Journal of Sustainable Watershed Science & Management 2 (1): 118–129, 2015
doi: 10.5147/jswsm.2015.0187

Aquatic Fate of Aerially Applied Hexazinone and Terbuthylazine in a New Zealand Planted Forest

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Received: December 4, 2014 / Accepted: March 4, 2015

Journal of Sustainable Watershed Science & Management - ISSN 1949-1425. Published By Atlas Publishing, LP (www.atlas-publishing.org)

Abstract

Herbicides are used to control competing vegetation during tree establishment, and are often critical to the productivity and economic viability of a planted forest crop. Despite increasing public concern over herbicide use in planted forests and potential impact on the environment, there is limited information on the aquatic fate of many of these herbicides when applied in forests according to standard operational procedures. Two herbicides commonly used in New Zealand's planted forests, terbuthylazine and hexazinone, were aerially applied during two consecutive years at 7.4 kg and 1.1 kg ha^{-1} respectively, to a 12.5 ha catchment of newly planted *Pinus radiata* (Radiata pine) in the Bay of Plenty region of New Zealand. One hundred percent of the area was sprayed during Year 1 while 85% of the area was sprayed during Year 2. The highest concentrations of both herbicides were measured in stream water, sediment and algal samples on the day of herbicide application during Year 1 (September 2012 to June 2013), mainly as a result of spray drift, and in stream water during Year 2 (September 2013 to April 2014) at the time of a rainfall event seven days after herbicide application. Terbuthylazine concentrations exceeded New Zealand and World Health Organisation drinking water standards for <24 hours on both occasions. For the remainder of the trial period, concentrations of both herbicides were below safe drinking water standards. Herbicide concentrations in stream flow declined immediately below the trial site and were close to or below detection limits at the bottom of the catchment. The concentrations of terbuthylazine and hexazinone in stream flow during this trial, posed a short-term and low risk to algae. Peak concentrations of both herbicides were several orders of magnitude lower than Lethal Concentration (LC)50 concentrations for Daphnia and rainbow trout (*Oncorhynchus mykiss*). These results highlight the need to include data from both field and laboratory based trials when assessing the aquatic risk of these two herbicides when applied under operational conditions in planted forests.

Keywords: Herbicide, hexazinone, terbuthylazine, aerial application, water quality, sediment, algae, planted forest, New Zealand.

Introduction

Herbicides are used in forestry for a range of purposes such as reducing competing vegetation, managing species composition, controlling invasive weeds, managing wildlife habitat, and maintaining facilities and access ways (Richardson, 1993; Shepard et al., 2004; McCarthy et al., 2011). In particular, control of vegetation competing with the planted tree crop is an important management intervention in maximising productivity and maintaining commercial viability of planted forests (Wagner et al., 2006). Herbicides are the most widely used method for weed control in forests and have been selectively incorporated into site establishment and post-harvest vegetation management programmes in the past several decades because of their lower costs, high efficacy, elimination of soil disturbance, and lack of adverse effects on water quality (Neary and Michael, 1996; Little et al., 2006).

However, there are widespread public concerns regarding the risk of herbicide use in forests as these lands often have high aesthetic, recreational, wildlife, fishery and water resource values (Wagner et al., 1998; United Nations, 2014). In addition, national legislative and policy requirements and forest certification schemes such as the Forest Stewardship Council (FSC) promote the judicious use of herbicides in forests (Larson et al., 1997; Shepard et al., 2004; Forest Stewardship Council, 2005; Little et al., 2006). As a result, there is on-going and increas-

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ing pressure on forest managers to reduce herbicide use, and to adopt and integrate alternate methods to herbicides (Little et al., 2006; McCarthy et al., 2011; Rolando et al., 2011). However, other alternatives such as manual and mechanical methods, prescribed fire and biological control, also have potential negative aspects that need to be taken into consideration such as the risk of increased soil erosion, loss of nutrients, risk of wildfire, air pollution, efficacy and financial cost (Neary and Michael, 1996; Little et al., 2006; Rolando et al., 2011).

In New Zealand, planted forests cover 1.7 million ha (6% of New Zealand's total land area) with *Pinus radiata* D. Don comprising around 90% of the total planted forest estate. Fifty-six percent of New Zealand's planted forests are FSC certified (Forest Owners Association & Ministry for Primary Industries, 2013). Similar to elsewhere in the world, using herbicides to control competing vegetation is a critical component of inter-rotation forest management in New Zealand's planted forests (Rolando et al., 2011). A recent review by Rolando et al. (2013) on herbicide use in New Zealand's planted forests identified glyphosate (N-(phosphonomethyl) glycine), terbuthylazine (N2-tert-butyl-6-chloro-N4-ethyl-1,3,5-triazine-2,4-diamine) and hexazinone (3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4-(1H,3H)-dione), as the three most widely used herbicides for control of weeds. These three herbicides account for 90% of the estimated 447 Mg of active ingredient used in forestry within New Zealand. Two of these herbicides, terbuthylazine and hexazinone, are used in combination for post-plant control of weeds and are the focus of this study.

Terbuthylazine is a broad spectrum herbicide that belongs to the triazine group (Tomlin, 2006). Adsorption of terbuthylazine onto soil organic matter is strong (soil organic carbon affinity coefficient (Koc) of 162 to 178) (Watt et al., 2010) and water solubility is low (Table 1), indicating that transport to water bodies is more likely via sediment and organic matter, than in a solute form. Terbuthylazine degrades very slowly under aerobic aquatic conditions and persists in most aquatic environments. It is phytotoxic to aquatic plants, slightly toxic to aquatic invertebrates and moderately toxic to both cold and warm water fish (Table 1) (Environmental Protection Agency, 1995; Tomlin, 2006). When using the octanol/water partition co-efficient (log Kow) to assess bioaccumulative risk, a (log Kow), of ≥ 3 is a common international trigger point for concern and terbuthylazine exceeds this limit (Table 1). In contrast, when using the bioaccumulation factor (BCF: the ratio of the concentration of a chemical in an organism compared with that in water), a BCF of < 100 is considered a low risk (Beek et al., 2000) and terbuthylazine is below this limit (Table 1). These guidelines, give contradictory assessments on the potential risk of terbuthylazine bioaccumulating in freshwater environments (Table 1). There are potential risks of downstream cumulative effects on estuarine and marine invertebrates (Environmental Protection Agency, 1995). However, the potential for terbuthylazine leaching to groundwater and surface waters in New Zealand's planted forests is likely to be low due to the high organic carbon content and low pH of most forest soils.

Hexazinone also belongs to the triazine group (Environmental Protection Agency, 1994; Tomlin, 2006). It is highly soluble in water (Table 1), increasing the potential for surface and groundwater contamination through surface and sub-surface run-off and leaching through the soil profile. Both hexazinone and its metabolites (A-H) are mobile and can persist in some aquatic environments (Tu et al., 2001). Hexazinone can be highly toxic to algae but it is of low toxicity to aquatic invertebrates and fish (Table 1) (Berrill et al., 1994; Kreutzweiser et al., 1995; Nieves-Puigdoller et al., 2007). Due to its high water solubility, hexazinone does not bioaccumulate and has a low BCF factor (Table 1).

Terbuthylazine is rated slightly hazardous (Class III) and hexazinone moderately hazardous (Class II) under the World Health Organization classification of pesticides (World Health Organization, 2010).

