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Runoff of Silvicultural Herbicides Applied Using Best Management Practices

Matthew W. McBroom
Stephen F Austin State University, mcbroommatth@sfasu.edu

Jeff Louch

R Scott Beasley

Mingteh Chang

George G. Ice

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Matthew W. McBroom, Jeff Louch, R. Scott Beasley, Mingteh Chang, and George G. Ice

Abstract: Nine small (2.2–2.9 ha) and four large (70–135 ha) watersheds in East Texas, USA, were instrumented to compare herbicide runoff under different silvicultural systems with best management practices (BMPs). Two treatments were evaluated: *conventional*, with clearcutting, aerial herbicide site preparation, and hand-applied banded herbaceous release; and *intensive*, in which subsoiling, aerial fertilization, and a 2nd-year aerial herbicide application were added. Herbicides were applied as operational tank mixes. The highest imazapyr concentration found in stream water was 39 $\mu g\ L^{-1}$ during the first storm after application (23 days after treatment [DAT]) and in-stream concentrations during runoff events dropped to $<1\ \mu g\ L^{-1}$ in all streams by 150 DAT. The highest hexazinone concentration was 8 $\mu g\ L^{-1}$ for the banded application and 35 $\mu g\ L^{-1}$ for the broadcast application the following year and fell to $<1\ \mu g\ L^{-1}$ in all streams by 140 DAT. The highest sulfometuron methyl concentration found during a runoff event was 4 $\mu g\ L^{-1}$ and fell to $<1\ \mu g\ L^{-1}$ in all streams by 80 DAT. Approximately 1–2% of applied imazapyr and <1% of hexazinone and sulfometuron methyl were measured in storm runoff. Herbicide was found in streams during storm events only (all herbicides were $<1\ \mu g\ L^{-1}$ in all true baseflow samples), and peak concentrations during runoff events persisted for relatively short times (<24 h). These results suggest that silvicultural herbicide applications implemented with contemporary BMPs are unlikely to result in chronic exposure of aquatic biota; therefore, herbicide use under these conditions is unlikely to degrade surface waters. FOR. SCI. 59(2):197–210.

Keywords: herbicides, silviculture, best management practices, streamside management zones, surface water quality

The United States harvests approximately 708,000,000 m^3 of wood annually, the highest rate of timber removal of any nation (Juslin and Hansen 2002) but is still a net importer of wood products. Even though the total annual growth rate of wood (1,044,000,000 m^3) exceeds harvest levels, some of this growth is occurring on forestlands reserved for other uses and will not be harvested for timber products. The 13 southeastern states (collectively referred to as the South) sustainably produce 60% of the forest products in the United States, more timber products than any other country (outside the United States) in the world (Wear and Greis 2002). To sustain these volumes, forest management in the South has intensified over the past 2 decades and is expected to continue to intensify into the future.

One crucial component of intensive silviculture is the use of herbicides to control competing vegetation. Herbicides are applied to an estimated 2.0 million acres annually in the South, primarily associated with loblolly pine (*Pinus taeda* L.) plantation establishment and stand management (Wear and Greis 2002). Prescribed burning for vegetation control has declined during the past 2 decades, primarily due to concerns about liability from fire escapes and smoke management. Mechanical site preparation has also declined as more existing plantations and fewer naturally regenerated forests are harvested and replanted. Mechanical site preparation can also cause accelerated erosion losses (Beasley 1979, Blackburn et al. 1986, McBroom et al. 2008a). Replacing mechanical site preparation practices with herbicide applications lowers the potential for sediment and nutrient pollution of surface waters (Neary and Michael 1996).

Another significant factor in minimizing the impacts of forest management on water resources is the use of best management practices (BMPs). Voluntary forestry BMPs are successfully implemented on 91.5% of silvicultural operations in Texas (Simpson et al. 2008), with comparable rates throughout the South. BMP-implementation rates have generally been increasing over the last 2 decades, although additional efforts are needed to increase implementation, especially for small, nonindustrial private landowners (Simpson et al. 2008).

