MSM detections (≤0.030 µg/L) consistently occurred during the first storm event at sampling locations closest to the treated harvest unit. Results indicate that proximity to the treatment site, time from application, and rainfall influence herbicide presence and concentrations in surface water. Furthermore, detections of trace SMM and MSM concentrations were more than 25 000-fold and 60 000-fold below federal human health safety benchmarks for chronic exposure, respectively. We provide empirical context for understanding surface water herbicide presence following aerial silviculture application under modern forestry best management practices and identify potential risk to ecological and human health. *Integr Environ Assess Manag* 2020;16:114–127. © 2019 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals, Inc. on behalf of Society of Environmental Toxicology & Chemistry (SETAC)

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INTRODUCTION

Forest management is necessary to the maintenance of forest health and sustaining the productivity of forest systems (Smith et al. 2011; Jackson and Finley 2016). In pursuit of goals specific to commercial forestry, herbicides gained a significant role in federal, public, and private forest land management in the 1960s (Wagner et al. 2004). Since then, it has been demonstrated that herbicides are effective in controlling undesirable or damaging vegetation and have become an essential tool for profitable timber production around the world. In the Pacific Northwest of the United States, forest managers commonly use a variety of herbicide ingredients and preparations, including glyphosate; clopyralid; triclopyr; 2,4-dichlorophenoxyacetic acid (2,4-D); and sulfometuron methyl (SMM) (Wagner et al. 2017).

On average, 1 to 3 herbicide products are applied during 1 to 2 application events in a rotation of 30 to 80 y. Although applications of forestry herbicides are infrequent and at lower rates than agricultural and other commercial uses, concerns remain regarding perceived nontargeted exposure and the potential human health risk (Bernstein et al. 2013) and aquatic biota (Murdock et al. 2013; Carpenter et al. 2016). Nontarget exposure may occur through herbicide mobilization, which can potentially contaminate surface water via drift and runoff, and groundwater via infiltration (Sopper 1975; Louchart et al. 2001; Fulton and West 2002), all of which are dependent on product solubility and soil sorption potential, climatic conditions, topography, and soil properties (Wauchope 1978; Capel et al. 2001). Consumption of contaminated water is a public health concern (Gasnier et al. 2009; Bernstein et al. 2013; Mesnage et al. 2013), and

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nontarget impacts on aquatic biota within treated areas pose an ecological concern (Hayes et al. 2002; Murdock et al. 2013; Orton and Tyler 2015; Carpenter et al. 2016). Consequently, research has focused on assessing potential herbicide exposure vectors (Bundschuh and McKie 2015), environmental fate and persistence (Capel et al. 2001; de Jonge et al. 2001; Tatum 2004; Newton et al. 2008; Chang et al. 2011), and risks to sensitive species that may encounter biologically relevant concentrations in the environments they inhabit (McComb et al. 2008; Forbes et al. 2015). In response, modern forestry best management practices (BMPs), including silvicultural chemical BMPs (SCBMPs), have been designed and implemented to reduce potential surface water and groundwater contamination (Michael 2004). For example, SCBMPs include specified widths of vegetated buffers between actively treated areas and stream channels to minimize surface water contamination by aerosolized herbicide during application and runoff after application (Borin et al. 2004; Michael 2004; Zhang et al. 2010; McBroom et al. 2013; Scarbrough et al. 2015). While it has been demonstrated that modern BMPs are effective at mitigating nontargeted herbicide mobilization (Borin et al. 2004; Michael 2004; Zhang et al. 2010; McBroom et al. 2013; Scarbrough et al. 2015), limited peer-reviewed studies exist (Louch et al. 2017) that describe the magnitude and duration of trace herbicide concentrations in stream-surface-draining timber lands. Furthermore, assessments of human and ecological risk from such exposures are warranted.

Due to such concerns in and around communities near forestry operations, current regulatory initiatives that aim to restrict forestry-related aerial herbicide application are being debated regionally, including ongoing efforts in Lincoln County, on Oregon's northern coast. Therefore, the purpose of this study was to determine whether aerially applied herbicides mobilize to stream-surface-draining treated timber units within Oregon's north coast range, including a municipal water source stream. We targeted anticipated episodic pulses and monitored the magnitude and duration of detectable herbicides during application, through the immediate months following application, and during subsequent rainfall events. Our 2-year study monitored streams of paired watersheds during a pilot study year, followed by targeted sampling of treated watersheds to further quantify and corroborate initial observations of herbicide mobilization to surface water during the second year.

METHODS

Approach

We monitored 1 treated and 2 control watersheds in 2016, and 2 treated and 1 control watersheds in 2017. All study watersheds were located in Oregon's north coast range, within 10 miles of Tillamook, Oregon (Figure 1). To monitor for aerial drift, samples were collected from treatment and control streams before, during, and immediately after herbicide application. To monitor for runoff, samples were collected before, during, and immediately after the first 3 storms forecasted to be greater than 0.5 inches of rainfall within 24 h.

Treated forestry units were located within the Killam Creek (2016, 2017), Short Creek (2016), and Bear Creek (2017) watersheds (Figure 1, Table 1), with sampling sites located in the sole perennial stream draining each of the treated units. These treatment streams were sampled at an upstream site immediately downhill of the associated timber unit and a downstream site near the timber company property boundary. During both years, treatment sites were paired with negative control streams (Figure 1). Treatment stream sampling sites were located to quantify herbicide mobilized during application (drift) and subsequent rainfall (runoff). Control stream sampling sites were located to quantify effects of legacy herbicide residue and the spatial extent of drift.

Study sites

2016 sites. Killam Creek is a second-order stream (Strahler 1954, 1957) that contributes to the Tillamook municipal water system. The Killam Creek watershed contains numerous active forestry units. The 23-hectare Powerline forestry unit is located 450 to 680 m above mean sea level (AMSL) and presents a west/southwest aspect with a mean slope of approximately 30%. Powerline was the only unit treated with herbicide within the Killam Creek watershed in 2016. Following harvest, herbicides were applied by helicopter in preparation for reforestation in July 2016. The sole perennial stream draining Powerline, Powerline Creek, a first-order stream less than 5 m bankfull width, represents the herbicide treatment stream (Figure 1). The 2 Powerline Creek sampling sites included an upstream site, 120 geodesic m from the base of the unit, and a downstream site, 2.7 geodesic km (3 stream km) downstream of the unit and 1.1 geodesic km (1.5 stream km) upstream from Tillamook's municipal water supply intake.

Surface water samples were also collected from an intrawatershed control stream in the adjacent subwatershed north of Powerline, designated as Killam Creek (Figure 1). At this location, Killam Creek is a first-order stream less than 5 m bankfull width; it drains harvest units not treated with herbicide in 2016. Killam Creek sites thus provided control associated with application drift and short-term legacy herbicide residue.

However, potential herbicide legacy existed within Killam Creek due to glyphosate, MSM, SMM, clopyralid, and triclopyr treatments during 2012 to 2015. As a result, a second, out-of-watershed, negative control stream was also sampled in 2016. Short Creek is a first-order stream less than 5 m bankfull width, located approximately 20 geodesic km (west/northwest [WNW]) of Killam Creek, north of Oceanside, Oregon (Figure 1). Aside from 2010 and 2013 targeted roadside herbicide applications, the Short Creek watershed had not been harvested or treated with herbicide in approximately 30 y. Including Short Creek as an additional negative control allowed for the evaluation of any long-term herbicide legacy effects.