The literature lacks information about the aquatic fate of terbuthylazine when applied under forest operational conditions. In contrast to terbuthylazine, there is a reasonable body of literature on aquatic fate of hexazinone in forested catchments, particularly in the southern U.S.A. (Fagg et al., 1982; Neary, 1983; Bouchard et al., 1985; Neary et al., 1985; Lavy et al., 1989; Michael et al., 1999; McBroom et al., 2013). The highest risks of herbicide contamination of water bodies were associated with herbicide application directly over perennial and ephemeral stream channels and in the first high flow event after spraying. Thereafter, concentrations in receiving freshwater environments usually declined within days or several months of application to concentrations <10 µg L^{-1}, or below detection limits (Fagg et al., 1982; Leitch and Flinn, 1983). Field studies on the aquatic fate of hexazinone in forests found that when used according to manufacturer's instructions and applied using the Best Manage-

Table 1. Freshwater environmental persistence and toxicology data for hexazinone and terbuthylazine (Tu et al., 2001; World Health Organization, 2003; Tomlin, 2006; Ministry of Health, 2008).

	Water solubility	**Average half-life in water**	**EC_{50}[†] (72 hr) algae**	**LC_{50}[‡] (48 hr) Daphnia**	**LC_{50} (96 hr) trout**	**K_{ow}[#] log**	**BCF[*f*]**	**DWS[§] New Zealand**	**DWS[§] WHO**
Herbicide	**mg L^{-1}**	**days**	**µg L^{-1}**	**µg L^{-1}**	**µg L^{-1}**			**µg L^{-1}**	**µg L^{-1}**
Terbuthylazine	8.5	50	16-24	442×10^3	$3.8\text{-}4.6\times10^3$	3.2	34	8	7
Hexazinone	28900	90	7-210	$21\text{-}51\times10^3$	$>320\times10^3$	1.2	7	400	-

[†] EC_{50} is the median effective concentration

[‡] LC_{50} (lethal concentration) is the concentration in water that kills 50% of the test organisms.

[#] Kow (octanol-water partition coefficient) is the ratio of the concentration of a chemical in octanol and in water at equilibrium.

[f] BCF (bioaccumulation factor) http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm. Accessed 4/6/2014.

[§] DWS (Drinking water standards).

Journal of Sustainable Watershed Science & Management - ISSN 1949-1425. Published By Atlas Publishing, LP (www.atlas-publishing.org)

ment Practices (BMPs) (i.e. set-backs from waterways, optimal weather conditions), the potential risk to human health, water quality and the aquatic environment was low (Mayack et al., 1982; Neary et al., 1993; Rolando et al., 2013).

Currently there is no information on the aquatic fate of either of these herbicides in New Zealand's planted forests, when applied according to standard operational practice. This highlighted the need for empirical catchment-scale studies on the persistence, and environmental fate of these herbicides in planted forest ecosystems to provide a scientific foundation for any policy decisions on the use of hexazinone and terbuthylazine. The objective of this study was to assess the fate of terbuthylazine and hexazinone in the aquatic environment following an operational aerial application of these two herbicides in a New Zealand planted forest catchment for post-plant weed control. This study is supported by associated research on the environmental fate of these two herbicides in the soil environment (Garrett et al., 2015).

Methods

Study Site

The trial area is located in the Pekepeke catchment in Kaingaroa Forest in the Bay of Plenty region of New Zealand (Fig. 1). This site was chosen because of the leaching potential of the deep well-drained sandy loam Immature Orthic Pumice Soils (Garrett et al., 2015). The underlying geology in the Pekepeke catchment is comprised of rhyolitic ignimbrite with a small outcrop of greywacke in the headwaters of the trial catchment (Leonard et al., 2010). Median annual rainfall in the area is 1300 mm (NIWA, 2012). The Pekepeke stream drains the eastern slopes of the Kaingaroa Plateau flowing into the Rangitaiki River and deeply dissects the landscape in places (Fig. 1C). Most of the Pekepeke catchment is in rolling, strongly rolling and moderately steep slopes (Ministry of Works and Development, 1978a; Ministry of Works and Development, 1978b). The catchment is in mixed age classes of *P. radiata*.

The trial site (12.5 ha) (Fig. 1A & B) is gently rolling to steep and dissected by several small first and second-order spring-fed perennial streams. The trial site was harvested in 2011 and residual logging slash (branches, twigs, needles) lay across the stream channels throughout most the stream network. Site preparation prior to re-planting consisted of an aerial application of metsulfuron, glyphosate and organosilicone in March 2012 to control weeds. Re-planting with a third-rotation crop of *P. radiata* was completed in July 2012 at 800 stems per hectare. No terbuthylazine or hexazinone had been applied to this catchment, prior to this trial.

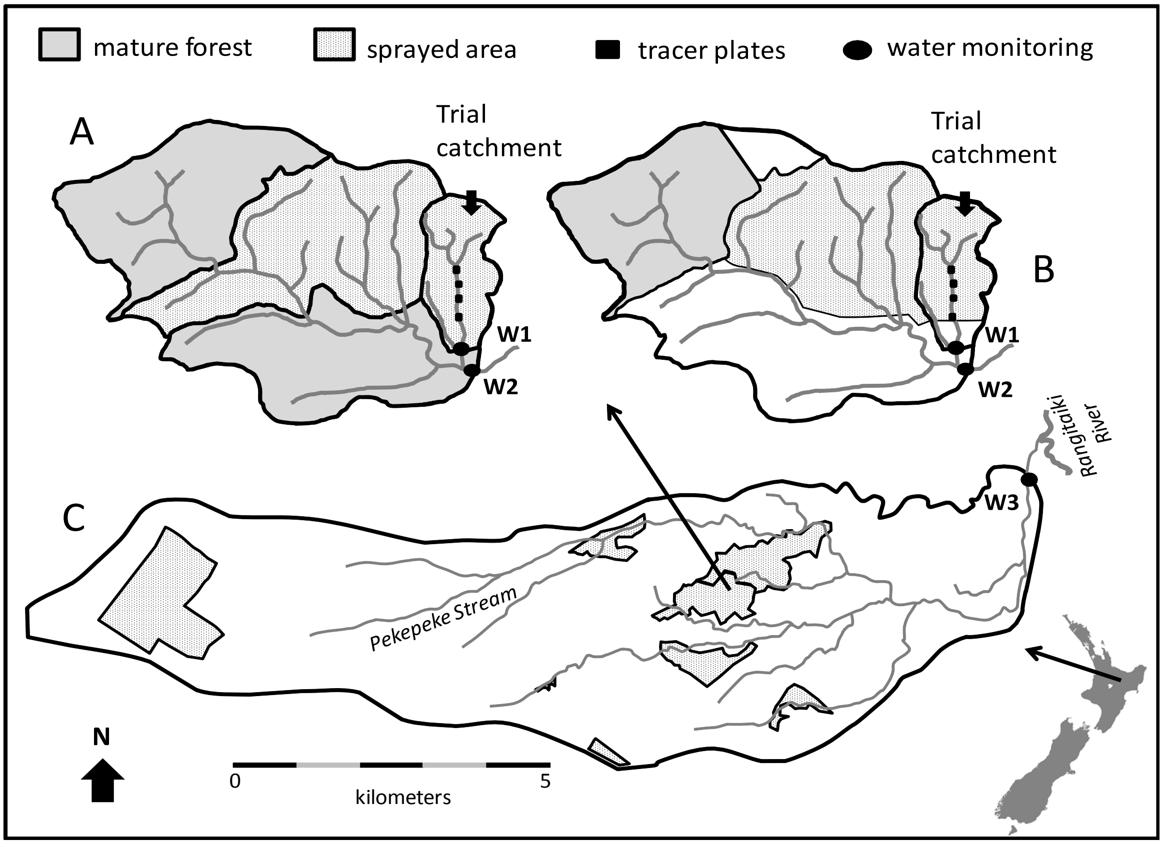

Figure 1. Trial area in the Pekepeke Stream catchment, Kaingaroa Forest, Bay of Plenty, New Zealand. A – water monitoring point at the base of the trial catchment (W1) and downstream of the trial catchment (W2) showing the area sprayed in Year 1; B – same as for A but showing the area sprayed in Year 2; C - water monitoring point at the base of the Pekepeke Stream catchment (W3) showing areas sprayed in the catchment in Year 2.

Site Treatment

The trial site was aerially sprayed with Release KT^{TM} (Orion Crop Protection Limited, Christchurch) (435 g L^{-1} terbuthylazine and 65 g L^{-1} hexazinone), on 01 November 2012 and again on 30 October 2013, applied at 17 L ha^{-1}. For both years the same aircraft and application set-up was used. A Bell 205 UH-1H Iroquois helicopter was fitted with 72 x D6 nozzles (Spraying Systems Co., 2011) evenly spaced along an 11 m long boom, within 80% of the rotor diameter. The aircraft operated at a ground speed of 60 to 65 knots (111 to 120 km hr^{-1}) and the spray release height was 8 to 10 m above ground level. At the above application parameters, the droplet spectra is classified as extremely coarse (American Society of Agricultural and Biological Engineers, 2009) with a volume mean diameter (VMD) of approximately 800 μm. The aircraft was calibrated to deliver 100 L ha^{-1} with an effective swath width of 28 m. In order to achieve an even spray pattern the area was sprayed with a half overlap pattern. Flight direction was approximately at right-angles to the stream channel. Operational BMP's required a 'no-spray' zone of 10 m from any visible flowing water. The wind speed during herbicide application for Year 1 and Year 2 averaged 4.5 and 3.1 km hr^{-1}, respectively.

In the first year (September 2012 to June 2013), the entire trial area upstream of the first water monitoring point (W1) (12.5 ha) was sprayed with Release KT^{TM} (Fig. 1A). At a second water monitoring point (W2), established approximately 70 m downstream to measure dilution rates (Fig. 1A), 45% (51.78 ha) of the 116.24 ha catchment was sprayed with Release KT^{TM}. In the second year (September 2013 to April 2014), 10.6 ha (85%) of the trial site was sprayed with more conservative 'no-spray' boundaries maintained along the stream edge. Downstream at W2, 43.21 ha (37%) of the upstream catchment area was sprayed (Fig. 1B). In Year 2, a third water monitoring point was established at the base of the Pekepeke catchment, approximately 8.1 km downstream of W1 (Fig. 1C (W3)). The upstream area was 4949 ha of which 544 ha (11%) was sprayed with Release KT^{TM} between September and December 2013.

Data Collection

The PLC meteorological station (Caboolture QLD 4510, Australia) was set up in the vicinity of the trial site on 01 October 2012 (Year 1) and 14 October 2013 (Year 2). Measurements taken at 1.8 m above the ground were: rainfall, wind speed, wind direction, temperature, relative humidity, and photosynthetically active radiation, at 10 minute intervals for the duration of the trial.

To measure spray deposition in the Pekepeke stream during each herbicide application, 10 stainless steel plates (76 x 152 mm) were placed horizontally at 1 m intervals either side of the stream channel prior to spraying and replicated 4 times along the stream channel (4 sets, 40 plates in total) (Fig. 1A & B). The dye tartrazine was added to the herbicide mixture at the rate of 0.005 kg L^{-1}. Tartrazine is photo-stable, non-toxic and has no impact on the performance of the herbicide and atomization characteristics of the nozzle or spray system, and it produces the same results as the herbicide active ingredient when used as a tracer in spray deposition studies (Pergher, 2001; Richardson and Thistle, 2006; Fritz et al., 2011). The steel plates were collected after spraying and returned to the laboratory for analysis.

Concentrations of terbuthylazine and hexazinone and one of the main metabolites of terbuthylazine (terbuthylazine-desethyl) found in the aquatic environment (Bottoni et al., 2013) were monitored in stream water, sediment and algae at the trial site (W1), and in stream water at W2 and W3 (Year 2 only) (Fig. 1). In Year 1 and Year 2 at the trial site (W1), stream water and stream sediment were sampled twice prior to spraying. Algae were sampled once at W1 prior to spraying as there was insufficient material in the stream channel for a second sample. On spray day, 500 ml stream water samples were taken every 15 minutes for the first two hours after spraying. Thereafter composite hourly samples (four 15 minutes samples) were taken for a further 6 hours. Sediment and algal samples were collected as well. In Year 2 only, in order to better capture the decay rate of both herbicides, water samples were collected on days 1, 2, 5, 8, 12, and 20 after spraying. In both years, water, sediment and algae (when present in stream channel) were sampled at monthly intervals after spray day until the following June in Year 1 and April in Year 2. In addition, the stream water was sampled for herbicide analysis for two rainfall events in Year 1 and three rainfall events in Year 2 (details in results).

At W2, water samples were collected for herbicide analysis prior to spray day (Year 2 only), on spray day, monthly and during rainfall events. At W3 (Year 2 only), water samples for herbicide analysis were collected prior to spray day, monthly and during high rainfall events (both years). A single water sample for water quality analysis was collected at each of the three water monitoring sites each time the sites were visited during the trial period. Samples were labelled, cooled and stored in insulated containers for transportation to the laboratory for analyses. A chain-of-custody form was used for all sample handling from the trial site to RJ Hills analytical laboratory (RJ Hill Laboratories, Hamilton, New Zealand; http://www.hill-laboratories.com/). Flows were measured using a Hach FH950 portable velocity meter and were taken at the same time as the water samples. The exceptions to this were on the days of herbicide application where water samples were taken over several hours. As the base flows were steady during this time, a single flow measurement was taken. Where water samples were collected over several hours during a rainfall event, flow measurements were taken on an hourly basis.

Laboratory Analyses

Laboratory evaluations of tracer deposition on the four sets of tracer plates compared the light absorbance of processed samples with the light absorbance from a set of reference samples with known dye concentrations. From this, the actual amount of dye in the sample and thus the concentration in each sample was calculated (Richardson et al., 1989). This was accomplished with the light absorbance of the sample measured at 427 nm using a PG instrument, T70 spectrophotometer. The average concentration for each set of 10 plates was used to calculate the percentage of the full application rate that reached the stream channel.

Water samples collected for herbicide analysis were extracted into dichloromethane using a liquid/liquid separating funnel technique. A 250 mL sub-sample was then quantitatively extracted into a final volume of 0.5 mL of solvent. A deuterated internal standard was used to determine selected compounds. Samples were run on a GC - Agilent 6890N MS - Agilent 5975B using a 30 m 250 µm x 0.25 µm DB-XLB column (http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3510c.pdf).

Sediment samples were extracted into ethylacetate using a sonication technique. About 8.5 g of sample was then quantitatively extracted into 20 mL of solvent. A portion of the extract was concentrated by a factor of 4. A deuterated internal standard was again used for selected compounds. Samples were run on a GC-MS, using a 30 m 250 µm x 0.25 µm DB-XLB column.