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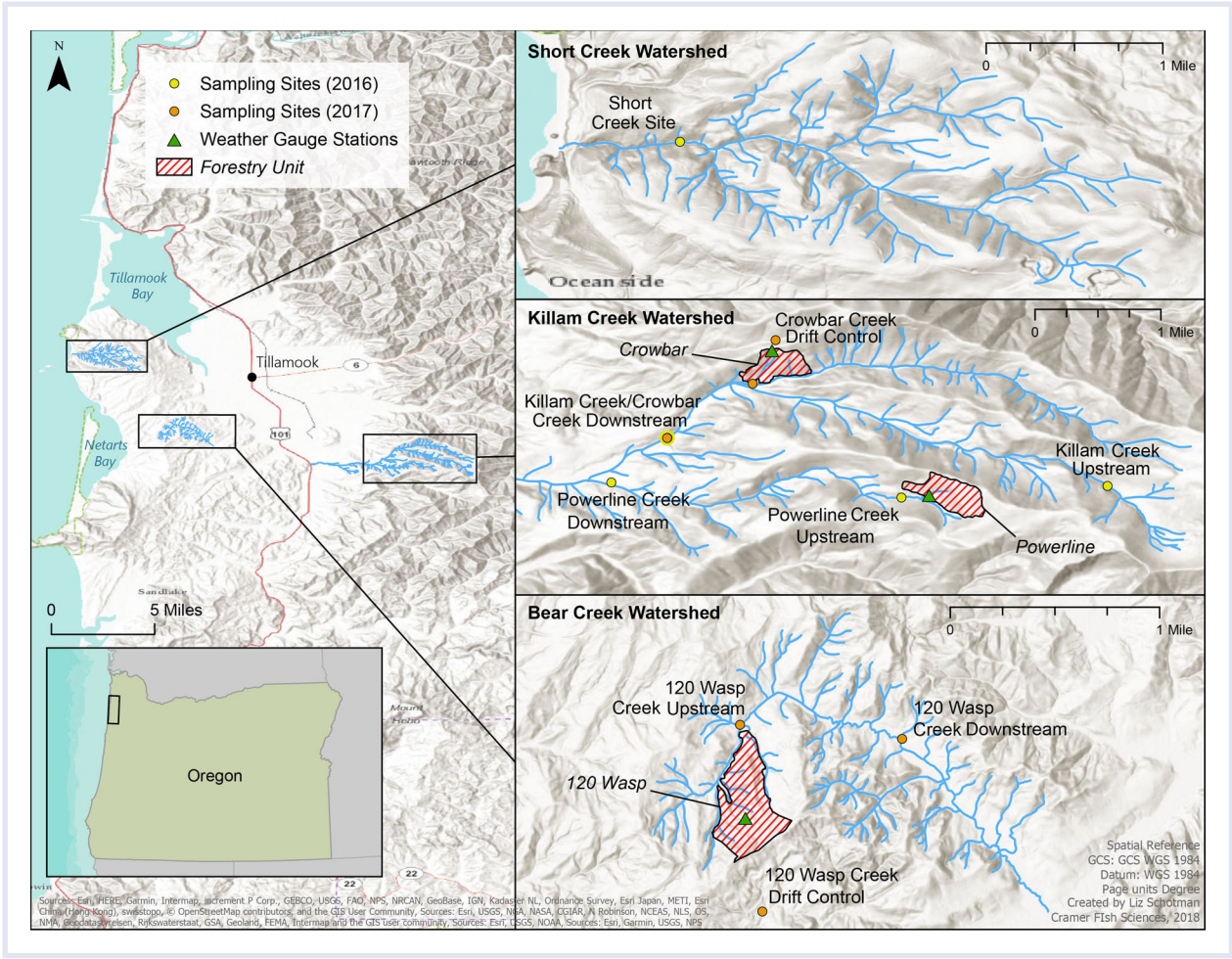

Figure 1. Map indicating locations of study area, forestry units, treated watersheds, control and treatment streams, sampling sites, and weather stations.

2017 Sites. Three sites were sampled within the Killam Creek watershed and 3 within the Bear Creek watershed, which drains into a tributary of the Tillamook River.

Crowbar is a 19-hectare forestry unit within Killam Creek and was the only unit within the watershed herbicide treated in 2017. Crowbar is located 100 to 200 m AMSL and

Table 1. Sampling site location summary and design function

Study Year	Watershed	Unit or stream	Position	Design function
2016	Killam Creek	Powerline	Upstream	Treatment (adjacent)
			Downstream	Treatment (distant)
		Killam	Upstream	Negative control (short-term, adjacent)
			Downstream	Negative control (short-term, distant)
	Short Creek	Short Creek	N/A	Negative control (long-term)
2017	Killam Creek	Crowbar	Upstream	Treatment (adjacent)
			Downstream	Treatment (distant)
		Crowbar drift control	N/A	Negative control (drift)
	Bear Creek	120 Wasp	Upstream	Treatment (adjacent)
			Downstream	Treatment (distant)
		120 Wasp drift control	N/A	Negative control (drift)

N/A = not applicable.

presents a generally south/southwest aspect with a mean slope of approximately 32%. In July 2017, Crowbar was herbicide-treated by helicopter to release the stand from competitition with nontarget plants. The sole perennial stream draining Crowbar, Crowbar Creek, represents an herbicide treatment stream. The Crowbar upstream sampling site was located 70 geodesic m from the base of the Crowbar unit, at a location where Crowbar Creek is a first-order stream less than 5 m bankfull width with peak observed flows <10 cfs (0.28 cms). The downstream Crowbar Creek site was located 1.4 geodesic km (1.6 stream km) downstream of the unit, at a location where Crowbar Creek is still a first-order stream approximately 10 m bankfull width with peak observed flows of approximately 50 cfs (1.42 cms). To quantify application drift effects, surface water samples were also collected from an unnamed tributary stream in the adjacent subwatershed. Crowbar Control Creek (aka Mill Creek) is located approximately 110 m north of the northern (uphill) end of the unit. At the sampled location, Crowbar Control Creek is a first-order stream less than 5 m bankfull width.

120 Wasp is a 33-hectare forestry unit and was the only unit treated with herbicide within the Bear Creek watershed in 2017. 120 Wasp is located 20 to 120 m AMSL and presents a generally northwest aspect with a mean slope of approximately 11%. Following harvest in July 2017, 120 Wasp was herbicide-treated by helicopter in preparation for subsequent planting. Aside from targeted roadside treatments in 2006, 2010, 2013, and 2016, no units within the watershed had been treated with herbicide during the previous 10 y. The sole perennial stream draining the 120 Wasp unit, 120 Wasp Creek, represents a treatment stream for the 2017 study. The 120 Wasp upstream site was located 300 geodesic m from the base of the unit, at a location where 120 Wasp Creek is a first-order stream less than 10 m bankfull width with peak observed flows approximately 6 cfs (0.17 cms). The downstream site in 120 Wasp Creek was located 1.5 geodesic km (1.9 stream km) downstream of the unit, at a location where 120 Wasp Creek is still a first-order stream approximately 10 m bankfull width with peak observed flows approximately 15 cfs (0.42 cms). To control for application drift effects, surface water samples were collected from a single site within an unnamed tributary stream in the adjacent subwatershed, which we refer to as 120 Wasp Control Creek, located approximately 375 m south of the southern (uphill) end of the unit.