Hexazinone, terbuthylazine, and the metabolite terbuthylazine-desethyl concentrations in algae were determined by extraction of algal biomass samples into ethyl acetate via homogenization. About 1 g of sample was quantitatively extracted into 40 mL of solvent. The extract was cleaned up by a combination of Gel Permeation Chromatography (GPC) and Solid Phase Extraction (SPE). An internal standard was used for quantification of residues. Samples were run on a GC-MS, using a 30 m x 250 µm x 0.25 µm DB-XLB column.

The extraction method for sediment and algae was developed in-house by Hills Laboratory, based on the published method of Roos et al. (1987). Detection limits for hexazinone and terbuthylazine in water ranged from 1 to 10 µg L^{-1} on spray day at Site 1 in Year 1 to 0.02 to 0.10 µg L^{-1} at all sites for the remainder of the monitoring in both years. The detection limit for terbuthylazine-desethyl was 0.04 µg L^{-1}. Detection limits for sediment ranged from 7 to 70 µg L^{-1} for hexazinone, 7 to 90 µg L^{-1} for terbuthylazine, and 14 to 140 µg L^{-1} for terbuthylazine-desethyl. Detection limits for algae ranged from 10 to 100 µg L^{-1} for hexazinone, 10 to 40 µg L^{-1} for terbuthylazine, and 10 to 100 µg L^{-1} for terbuthylazine-desethyl.

The stream water collected for water quality was analysed for pH, electrical conductivity, total suspended solids (TSS) and dissolved organic carbon. The laboratory analyses followed the methods of APHA 4500-H+, APHA 2510 B, APHA 2540 D, and APHA 5310 B (APHA, 2012).

Results

Rainfall

During the first year of the trial, the Bay of Plenty region, along with the rest of the North Island of New Zealand, experienced record-breaking drought conditions in the austral summer and autumn of 2013 (NIWA, 2014a). During Year 2 rainfall was above average in the Bay of Plenty region in the first two months after spraying (November and December 2013) with below average rainfall for most of the remainder of the monitoring period (NIWA, 2013; NIWA, 2014b; NIWA, 2014c; NIWA, 2014d). As a result, the rainfall at the trial site was lower in Year 1 compared with Year 2, with fewer high rainfall events (Fig. 2).

Water Quality and Flow

Stream water was of neutral acidity and the pH was similar at all three sites (Table 2). TSS increased down the catchment with electric conductivity (EC) higher at W3 than the two upstream sites (Table 2). Dissolved organic carbon (DOC) showed a reverse trend to TSS with higher concentrations at the two upstream sites (Table 2).

Mean water depths at the three sites during the trial period ranged from 40 to 170 mm for W1, 60 to 220 mm for W2 and 220 to 370 mm for W3. Flows at W1 and W2 ranged from 0.4 to 4.0 L sec^{-1} and 2.0 to 19.0 L sec^{-1}, respectively, over both years of the trial (Fig. 3A & B) with flows at the upper end of the range at all three sites associated with the higher rainfall events. Flows at W3 (Year 2 only) were in order of two magnitudes higher than at the trial site (W1), ranging from 106 to 238 L sec^{-1} (Fig. 3B). Flow was positively correlated with DOC at W1 (r = 0.52). At W2, EC was negatively and TSS and DOC were positively correlated with flow (r = 0.53, 0.47 and 0.78 respectively). At W3, pH and EC were negatively and TSS positively correlated with flow (r = 0.74, 0.90 and 0.78, respectively). All these relationships were significant (Table 2).

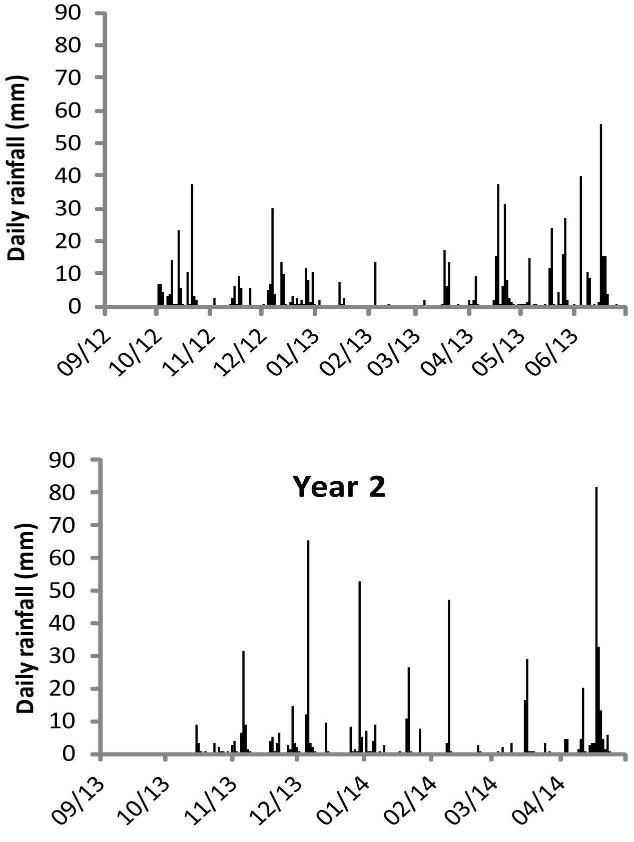

Fig. 2. Rainfall at the trial site in Year 1 and Year 2.

Table 2. Mean water quality characteristics, at the three (W1-W3) water monitoring sites. The ranges are in parentheses. Data from both years were combined.

Site	W1	W2	W3
Sample size	22	20	9
pH	7.2 (6.7-7.6)	7.0 (6.6-7.4)	**7.1** (6.8-7.3)
EC† (mS m^{-1})	8.5 (8.1-9.1)	**8.1** (7.5-8.5)	**9.3** (8.9-9.8)
TSS† (g m^{-3})	6.5 (1.5-19)	**8.8** (1.5-26)	**18.1** (6-36)
DOC† (g m^{-3})	**5.7** (2.0-18.8)	**6.7** (3.2-18)	3.7 (1-7.3)

† EC (electric conductivity), TSS (total suspended solids), DOC (dissolved organic carbon); Water quality values in bold were significantly related with flow (P < 0.05).

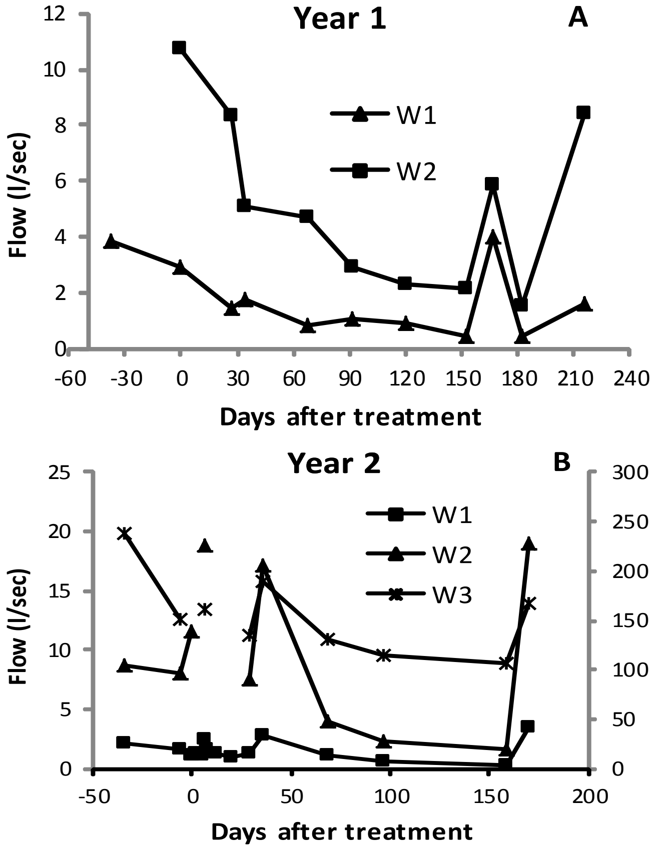

Fig. 3. Flows at W1 and W2 in Year 1 (A) and W1-W3 in Year 2 (B). W3 flows are shown on the secondary y axis.Negative 'Days after treatment' figures refer to the days before the herbicides were applied. In Fig. 3B the lines are disconnected for W2 and W3 as flows weren't measured at these two sites at the same intensity as at W1 in the first month after herbicide application.

Herbicide Concentrations in Water

During Year 1, no herbicide residues were detected in the stream water prior to herbicide application at the trial site (W1) (Fig. 4B & C). On the day of herbicide application, the results from the tracer plates showed that an average of 14 to 36% of the full application rate of Release KT^{TM} reached the stream channel. Terbuthylazine peaked at 1160 µg L^{-1} at W1 (Fig. 4A) at the start of the monitoring period, declining to 12 µg L^{-1} after eight hours of monitoring. Concentrations were less than 0.4 µg L^{-1} for the remainder of the trial period (Fig. 4B). Terbuthylazine-desethyl concentrations (data not shown) were 0.2 µg L^{-1} at the beginning of monitoring on the spray day but were below detection limits eight hours later and remained close to or below detection limits to the end of the monitoring period (216 days after treatment (DAT)). Highest hexazinone concentrations were also recorded at the start of the monitoring period on the day of spraying at 230 µg L^{-1} (Fig. 4A), declining to 1 µg L^{-1} at the end of monitoring on the spray day. Hexazinone concentrations were ≤ 1 µg L^{-1} for the remainder of the trial period (Fig. 4C). After the spray day, the highest concentrations for both terbuthylazine and hexazinone in the post-spray period in Year 1, were recorded during two small rainfall events; one 34 DAT (6.6 mm in the preceding 24 hours), the other 167 DAT (24.6 mm in the preceding 24 hours). Concentrations for both herbicides in both rainfall events ranged from 0.24 to 1.05 µg L^{-1}.

Downstream at W2, terbuthylazine and hexazinone concentrations on the spray day in Year 1 measured 32 and 7 µg L^{-1} respectively, around one-fifth of the average concentrations at W1 (Fig. 5A). For the remainder of Year 1 the concentrations of both herbicides at W2 remained below 1.5 µg L^{-1} (Fig. 5A).

The terbuthylazine and hexazinone concentrations and flow rates for the spray day were used to calculate the amount of herbicide exported from the trial site (W1) in the first 24 hours after spraying. Of the actual 92 kg of terbuthylazine and 14 kg of hexazinone applied to the site, 0.01% of the total amount applied for both herbicides, was exported on spray day (0.008 and 0.002 kg, respectively). This was the period of highest herbicide concentrations measured for the duration of the trial in Year 1 (Fig 4B & C).

During Year 2, neither terbuthylazine (Fig. 4E) nor terbuthylazine-desethyl (data not shown) was detected at the trial site (W1) prior to the herbicide application but hexazinone was detected at < 0.2 µg L^{-1} (Fig. 4F). On the day of herbicide application, an average of 9 to 20% of the full application rate of Release KT^{TM} reached the stream channel at the three upstream sets of tracer plates. The lower set of tracer plates averaged 2% of the full application rate and was likely a result of its location close to the lower spray boundary in Year 2 (Fig. 1B). Terbuthylazine concentrations on the spray day peaked at 4 µg L^{-1} (Fig. 4D), and were much lower than in Year 1 (Fig. 4A), most likely a result of spraying 85% of the area at the trial site (Fig. 1B) and the more conservative spray regime around the stream channel in Year 2.

Higher terbuthylazine concentrations were measured in the first rainfall event 7 DAT (31.6 mm in the preceding 24 hours) peaking at 210 µg L^{-1} (Fig 4E) and declining to 7.5 µg L^{-1} 24 hours later. At the second monitored rainfall event 36 DAT (36.6 mm in the preceding 24 hours), peak concentrations reached 5 µg L^{-1}. During the third rainfall event and final measurement for the trial 170 DAT (49.4 mm in the preceding 24 hours), terbuthylazine residues had declined to 0.2 µg L^{-1} (Fig. 4E).

Hexazinone concentrations peaked at 3 µg L^{-1} on the spray day in Year 2 (Fig. 4D), two orders of magnitude lower than the previous year (Fig. 4A). Similar to terbuthylazine, higher concentrations (maximum 7 µg L^{-1}) (Fig 4F) were recorded in the first rainfall event 7 DAT (31.6 mm in the preceding 24 hours). Thereafter hexazinone concentrations were less than 3 µg L^{-1} for the remainder of the monitoring period with highest concentrations recorded in the second rainfall event 36 DAT (36.6 mm in the preceding 24 hours) (Fig. 4F).

On the spray day during Year 2, 78 kg of terbuthylazine and 12 kg of hexazinone were applied to the trial site. The amount of terbuthylazine and hexazinone exported from the trial site (W1) over a 24 hour period during the first rainfall event (7 DAT), the period of highest herbicide concentrations recorded during Year 2, was calculated at 0.01% of the actual total amount applied for both herbicides (0.006 kg and 0.001 kg for terbuthylazine and hexazinone, respectively).

Downstream at W2, terbuthylazine concentrations measured 0.2 µg L^{-1} on the day of herbicide application in Year 2 (Fig. 5B). Terbuthylazine concentrations increased to 7 µg L^{-1} during the first rainfall event (7 DAT) and were below 1.5 µg L^{-1} for the remainder of the monitoring period (Fig. 5B). Terbuthylazine-desethyl first appeared at W2 in the first rainfall event (7 DAT) (data not shown). Highest concentrations were detected 36 DAT (0.4 µg L^{-1}) and were close to or below detection limits for the remainder of the trial period. Traces of hexazinone were detected at W2 (≤ 0.2 µg L^{-1}) prior to herbicide application in Year 2 and on the spray day (Fig. 5B). In the first rainfall event (7 DAT) hexazinone concentrations measured 4 µg L^{-1} and were below 1.3 µg L^{-1} for the remainder of the monitoring period (Fig. 5B). At the bottom of the catchment (W3), highest terbuthylazine and hexazinone concentrations were recorded during the 7 DAT rainfall event (0.9 and 0.4 µg L^{-1}, respectively), in Year 2 and remained close to or below detection limits for the remainder of the monitoring period (Fig. 5B). Terbuthylazine-desethyl was undetectable at W3.