Herbicide application

2016 Study. Beginning at 6:28 AM on 28 July 2016, under clear skies, with winds of 0 to 5 km/h from the northeast, and ambient air temperature approximately 18 °C, a mix of herbicide and surfactant plus adjuvant products was applied to the Powerline unit. From an elevation of approximately 6 m above the vegetation canopy, a helicopter applied a mix of Glyphosate 5.4® (Alligare) and SFM Extra® (Alligare). Glyphosate 5.4, with the active ingredient glyphosate, was applied at a target rate of 4.7 L/hectare. SFM Extra, with the active ingredients sulfometuron methyl (SMM) and metsulfuron methyl (MSM), was applied at a target rate of 280 g/hectare. Herbicide mixture adjuvants included Crosshair® (Wilbur-Ellis), for drift and deposition control at a target rate of 290 mL/hectare, and Syl-Tac® (Wilbur-Ellis), a surfactant, at a target rate of 440 mL/hectare.

2017 Study. Beginning at 10:10 AM on 13 July 13 2017, under high clouds and intermittent fog, with winds of 0 to 5 km/h from the south to southwest, and ambient air temperature approximately 16 °C, a mixture of herbicide and surfactant and adjuvant products was applied to the Crowbar unit. From an elevation of approximately 9 to 15 m above the vegetation canopy, a helicopter applied a mixture of Oust® XP (Bayer) and Transline® (Dow Agro). Oust XP, with the active ingredient SMM, was applied at a target rate of 200 mL/hectare. Transline, with the active ingredient clopyralid, was applied at a target rate of 4.7 L/hectare. Crosshair was also included at a target rate of 290 mL/hectare.

Beginning at 9:10 AM on 17 July 17 2017, under clear skies, with winds of 0 to 5 km/h from the west, and ambient air temperature approximately 15 °C, a mixture of herbicide and surfactant and adjuvant products was applied to the Powerline unit. From an elevation of approximately 9 to15 m above the vegetation canopy, a helicopter applied a mixture of, Oust® Extra (Bayer) and Glyphosate 5.4. Oust Extra, containing the active ingredients SMM and MSM, was applied at a target rate of 290 mL/hectare. Glyphosate 5.4 was applied at a target rate of 4.7 L/hectare. Crosshair and Syl-Tac were applied with target rates of 290 mL/hectare and 440 mL/hectare, respectively.

Water sampling

Sample collection included both structured time series during application and rain events, and grab samples collected at strategic baseline time points and upon retrieval of autosamplers. During each year, sampling occurred 1) prior to application (preapplication baseline grabs); 2) during and immediately following application (application time series); 3) monthly after application but before the rainy season (postapplication baseline grabs); and 4) during and after the first 2 (2016) or 3 (2017) rain events delivering more than 13 mm (0.5 inches) in 24 h (storm time series). Within application and storm events, sampling intervals were designed to capture anticipated pulses of herbicide, as described by Dent and Robben (2000) and more recently validated by Louch et al. (2017). To minimize potential contamination, surface water and tank samples were collected and transported independently by study team personnel to provide isolation from potential contact by forestry operations personnel.

Application and storm time series samples were collected by autosamplers (ISCO® 6712; Teledyne Technologies Inc, Lincoln, Nebraska). Autosamplers collected 300 mL water samples into clean glass bottles through clear vinyl suction

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tubing secured within the streambed with landscaping pins and substrate. Autosamplers were also secured to the stream bank. Upon sample retrieval, samples were transferred into clean amber glass bottles and maintained at 4 °C until analysis by Anatek Labs, Inc (Moscow, Idaho). Between each use, autosamplers, tubing, and bottles were washed and triple-rinsed with tap water.

Grab water samples were collected in duplicate prior to herbicide application from all treatment sites into clean amber glass bottles for herbicide analysis and into clean high-density polyethylene bottles for total suspended solids (TSS) analysis. Briefly, grab-sample collection involved facing the bottle opening upstream to fill with flowing water while not disturbing benthic substrate. Samples were generally collected near the surface layer of the stream. Most sampling locations were shallow enough that it was impossible to completely submerge the bottle opening.

2016. Monthly surface water–grab samples were collected from all treatment and control sites April 2016 to January 2017. For surface water collections by autosampler during and following application and storm events, 1 preprogrammed autosampler was installed at each of the 4 sampling sites within the Killam drainage. Programming for application events involved the collection of duplicate surface-water samples at 0, 6, 12, 24, and 32 h post treatment (HPT). Programming for rain events involved the collection of duplicate surface water samples at 0, 6, 12, 24, 48, and 72 h after the start of each storm.

2017. Monthly surface water–grab samples were collected from treatment and control sites June 2017 to January 2018, as described for 2016. One preprogrammed autosampler was installed at each of the 3 sites for each application and storm time series. Based on 2016 study results, sampling intervals were refined to more frequently collect samples to best capture the anticipated peak concentration. Autosamplers were programmed to collect duplicate samples every 2 h, from the scheduled time of application initiation through 12 HPT.

Due to very low duplicate sample variability in laboratory results from the 2016 study and the 2017 application event, singleton samples were collected more frequently throughout the duration of the storm events to best capture runoff and anticipated peak concentrations. Each autosampler was equipped with a cellular modem (ISCO 6712ci, Teledyne), enabling telephone-based remote control of the sampling program, and ensuring that each autosampler program start time was coordinated with the onset of the storm. Storm initiation was determined by remotely accessing rainfall data from a weather station placed on the 120 Wasp unit.

Laboratory analysis and quality assurance

Standard methods were used to detect acid equivalent (a.e.) values of clopyralid and triclopyr (US EPA Method 8151 with GC/MS/MS), and glyphosate and aminomethylphosphoic acid (AMPA) (US EPA Method 547 with HPLC). The US EPA Method 8321b with LC/MS/MS was used to detect the active ingredient (a.i.) of SMM and MSM, and SM 2540D for the quantification of TSS. Detections were reported relative to the practical quantification limits (PQL), the lowest calibration standard concentration, of each method for clopyralid and triclopyr (0.1 µg/L), glyphosate/AMPA (5 µg/L), SMM and MSM (0.01 µg/L), and TSS (1 mg/L).

For the extract preparation and detection of the sulfonylurea (SU) active ingredients by USEPA Method 8321b, 200 mL aliquots were acidified and subjected to solid-phase extraction eluted through a conditioned Strata X-33 cartridge, followed by concentration to 1 mL final volume. Sample extracts were analyzed using LC/MS/MS using the following parent–daughter transitions: MSM, 382 to 167 m/z and 382 to 199 m/z and SMM, 365 to 150 m/z and 365 to 199 m/z.

For the purposes of analytical quality control, laboratory control samples, matrix spikes, matrix spike duplicates, and method blanks were run prior to each analytical batch from a sampling event. The quantification of each analyte was compared against calibration standards, which were prepared from primary standard solutions for each analyte and analyzed in accordance with method-specific requirements.

Water quality, weather, and hydrology

During both years, water quality data were collected at the time and location of each grab water–sample collection and/or autosampler retrieval (data not shown). Water quality data included temperature and dissolved oxygen (ProODO, Professional Series, YSI Inc), pH (pH-Fix test strips, Macherey-Nagel), current velocity (Flow Probe FP111, Global Water), and conductivity (YSI Model 30 handheld salinity, conductivity and, temperature system, YSI Inc).

In 2016, a data-logging pressure transducer (Onset® HOBO® model U20L-04) was deployed at the upstream site of Powerline Creek to monitor stream depth (stage) continuously. Pressure data were adjusted to account for changes in regional air pressure using data from the nearest weather station (KTMK, located at the Tillamook, OR airport, 8 km WNW from study area) and converted to relative change in water depth compared with depth at the time of deployment. A rain gauge (Onset HOBO model RG3) was deployed continuously on the Powerline unit from 31 August 2016 to 15 December 2016, except 10 to 30 September 2016, when the gauge was removed for calibration and maintenance. During this period, regional rainfall data from the KTMK weather station were downloaded to provide an estimate of rainfall on the study area (WU 2017).

At each of the Crowbar and 120 Wasp units, a set of remote sensing modules was deployed on 21 June 2017 with continual weather data recording through January 2018. Temporary data interruptions occurred on 3 occasions associated with 2 events of wildlife disturbance to base stations (Onset HOBO H21 or RX3000) and an extremely

high-flow event that mobilized pressure transducers. Base stations were equipped with 1 electronic rain gauge (Onset HOBO RG3) to collect unobstructed incident rainfall, and each base station recorded data from all attached sensors. Pressure transducers and paired air pressure sensors (Onset S-BPB-CM50) were placed at upstream and downstream sites on each creek. Water pressure data were adjusted by subtracting time-matched air pressure measurements and then converting to depth.

Aquatic safety risk

Aquatic safety risk thresholds for salmonids, aquatic invertebrates, and aquatic plants were determined by applying the 6X hypothesis (Tucker and Leitzke 1979; USEPA 2004) to herbicide concentrations demonstrated to be lethal to half (50%) of a test population (LC50). Accordingly, the aquatic risk value was determined by dividing the lowest reported LC50 values (AQUIRE 2010) by 6. However, if a no observable adverse effect concentration (NOAEC) designation was available in the current literature, the lower of the NOAEC or the product of the 6x rule was selected as the aquatic risk value. Safety risk values for salmonids were calculated by dividing the lowest reported LC50 value by 20, to account for nonlethal effects such as olfactory system damage or impairment (Hasler and Scholz 1983) in light of observed deleterious effects of pesticide exposure on salmonid olfaction (Hay 1990; Moore and Waring 1996, 2001; Tierney et al. 2007a, 2007b, 2008).

RESULTS

Weather and hydrologic conditions

During both years of study, trace precipitation fell on the studied units between herbicide application and the first sampled storm event, with maximum daily rainfall of 0.8 cm. In 2016, the first sampled storm delivered 2.3 cm of rain to the Powerline unit during 48 h, with the majority falling during the first 24 h. The second sampled storm event delivered 6.8 cm of rain during 9 days. In 2017, the first sampled storm delivered 9.9 cm and 7.6 cm of rain to the 120 Wasp and Crowbar units, respectively, with the majority falling on the second and third days. The second sampled storm delivered 19.6 cm and 16.5 cm of rain to the 120 Wasp and Crowbar units, respectively. The third sampled storm was prolonged with modest rainfall, and delivered 2.3 cm and 1.78 cm of rain to the 120 Wasp and Crowbar units, respectively, during 6 days of near or slightly above 1.2 cm of rainfall per day.

During both years, streamflow at all sites responded strongly to rainfall, with timing of peak flows slightly lagged compared with peak rainfall intensity. Within each site, hydrologic response to storms differed as the rainy season progressed. Flow response to the first storm was muted compared with more the pronounced flow responses observed during subsequent storms.

Water quality

During 2016, water quality parameter values were generally similar at all sites within Powerline and Killam Creeks and at the Short Creek site, with the exception of conductivity being higher in Short Creek than in the Killam Creek watershed sites (data not shown). Water temperature, pH, conductivity, and dissolved oxygen (DO) exhibited seasonal variation at each site, and values from both sites within a stream generally fluctuated in parallel. During summer 2016, Short Creek and both downstream sites in the Killam Creek watershed were approximately 2 °C warmer than the upstream sites.

During 2017, water quality parameter values in Crowbar Creek and 120 Wasp Creek were generally similar at all sites (data not shown). Water temperature, pH, conductivity, and DO exhibited seasonal variation at each site, and values from both sites within a stream generally fluctuated in parallel. During summer 2017, 120 Wasp Downstream was approximately 2 °C warmer than other sites, while 120 Wasp Upstream exhibited lower DO and lower pH values compared with other sites.

Herbicide detections in surface water

Across both study years, all tested herbicides were not detected in surface water samples collected from control streams, and in preapplication baseline grab samples from the 3 treatment watersheds. Additionally, glyphosate and AMPA were not detected in any surface water samples from preapplication through poststorm grab samples in both study years. SMM, MSM, and clopyralid detections occurred during and following the application events, with maximum detections in both years observed during application or during the first subsequent storm event at the upstream treatment sites. For all downstream sites, herbicide detections were generally delayed and at lower concentrations compared with upstream sites. Following the first storm event in both years, concentrations of all tested herbicides from monthly baseline collections diminished to laboratory detection limits or nondetectable concentrations at all sites.

Powerline Creek upstream site had herbicide detections immediately following treatment, with SMM and MSM detected at 0.03 µg/L and 0.01 µg/L, respectively, at 32 HPT. Peak SMM and MSM concentrations occurred 49 days posttreatment (DPT) during the first storm event, at 0.08 µg/L and 0.07 µg/L, respectively (Figure 2A). By 111 DPT, SMM dissipated to <0.01 µg/L, and was maintained through the last collection at 179 DPT (Figure 2A). Similar trace SMM concentrations were observed at the Powerline Creek downstream site; however, MSM was not detected at either site (Figure 2B).

Similar to observations from Powerline in 2016, peak herbicide concentrations at both upstream sites of Crowbar and 120 Wasp were observed at approximately 2 to 5 h following application initiation, with gradual dissipation to <0.20 µg/L for the remainder of the sampling time

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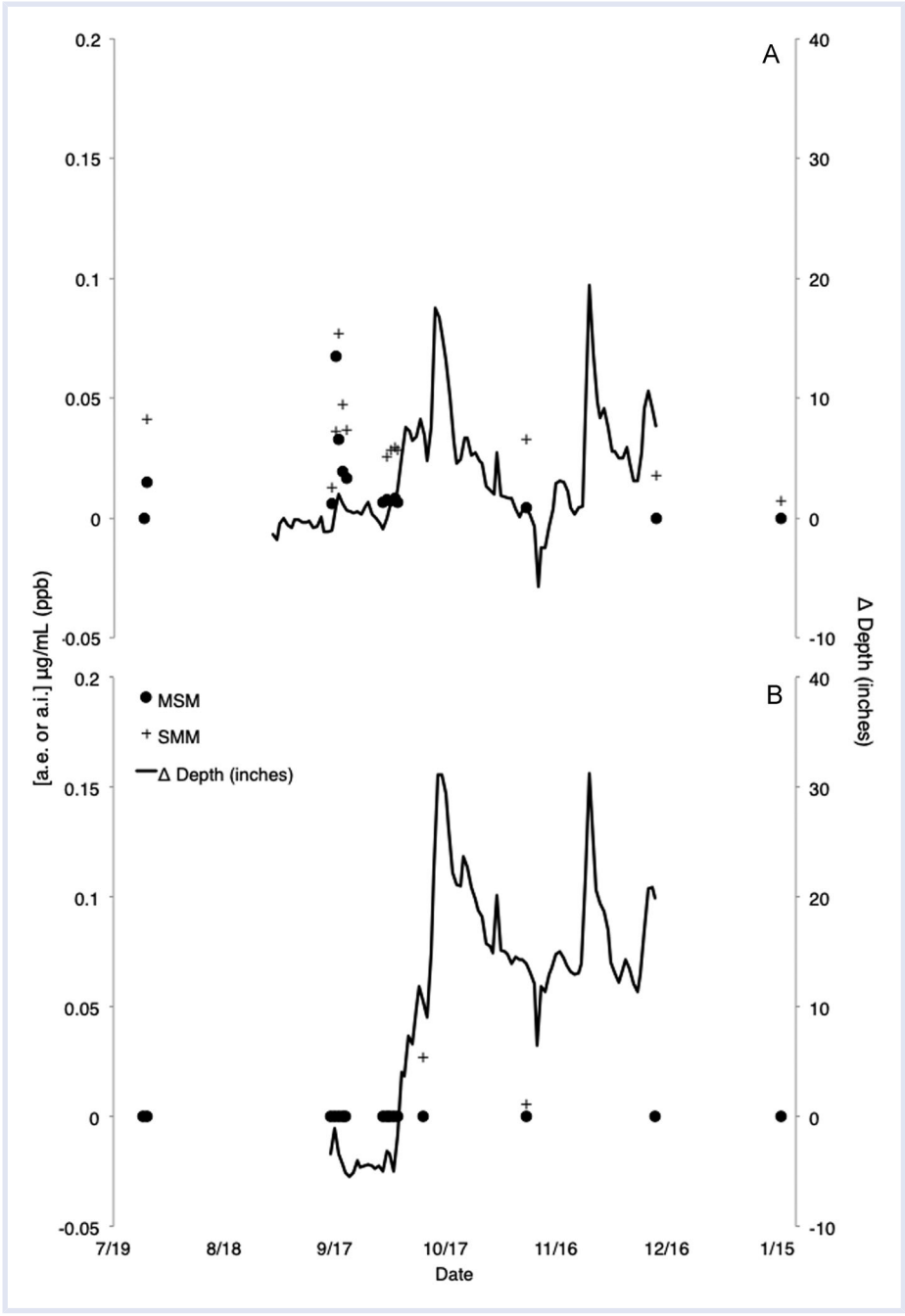