Herbicide Concentrations in Sediment and Algae

The highest concentrations of terbuthylazine in the stream sediments were recorded on spray day in both years (3300 µg kg^{-1} Year 1; 1610 µg kg^{-1} Year 2). In both years, while not detected on all sampling occasions, terbuthylazine persisted in the sediment until the end of the trial (50 µg kg^{-1}, 216 DAT during Year 1 and 50 µg kg^{-1}, 159 DAT during Year 2). No terbuthylazine-desethyl was detected in stream sediments at the trial site during Year 1. However it was recorded in stream sediments during Year 2 at 29 and 68 DAT (120 and 70 µg kg^{-1} respectively). On spray day, hexazinone concentrations in sediment measured 220 µg kg^{-1} and 210 µg kg^{-1} during Years 1 and 2 respectively, and remained below detection limits during Year 1 until the last measurement 216 DAT (20 µg kg^{-1}). During Year 2, hexazinone was present in sediment until 68 DAT and below detection limits for the remainder of the monitoring period.

No herbicide residues were detected in algal samples prior to herbicide application during both years. During Year 1, terbuthylazine, terbuthylazine-desethyl and hexazinone concentrations in algae were 8100, 33 and 600 µg kg^{-1} respectively, on the spray day but remained below detection limits up until the end of the trial (182 DAT). During Year 2, only terbuthylazine was detected in algal samples on the spray day (110 µg kg^{-1}) and again a month later 29 DAT (370 µg kg^{-1}).

Table 3. Summary of forested catchment studies on the aquatic fate of hexazinone in streams including the results of this study.

Location	Hectares	% treated	SMZ† width (m)	Application method (kg a.i. ha^{-1})	DL† (µg L^{-1})	Max. conc. On treatment day (µg L^{-1})	Trial length (DAT†)	DAT until conc. below DL	DAT when 1st rainfall event occurred (mm d^{-1})	Max. conc. in rainfall event (µg L^{-1})
Alabama, USA[1]	17.4	4.6		air- pellet (1.8)	20	2400	265	6	10 (13)	<DL
Victoria, Australia[2]	28	100	100	air - spray (4.0)	50	<DL	35	0	9 (37)	<DL
Georgia, USA[3]	1	100		ground - pellet (1.68)	1	<DL	390	114	3 (50)	442#
Tennessee, USA[4]	194	35		air - pellet (1.68)	10	<DL	230	0	30 (50)	<DL
Victoria, Australia[5]	46.4	100	30	air - spray (2.0)	2	4	63	7	31 (64)	<DL
West Virginia, USA[6]	16	63	15	ground - spot (1.36)	0.2	<DL	1290	1290	68 (60)	16
Michigan, USA[7]	4400	-		air - spray (1.7)	-	< 1	116	1	- (-)	<DL
Arkansas, USA[8]	11.5	100		ground - spot (2.0)	1	<DL	365	> 365	- (56)	14
Texas, USA[9]	2.2-135	100	15	ground-spray (0.28-0.55)	1	<DL	-	254	71 (-)	7.7#
			15	air - spray (0.55)	1	<DL	-	207	24 (-)	29.9#
Bay of Plenty, NZ[10]	12.5	100(Y1‡)	10	air - spray (1.1)	0.02-10	230	216	> 216	34 (7)	0.3
		85(Y2‡)	10	air - spray (1.1)	0.02-0.10	3	170	> 170	7 (32)	7

[1]Miller and Bace, 1980; [2]Fagg et al., 1982; [3]Neary et al., 1983; [4]Neary, 1983; [5]Leitch and Flinn, 1983; [6]Lavy et al., 1989; [7]Neary et al., 1985; [8]Bouchard et al., 1985; [9]McBroom et al., 2013; [10]this study. †SMZ (streamside management zone); DL (detection limit); DAT (days after treatment). ‡Y1 (Year 1); Y2 (Year 2). #average.

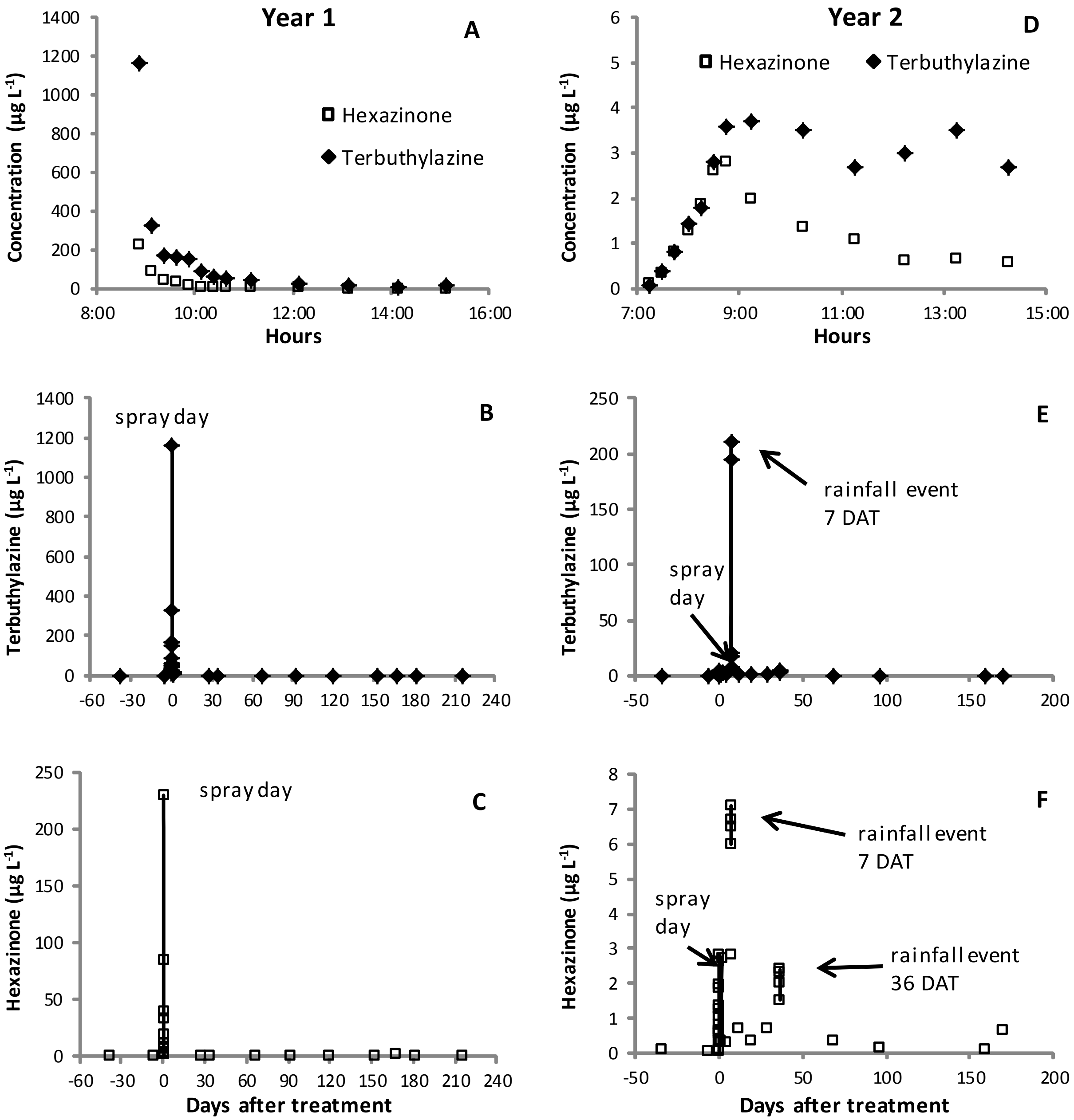

Fig. 4. Year 1: A - concentrations of terbuthylazine and hexazinone measured in stream water at the trial site (W1) on the day of herbicide application; (B) terbuthylazine and (C) hexazinone concentrations in stream water at W1 for the total trial period. Year 2: D - concentrations of terbuthylazine and hexazinone measured in stream water at the trial site (W1) on the day of herbicide application; (E) terbuthylazine and (F) hexazinone concentrations in stream water at W1 for the total trial period.