Figure 2. SMM (+) and MSM (●) maximum daily detections at Powerline Creek upstream (A) and downstream (B) sites. Samples were collected monthly by grab method and by autosampler for the 28 July 2016 application event and the first 2 storm events on 17–20 September 2016 (storm event 1) and 1–4 October 2016 (storm event 2). Change in water depth (black, solid) is represented on the right *y*-axis. a.e. = acid equivalent; a.i. = active ingredient; SMM = sulfometuron methyl; MSM = metsulfuron methyl. 54 × 79 mm (300 × 300 DPI).

series. Maximum concentrations during the application events were 1.4 µg/L clopyralid (Crowbar), 0.3 µg/L SMM, and 0.02 µg/L MSM (Figures 3A and 4A). Maximum herbicide concentrations during the first storm event were 1 µg/L clopyralid (Crowbar), 0.2 µg/L SMM, and 0.05 µg/L MSM, all within 21 h (Crowbar) and 72 h (120 Wasp) of the storm's first rainfall (Figures 3A and 4A). Herbicide concentrations diminished to trace (<0.15 µg/L) or nondetectable levels throughout the remaining 2017 storm events and baseline collections. Herbicide concentrations were detected more frequently at upstream sites than downstream sites, with clopyralid not exceeding 1 µg/L and SU <0.40 µg/L (Figures 3B and 4B).

Risk to the safety of salmonids and aquatic invertebrates

Assigned aquatic risk values were compared with maximum herbicide detections during both years of study (Table 1 and Figure 5). Maximum herbicide detections observed in

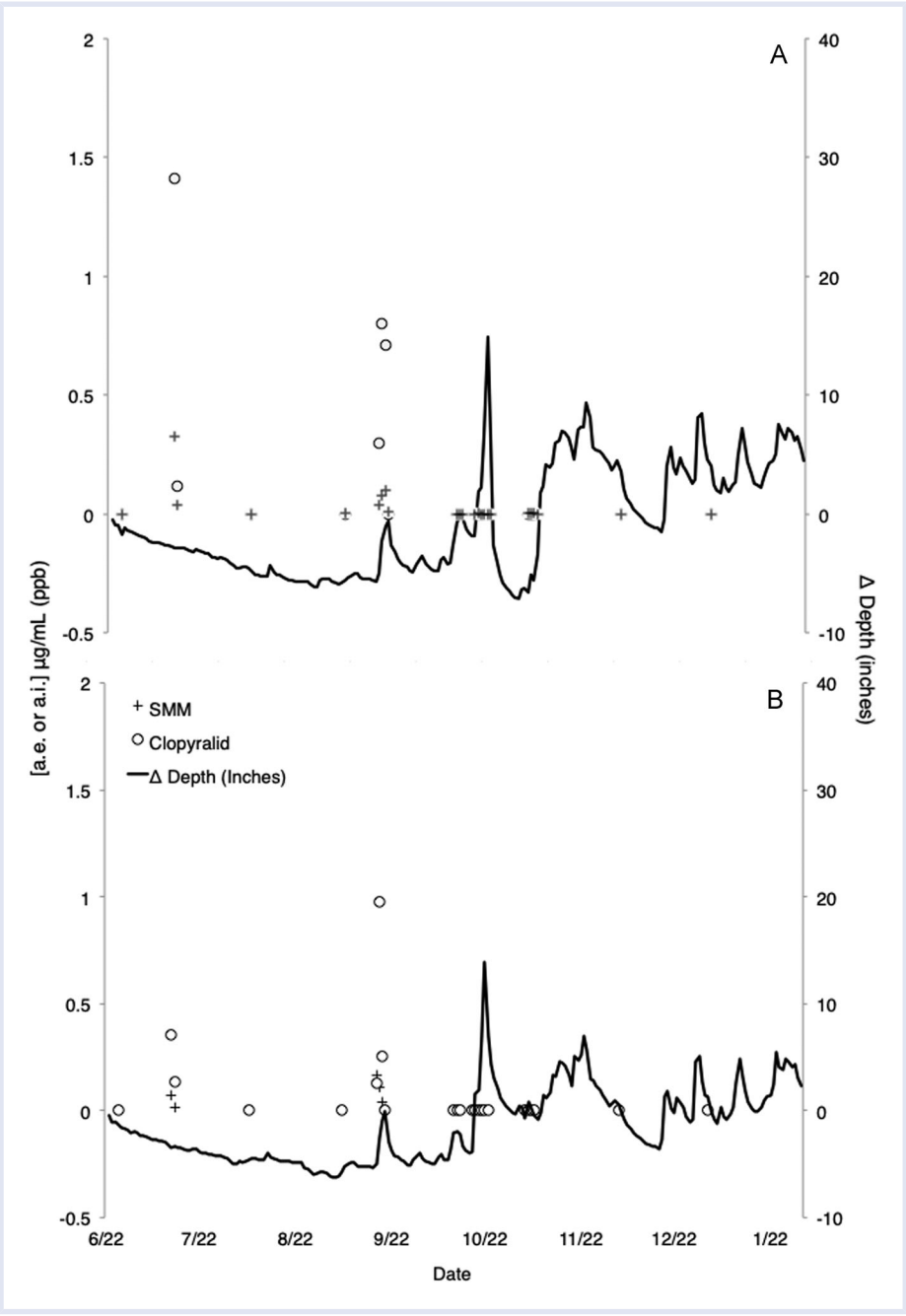

Figure 3. SMM (+) and clopyralid (○) maximum daily detections at Crowbar Creek upstream (**A**) and downstream (**B**) sites. Samples were collected monthly by grab method and by autosampler for the 13 July 2017 application event and the first 3 storm events on 17–19 September 2017 (storm event 1), 18–22 October 2017 (storm event 2), and 4–6 November 2017 (storm event 3). Change in water depth (black, solid) is represented on the right *y*-axis. a.e. = acid equivalent; a.i. = active ingredient; SMM = sulfometuron methyl. 54 × 79 mm (300 × 300 DPI).

2016 were approximately 1.6×10^5- to 2.1×10^6-fold below assigned risk threshold values for aquatic invertebrates and 8.0×10^3- to 1.9×10^6-fold below assigned risk threshold values for salmonids. Slightly higher herbicide concentrations were detected in 2017; therefore, ratios between detections and thresholds were greater. Maximum herbicide detections observed in 2017 were approximately 6.5×10^3- to 5.0×10^5-fold below assigned risk threshold values for aquatic invertebrates and 2.0×10^3- to 1.5×10^6-fold below assigned risk threshold values for salmonids.

Maximum detections and human health benchmarks

The USEPA and US Geological Survey (USGS) have established human health benchmarks for the protection of drinking water from surface and groundwater sources (Norman et al. 2018). Benchmarks for SMM, MSM, clopyralid, and glyphosate are provided in Table 2. In 2016, maximum herbicide concentrations in surface water draining the Powerline unit were found to be 22 000- to 22 900-fold below the human health safety thresholds. In 2017,

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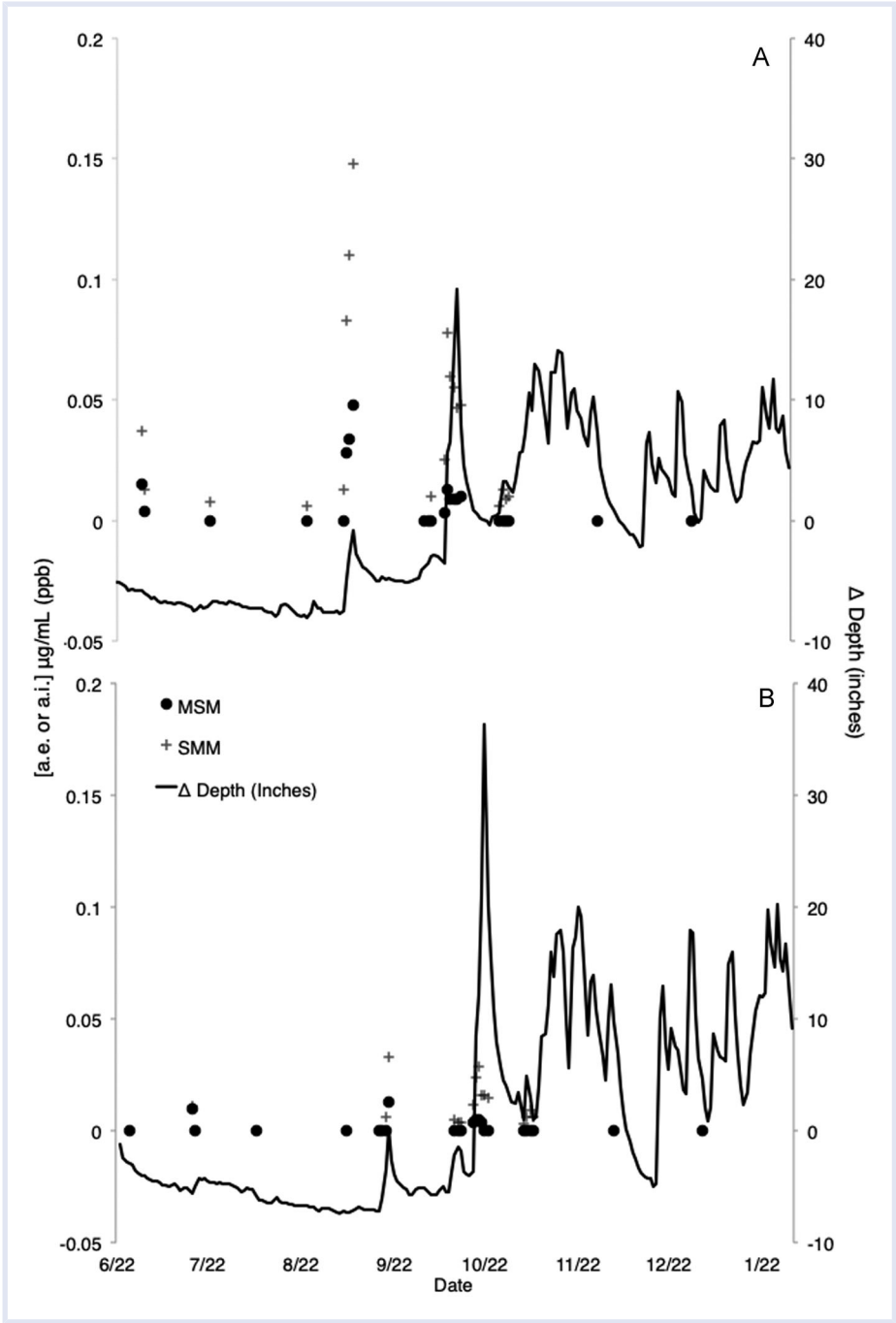

Figure 4. SMM (+) and MSM (●) maximum daily detections at 120 Wasp Creek upstream (A) and downstream (B) sites. Samples were collected monthly by grab method and by autosampler for the 17 July 2017 application event and the first 3 storm events on 17–19 September 2017 (storm event 1), 18–22 October 2017 (storm event 2), and 4–6 November 2017 (storm event 3). Change in water depth (black, solid) is represented on the right *y*-axis. a.e. = acid equivalent; a.i. = active ingredient. 54 × 79 mm (300 × 300 DPI).

the maximum concentrations of SMM (0.32 µg/L), MSM (0.05 µg/L), and clopyralid (1.41 µg/L) were found to be approximately 700- to 32 000-fold below the human health safety thresholds (Table 3, Figure 5).

DISCUSSION

We implemented a 2-year study monitoring surface water within drainages associated with 3 different forestry units to determine the magnitude and duration of herbicide presence before, during, and after aerial herbicide application. This study targeted and captured episodic herbicide pulses through treated drainages immediately following application and during subsequent posttreatment storm events. Due to sensitive detection limits and the extended length of monitoring, this is the first study to report trace herbicide detections at lower concentrations and beyond previously investigated durations (Michael 2004; McBroom et al. 2013;