Discussion

When operationally applied on planted forest land, the highest concentrations of terbuthylazine and hexazinone in this study were detected in stream water at W1, either on the day of spraying (Year 1) (Fig. 4A) or in a rainfall event occurring shortly after application (7 DAT) (Year 2) (Fig. 4 E & F), as well as on spray day during Year 1 at W2 (Fig. 5A). In these instances terbuthylazine concentrations exceeded New Zealand and World Health Organisation drinking water standards (Table 1) at W1 for 24 hours or less. Subsequently, concentrations were well below drinking water standards for both herbicides for the remainder of the trial period in both years with concentrations close to and frequently below detection limits at the bottom of the catchment.

In the steep to moderately steep dissected hill country of this trial, the topography sometimes limits the ability to aerially apply herbicides along flight lines running parallel to waterways, particularly in headwater streams. Instead, flight lines ran approximately at right angles to the stream channel. The spray applicators were switched off when traversing the stream channel to maintain the required 10 m buffer but the forward momentum of the spray drift meant that anywhere from 9%-27% of the full application rate reached the stream channel at the trial site. The

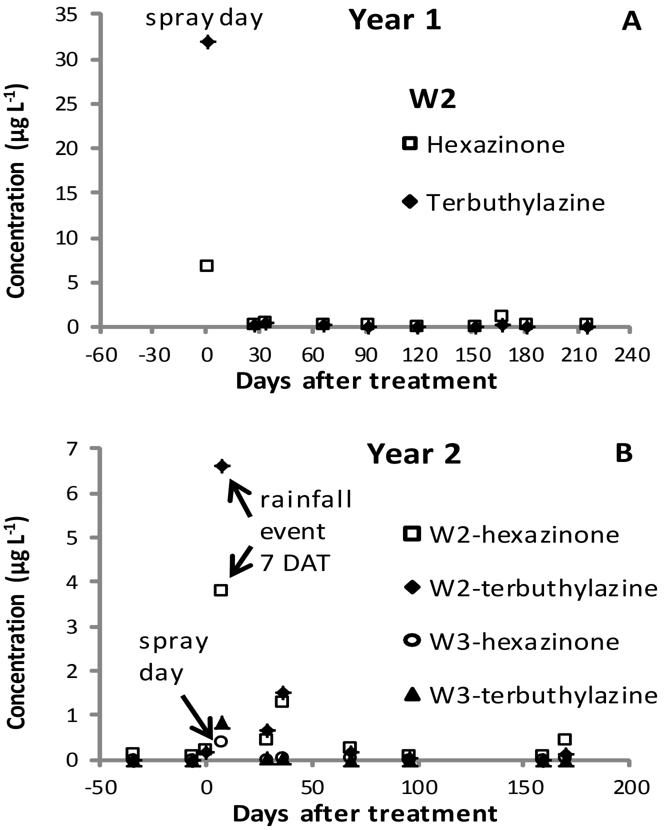

Fig. 5. Concentrations of terbuthylazine and hexazinone measured in stream water downstream of the trial site at W2 in Year 1 (A) and W2 and W3 in Year 2 (B).

two main sources of herbicides in the stream channel were from spray drift where flowing water was visible and direct application over ephemeral channels or channels screened by logging slash. Logging slash across the stream channels would have reduced the amount of spray drift reaching the water surface and provided sites for herbicide retention and degradation (Garrett et al., 2015). Additionally, during Year 2, the more conservative spray boundaries and partial spraying of the catchment (85%) substantially reduced the concentrations of both herbicides detected in stream water.

Comparable fate studies in forests for terbuthylazine were not found in the literature. However, when comparing the hexazinone measured in the stream waters of this study with other forest operational studies (Table 3), concentrations were intermediate between the higher concentrations associated with direct application over the stream channel (Miller and Bace, 1980), and the lower concentrations where management practices such as ground application and retention of 'no-spray' streamside management zones (SMZs) minimised spray drift (Table 3).

Following herbicide application, similar to this study, herbicide concentrations peaked in the first high rainfall event after application (Table 3), usually declining in subsequent rainfall events (Neary et al., 1983; Lavy et al., 1989; McBroom et al., 2013). This finding was most likely a combined effect of the timing (DAT) and the quantity and duration of rainfall along with other factors such as the presence of SMZ's, preceding catchment saturation, geology and soils, hydrology and flow pathways (Neary et al., 1983; DeGraff et al., 2007). In other studies, greater quantities of hexazinone tended to reach streams in wet conditions or where the first storm event occurred shortly after herbicide applications (Neary et al., 1983; Michael et al., 1999; McBroom et al., 2013) with lower concentrations associated with drier climatic conditions (Leitch and Flinn, 1983; this study). The persistence of hexazinone in the aquatic environment (as indicated by the DAT until concentrations fell below detection limits in Table 3) varied between studies, with trace concentrations persisting for several years after application in some instances (Table 3). These results were influenced by detection limits that have increased in sensitivity over time (Table 3).

Processes Influencing Herbicide Fate in Streams

After spray application, terrestrial herbicide residues have the potential to migrate off-site and into water bodies via indirect pathways such as overland and sub-surface flow, drainage to ground water systems or transport via sediment erosion into waterways (Larson et al., 1997; Sarmah et al., 2004; Holvoet et al., 2007). The highest stream water concentrations were often associated with overland and sub-surface flow (i.e. Neary et al., 1983; Lavy et al., 1989; Michael et al., 1999).

Pumice soils are susceptible to leaching (Landcare, 2014); however, it is unlikely that leaching and transfer of terrestrial herbicide residues to the stream channel via overland and subsurface flow and erosion processes occurred at this site, due to the low rainfall pattern, particularly in Year 1 (Fig 2A & E). During Year 2, the three rainfall events (7 DAT, 36 DAT, 170 DAT) where herbicide residues were monitored in stream water were similar to the time periods when drainage was predicted in the catchment (7 & 8 DAT, 36 & 37 DAT and 170 DAT) (Garrett et al., 2015). During these events, there was a low potential risk to groundwater due to limited herbicide movement down the soil profile, and high on-site retention of herbicide residues, (particularly terbuthylazine) in terrestrial organic matter (Garrett et al., 2015). The potential for terbuthylazine leaching to groundwater and surface waters in New Zealand's planted forests is likely to be low due to the high organic carbon content and low pH of most forest soils (Watt et al., 2010; Rolando and Watt, 2012).

Other potential sources of herbicide residue detected in stream water at this site could have included: 1) deposits on overlying or in-situ logging slash and vegetation washed off into the stream during rainfall events; 2) localised run-off from adjacent riparian areas; 3) herbicide residues collected from channel edges and ephemeral stream channels during high flow events, along with; 4) the re-suspension and mobilisation of any remaining herbicide residues in in-stream sediment and organic matter (Larson et al., 1997; Holvoet et al., 2007).