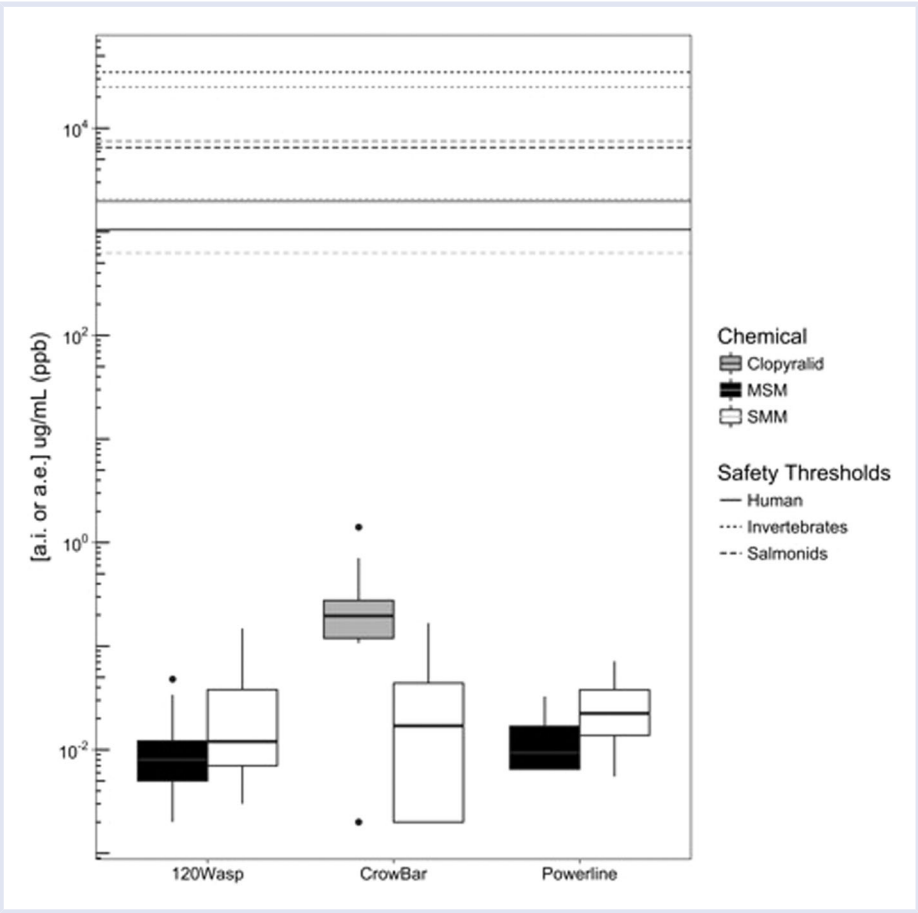

Figure 5. SMM, MSM, and clopyralid detections on logarithmic scale across all sites at Powerline, Crowbar, and 120 Wasp creeks across the entire 2016 to 2018 sampling period, compared with the range of aquatic safety values and human health limits and benchmarks. a.e. = acid equivalent; a.i. = active ingredient; SMM = sulfometuron methyl; MSM = metsulfuron methyl; boxes = 25th and 75th percentile data ranges; whiskers = maximum and minimum observed herbicide concentration; horizontal line within box = median observation; dots = outliers. All aquatic safety values (salmonids and invertebrates) and human health thresholds are represented by the horizontal lines. 39 × 39 mm (300 × 300 DPI).

Louch et al. 2017). Herbicide concentrations measured from in-basin and out-of-basin control streams in this study confirmed that aerial herbicide application did not have broad-reaching effects on surface waters beyond the study streams draining the treatment units. Throughout the duration of all sampling periods, nondetections were common. When detected, herbicide concentrations were low, including maximum peak detections observed during application and first storm events. We conclude that surface water from treatment drainages postsilviculture treatment pose minimal risk to aquatic safety and human health. In addition, we corroborate the efficacy of modern SCBMPs for the protection of riparian areas within herbicide treated drainages in Oregon's north coast range.

This study is also the first to report trace detections of SU during a period of months following 2 aerial silviculture applications. Herbicides were detected at concentrations as low as 0.01 µg/L (PQL) and 0.002 µg/L (minimum detection limit [MDL]), which is 2 to 3 orders of magnitude lower than previous studies (e.g., Michael 2004; McBroom et al. 2013; Louch et al. 2017) that reported MDLs of approximately 1 µg/L. Across 2 y of study and 3 timber units, we 1) quantified anticipated pulses of SU during application and the first storm event; 2) characterized the subsequent declines in herbicide persistence; and 3) further detected trace concentrations (<0.03 µg/L) throughout subsequent monitoring for more than 5 mo after treatment.

Chemical persistence of herbicides in the environment is largely dependent on their physicochemical properties. The stability and persistence of SU, specifically, are also affected by pH and temperature, with the environmental half-life of SU being inversely proportional to both (Tomlin 2009). Furthermore, herbicide degradation is driven primarily by hydrolysis and photolysis; when soil and water conditions are neutral or basic, rates of hydrolysis decrease and aqueous solubility increases (Hay 1990). Across the treatment watersheds, we generally observed surface water with neutral pH and cool temperatures, explaining relatively long half-lives and mobilization potential from treated areas into downstream surface water.

In addition to physicochemical characteristics, site-specific factors also determine the rate at which herbicides are mobilized to surface water. For example, meteorological conditions, soil type, drainage input, and topography

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Table 2. Risk to aquatic safety thresholds and maximum herbicide concentrations across all sites during 2016 and 2017

	Reported LC50 or EC50 range, or NOAEC* (µg/L)			Assigned aquatic risk value (µg/L)			Maximum detections: risk value					
							Powerline		Crowbar		120 Wasp	
	SMM	MSM	Clopyralid	SMM	MSM	Clopyralid	SMM	MSM	SMM	Clopyralid	SMM	MSM
Salmonids (*O. mykiss*)	12 500	150 000	103 500	625	75 000	6525	1:7813	1:1.9 mil	1:1953	1:20 391	1:4167	1:1.5 mil
Invertebrates (*D. magna*)	12 500–1 000 000	150 000	208 000–245 000	2080	25 000	34 700	1:156 250	1:2.1 mil	1:6500	1:24 610	1:15 200	1:0.5 mil

NOAEC = no observable adverse effect concentration; LC50 = concentration resulting in 50% lethality; EC50 = median effective concentration; SMM = sulfometuron methyl; MSM = metsulfuron methyl; mil = million. Aquatic risk values were derived from LC50 ranges for salmonids EC50 ranges or NOAEC for aquatic invertebrates (USEPA 2018; AQUIRE 2010)

influence herbicide presence and fate. When SU concentrations were compared between the Crowbar Creek and 120 Wasp Creek sites, SMM was present in surface water sooner after application and at higher concentrations at Crowbar Creek sites than at 120 Wasp Creek sites. Because target prescriptions of SMM were similar for both units, it is plausible that the approximately 10% concentration difference could have resulted from differences in attributes of these forestry units and their surrounding environments. For example, the mean slopes of the Crowbar and 120 Wasp units were 32% and 11%, respectively. During the first storm event at the upstream sites, peak SU was detected at Crowbar approximately 24 h prior to peak concentrations at 120 Wasp, likely reflecting the steeper terrain and associated faster runoff at Crowbar.

Herbicide detections during application at the proximate sampling locations for all 3 units cannot precisely be compared between the 2016 and 2017 study years, due to autosampler malfunction at the upstream site of Powerline. However, given results from 2017, and findings from previous studies monitoring similar application protocols (McBroom et al. 2013; Louch et al. 2017), it is reasonable to suspect that SMM and MSM concentrations at Powerline did not exceed 1 µg/L and 0.5 µg/L, respectively, at the upstream site.

Maximum SU detections in Killam and Bear Creeks occurred within 24 h of the second storm event, consistent with previously reported increases during the 12- to 72-h period after the initial rainfall (Scarbrough et al. 2015; Louch et al. 2017). By the second 2016 storm event, SU concentrations decreased from 0.08 µg/L (Powerline) and 0.20 µg/L (Crowbar, 120 Wasp) during the first storm to approximately 0.03 µg/L. Decreased concentrations during this second storm event did not appear to be driven by storm intensity because the second storm in 2016 delivered less precipitation, resulting in negligible change in stream depth, compared with 2017. By the third storm event in 2017, SU concentrations at Crowbar and 120 Wasp sites decreased to approximately 0.01 µg/L or at nondetection, and remained at trace or undetectable levels for all remaining baseline collections. Similar results were observed after the second rain event at the Powerline sites in 2016.