Once in the stream, a range of in-stream transformation, phase transfer and transport processes influence the decomposition and transport of herbicides (Larson et al., 1997; Holvoet et al., 2007). As terbuthylazine is stable to aqueous photolysis and hydrolysis (≈ half-life of 250 days in the pH neutral stream waters in this trial) and volatilisation from surface waters was unlikely (Environmental Protection Agency, 1995; http://toxnet.

nlm.nih.gov/ downloaded 2/7/2014), these processes were not considered major contributors to the aquatic fate of this herbicide. Nevertheless, the presence of terbuthylazine desethyl (up to 170 DAT) indicated that decomposition processes were occurring in the stream. Neither photolysis nor volatilisation was considered an important process for hexazinone degradation in the aquatic environment, and its adsorption potential is low (Tu et al., 2001; Tomlin, 2006; http://toxnet.nlm.nih.gov/ downloaded 2/7/2014). Therefore, given the rapid decline in herbicide concentrations following herbicide application, the most likely processes influencing the aquatic fate of both terbuthylazine and hexazinone would have been downstream dilution and dispersal.

However, primary transport pathways in running water differ between the two herbicides. Because of its high water solubility, hexazinone is unlikely to persist in stream sediments. Residues in stream sediment were detected on the day of herbicide application and up to 70 DAT in this and other studies, often at similar or lower concentrations than in stream water (Neary et al., 1983; Lavy et al., 1989; Michael et al., 1999). Consequently, hexazinone is primarily transported off-site in a dissolved state, the speed determined by flow rates in the catchment (Larson et al., 1997).

Because of terbuthylazine's greater adsorption capacity, terbuthylazine concentrations in in-stream sediment were higher and persisted for longer than hexazinone in this study. The sorption/desorption capacity of the stream sediments was not assessed in this trial and we were unable to quantify the contribution of this process on the aquatic fate of terbuthylazine. Terbuthylazine is expected to adsorb to suspended and benthic sediments and in-stream organic matter, accumulating in low energy depositional areas such as backwaters and pools. Therefore, terbuthylazine is primarily transported during high flow events (Larson et al., 1997; Kronvang et al., 2003). Michael et al. (1999) measured a biomodal response in stream sediments where hexazinone concentrations initially declined but increased again around 180 DAT. Michael et al. (1999) attributed this increase to the transport of additional terrestrial sediment sources and overland flow during intense rainfall events. Most of the soils in New Zealand's planted forests are high in organic carbon fraction, facilitating terbuthylazine adsorption (Watt et al., 2010) and Michael et al.'s (1999) study highlights the potential risk of off-site movement of terbuthylazine to receiving water bodies in planted forests with high erosion potential and subject to intense rainfall events.

Biological Significance

Highest concentrations of terbuthylazine and hexazinone in algal samples occurred on the day of herbicide application and for terbuthylazine in a rainfall event 7 DAT during Year 2. While these concentrations and the concentrations in water exceeded the EC50 (72 hr) thresholds for algae (Table 1) on occasion (Figs. 4 & 5), any impacts were short-term and no dead algae were evident in the monthly stream measurements after spray day. These two herbicides can be toxic to aquatic plants (Table 1) (Tu et al., 2001) with possible flow on effects up the food chain. However, the potential for bioaccumulation for both these herbicides is low (Table 1) and operationally, exposure time to herbicides was of a short duration with concentrations declining rapidly on the day of application as the herbicides were flushed from the system. These results concur with Schneider et al. (1995) where algae communities recovered from exposure to hexazinone concentrations within the range of this study. When applied under operational conditions in forested catchments in Georgia, U.S.A., hexazinone and its metabolites were detected on only a few occasions in aquatic macrophytes (Mayack et al., 1982).

When comparing the concentrations and duration of both these herbicides in stream water (Figs. 4 & 5) with the concentrations and duration required to adversely impact aquatic animals such as Daphnia and trout (Table 1), concentrations in stream water were several orders of magnitude lower than the LC50 concentrations for both these species. These results indicate that the risk to aquatic animals from operational herbicide application under the field conditions in this study appeared to be very low. Two studies reported in the literature examined the effects of hexazinone, applied either under operational conditions (Mayack et al., 1982) or at three times the prescribed rate (Michael et al., 1999), on aquatic invertebrate communities. In both these studies, a number of metrics were used to assess the effects of hexazinone on aquatic invertebrate communities and no discernible effects were found.

These results highlight the difficulty of using laboratory based toxicology tests as the basis for restricting herbicide use in the field, when the actual test of toxicity is the effect on the environment when applied under operational conditions. Toxicology concentrations are usually based on constant exposure for around 48 to 96 hours (Table 1), whereas in the field, peak concentrations tend to be of short duration (several hours) in forested streams as the herbicide is rapidly diluted and dispersed along the stream network once spraying or the rainfall event has ceased. Herbicide use is infrequent over the forestry growing cycle in New Zealand and the use of these two herbicides in two consecutive years in this trial is a maximum in an approximate 28-year growing cycle. In addition, around 50% of the planted forest area uses spot weed control which would substantially reduce the load of active ingredient applied to the site (Rolando et al., 2013). Power and McCarthy (1997) and others (Beek et al., 2000; Shepard et al., 2004) have highlighted the issue of extrapolating laboratory results to the field. Of concern is the limited number of aquatic organisms and indigenous organisms used in laboratory testing. For these two herbicides, toxicology information is lacking for New Zealand's indigenous aquatic biota.

Conclusions

The aquatic fate of terbuthylazine and hexazinone aerially applied in two consecutive years, was assessed on a moderately steep site with soils that had low adsorption capacity (Watt et al., 2010). The spray pattern involved flying at right-angles to the stream channel. Even under these operational conditions, terbuthylazine and hexazinone posed a low risk to ground and surface water quality. Highest risk was associated with terbuthylazine exceeding drinking water standards either on the day of herbicide application or in a rainfall event one week later, although exposure time was short and rapidly diluted downstream. The results of this study indicate that the BMPs and site conditions that facilitate 'no spray' SMZs to eliminate direct application to the stream channel and minimise spray drift, along with the use of ground application methods where suitable, and retention of organic matter on-site may further minimise environmental risk to aquatic ecosystems. If the infrequent spatial and temporal use of herbicides in New Zealand's planted forests is considered, the cumulative risk to downstream receiving environments is likely to be low. When evaluating the potential risk of herbicide use in forests, the assessment process should include the operational risks in the field when applied according to manufactures instructions and under BMP's, rather than laboratory based toxicology trials alone.

Given the lack of information on the aquatic fate of terbuthylazine operationally applied in forests, repeat studies are needed under the different soil, geological and hydrological conditions found in New Zealand's planted forests. Risks to surface waters such as streams, particularly from terbuthylazine, are likely to be higher in erosion prone forests subject to intense rainfall events where stream hydrology is dominated by overland and sub-surface flows. Further work is also needed to identify the risk of these two herbicides when used in combination to indigenous freshwater organisms and downstream cumulative effects on estuarine and marine receiving environments.

Acknowledgements

Funding was provided by the Undermining Weeds project (contract C10X081) with AgResearch, New Zealand. The cooperation and support of the forest company who provided access to the research site and managed the logistics of spray application is gratefully acknowledged. The authors would like to thank Hills Laboratory for the herbicide and water quality analyses. Support and contributions from Loretta Garrett, Caroline Gous and Tia Uaea are gratefully acknowledged.

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