Trace concentrations were observed at each downstream location in each treatment stream for all collections. Although elucidiating mechanisms underlying environmental kinetics was beyond the scope of this study, decreased downstream concentrations were likely due to a combination of dilution (by tributary water inputs downstream of the treated unit), adsorption and retention (by soil and other organic material within the stream channel), and degradation (e.g., hydrolysis, photolysis, and biolysis). While not explored quantitatively, differences in stand density among units treated for release and those treated for site preparation may have affected differences in measured surface water concentrations among units, for example, Powerline versus 120 Wasp.

Unlike our observations associated with SU compounds, we observed early but nonpersistent clopyralid

Table 3. Human health risk thresholds and maximum concentrations of herbicides applied across all sites at Crowbar Creek and 120 Wasp Creek

	USEPA limits or USGS benchmarks (µg/L)			Maximum herbicide concentrations (µg/L) vs fold-difference					
Herbicide	HHBP	HBSL	MCL	Powerline		Crowbar		120 Wasp	
SMM	1760	—	—	0.08	1:22 000	0.32	1:5500	0.15	1:11 733
MSM	—	1600	—	0.07	1:22 857	n/a	n/a	0.05	1:32 000
Clopyralid	960	—	—	n/a	n/a	1.41	1:681	n/a	n/a
Glyphosate	—	—	700	0	0	n/a	n/a	0	0

USEPA = US Evironmental Agency; USGS = US Geological Survey; HHBP = USEPA chronic noncancer Human Health Benchmarks for Pesticides; HBSL = USGS noncancer Health-Based Screening Levels water quality benchmarks; MCL = maximum contaminant level for public drinking water (USEPA); SMM = sulfometuron methyl; MSM = metsulfuron methyl; n/a = not applicable or no detections reported; – denotes benchmark not established by USEPA or USGS.
HBSL exists only if the HHBP or MCL are not established by the USEPA.
Risk values were derived from the most recent (May 2018) USEPA and USGS benchmarks.

detections in the Crowbar drainage. These observations are likely due to clopyralid's physicochemical properties. Because degradation of clopyralid is primarily attributed to photolysis rather than hydrolysis (O'Neil 2006), it is likely that, after application, much of the clopyralid in the Crowbar unit degraded during the sunny summer months of 2017. It is plausible that the bulk of the clopyralid residues mobilized during the first storm event due to its low sorption potential (K_{OC}, soil organic carbon/water partition coefficient) (O'Neil 2006). Clopyralid degradation and mobilization by the first storm likely resulted in nondetections through the remainder of our monitoring.

Neither glyphosate nor AMPA were detected at any sampling locations during all collection events in both years. Because our assay protocol defined an MDL of 1 µg/L, we could not definitively conclude the absence of glyphosate or AMPA. For example, Louch et al. (2017) observed glyphosate at approximately 0.060 µg/L immediately following aerial application and 0.115 µg/L during the first significant storm event in Oregon's north coast range using similar application prescriptions under modern BMPs. Because glyphosate and AMPA have low water solubility and high K_{OC}, moderate mobilization into surface water is expected during storm events via overland flow (Tatum 2004; Candela et al. 2007; Dollinger et al. 2015). If glyphosate were mobilized, however, this likely occurred during the first or second storm event when TSS concentrations ranged approximately 350 to 500 mg/mL, indicating substantial surface soil runoff.

During both 2016 and 2017, the magnitudes of observed peak herbicide concentrations resulting from these treatments were orders of magnitude below conservative and widely accepted safety thresholds for direct or indirect effects of herbicides on aquatic invertebrates and salmonids. Peak observations for SU was more than 6500-fold below assigned risk values for invertebrates (*D. magna*), more than 1950-fold below assigned risk values for salmonids (*O. mykiss*), and more than 8.3×10^8-fold lower than previously reported values associated with concentrations (NOAEC) (Table 1 and Figure 5). Compared with SU, peak clopyralid concentrations observed posed even less of a risk to salmonids and invertebrates, with maximum detections at approximately 20 000-fold less than assigned risk values for both taxa.

Further, our risk assessment involved conservatively assigned risk values for the aquatic ecosystem and human health. Specifically, we assumed risk to be associated with continuous (chronic) exposure and not actual exposure to episodic pulses of narrow duration. For example, risk to aquatic life assumes at least 96 h of static exposure with survival and growth as the biological endpoint. Similarly, the determination of human health risk thresholds (Figure 5) considers daily consumption during the course of a lifetime. Adoption of these chronic exposure thresholds thus provides a larger margin of safety.

Nonenforceable human health benchmarks developed by the USGS for the protection of drinking water from surface and groundwater sources (Norman et al. 2018) include Human Health Benchmarks for Pesticides (HHBPs) and Health-Based Screening Levels (HBSLs). The HHBPs for SMM and clopyralid are 1760 µg/L and 960 µg/L, respectively, and the HBSL for MSM is 1600 µg/L. The established drinking water Maximum Contaminant Level is 700 µg/L for glyphosate, where these US EPA metrics assume chronic exposure as daily consumption of 2.5 L of similarly contaminated water during a 70-year life-span (USEPA 2017). Maximum herbicide concentrations in our study were 4 orders of magnitude below these benchmarks (Figure 5). Specifically, we observed maximum SU and clopyralid concentrations of 0.32 µg/L and 1.41 µg/L respectively, across both years. In the case of glyphosate, we consistently observed nondetection. However, if the maximum detection was assumed to be just below the laboratory's MDL for glyphosate (1 µg/L), that concentration would still be 700-fold below US EPA's MDL. Measured herbicide concentrations observed in surface waters during both years of this study were thus determined not to be a risk to human health.

CONCLUSIONS

During both years of this study, all surface water herbicide detections were orders of magnitude below aquatic biota

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safety risk values and human health benchmarks. Aerial application of forestry herbicides appears to mobilize trace concentrations (approximately ≤1 µg/L) into surface water of treated drainages, similar to previous reports (Louch et al. 2017). Mobilization during aerial application is attributed to spray drift. Subsequent rainfall then drives herbicide runoff from the treated unit to surface waters, primarily during the first major autumn storm event (Dent and Robben 2000; McBroom et al. 2013; Louch et al. 2017). Consistent with the literature, similar observations of applied herbicide detections and concentrations in this study across 3 treatment units in 2 successive years indicated that chemical-specific physicochemical properties and rainfall primarily influence instream herbicide concentrations. Specifically, herbicide residues dissipate following the first storm event, with concentrations at or near nondetectable levels by the second or third storm event. On an hourly scale during application and storm events, unit topography appeared to affect herbicide concentration magnitude and duration (cf max detections at Crowbar vs 120 Wasp sites).

Results of this study provide a relevant empirical context for understanding the potential effects and associated ecological and human health risks of aerial herbicide application on surface water quality in a coastal coniferous ecosystem as found in northwest Oregon. Results of this study also indicated that aerial application in conjunction with modern forestry SCBMPs are effective in preventing deleterious surface water contamination by silviculture treatment. Application of the methods reported here to other forest ecosystems in other biomes or ecoregions could be useful for evaluating effects of specific herbicide treatments across an array of settings to further inform forestry and land use managers and minimize potential risk to ecosystem and human health.

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Disclaimer—The authors declare no conflicts of interest.

Data Availability Statement—Any data is available upon request. Readers should contact Lauren Courter at lauren.courter@mthoodenvironmental.com.

SUPPLEMENTAL DATA

An Excel spreadsheet with raw data across the entire period of study. The data includes: herbicide detections, stream depth, rainfall, miscellaneous environmental data, temperature, and observational field notes.

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