There is significant public concern that the use of herbicides in agriculture and forestry poses a risk to the environment in general and to aquatic ecosystems in particular. It is important to note that herbicide use in forestry differs significantly from that in agriculture. Compared with agriculture, forestry applications are infrequent (typically one or two applications in a rotation of 30–80 years), have low

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Matthew W. McBroom (mcbroommatth@sfasu.edu), Stephen F. Austin State University, College of Forestry, Nacogdoches, TX. Jeff Louch (jlouch@wcrc-ncasi.org), National Council for Air and Stream Improvement. R. Scott Beasley (sbeasley@sfasu.edu), Stephen F. Austin State University. Mingteh Chang (mchang@sfasu.edu), Stephen F. Austin State University. George G. Ice (gice@wcrs-ncasi.org), National Council for Air and Stream Improvement.

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application rates (typically less than the maximum allowed by the chemical label), and are targeted to only a small portion of the overall forestland base at any given time (Michael and Neary 1993, Neary and Michael 1996).

The environmental fate of an herbicide is determined by the properties of the product, amount and frequency of use, application method, and interaction of the physical, chemical, hydrological, climatic, and biological environment. Three commonly used herbicides in forestry are hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2, 4-dione], imazapyr [2-(4-methyl-5-oxo-4-propan-2-yl-1-*H*-imidazol-2-yl)pyridine-3-carboxylic acid], and sulfometuron methyl [2-(4,6-dimethylpyrimidin-2-yl carbamoylsulfamoyl) benzoate]. These herbicides tend to have properties that limit their potential for biomagnification and environmental impact due to offsite movement (Neary et al. 1993).

The potential for offsite movement to streams and other surface waters depends on timing and mode of application (liquid or pellet) and on whether BMPs like streamside management zones (SMZs) are used. Of the three silvicultural herbicides listed above, hexazinone is considered to have the greatest potential to move offsite after application because it has higher water solubility (3.3%) and lower adsorption to soil (Bouchard et al. 1985). Lavy et al. (1989) measured in-stream hexazinone (applied as Velpar L) concentrations after spot-gun applications of 1.36 kg ha^{-1}, leaving a 15-m herbicide-free buffer along each side of the stream, on two steeply sloping (40%) watersheds in north-central West Virginia. Approximately 4.7% of the applied herbicide moved offsite, with a maximum concentration of 16 $\mu g\ L^{-1}$. Bouchard et al. (1985) found similar results in a comparable study in northwest Arkansas, with maximum concentrations of 14 $\mu g\ L^{-1}$. Neary et al. (1983) reported on the effects of a 1.68 kg ha^{-1} pelletized hexazinone treatment applied directly in stream channels on small watersheds in Georgia. The maximum concentration was 442 $\mu g\ L^{-1}$, much higher than those reported above.

Fewer studies have examined offsite movement of imazapyr and sulfometuron methyl. Application rates of 2.2 kg ha^{-1} imazapyr on two watersheds, one with an herbicide-free streamside buffer and the other without, resulted in maximum concentrations of 130 $\mu g\ L^{-1}$ on the watershed with a buffer and 680 $\mu g\ L^{-1}$ on the watershed without a buffer (Michael and Neary 1993). Ground application of 0.42 kg ha^{-1} sulfometuron methyl without an herbicide-free buffer resulted in a maximum baseflow concentration of 7 $\mu g\ L^{-1}$, and no herbicide was detected in stormflow or stream sediment (Neary and Michael 1989).

In addition, a multitude of studies, reviews, and formal risk assessments have concluded that use of forest herbicides according to label directions poses negligible risk to aquatic biota (e.g., Solomon et al. 1996, 2008, Giesy et al. 2000, Solomon and Thompson 2003, Tatum 2004, USDA Forest Service 2009). Most herbicides labeled for forestry use have relatively low toxicity to periphyton and benthos (Sullivan et al. 1981, Mayack et al. 1982, Austin et al. 1991, Kreutzweiser et al. 1995, Fowlkes et al. 2003) and fish (Folmar et al. 1979, Mitchell et al. 1987). Overall, aquatic plants and algae are the organisms that are most sensitive to the three herbicides used in this study (Syracuse Environmental Research Associates, Inc. [SERA] 1997, 2004a, 2004b). However, in the case of sulfometuron methyl specifically, no observed effects concentrations (NOECs) for sensitive aquatic plants and algae are quite low; e.g., in its assessment of risk to aquatic systems, the USDA Forest Service (SERA 2004a) used NOECs of 2.5 $\mu g\ L^{-1}$ for sensitive algae species (*Selenastrum* spp.) and 0.21 $\mu g\ L^{-1}$ for sensitive aquatic plants (*Lemna* spp.). Note that these NOECs were developed using exposure periods ranging from 3 to 14 days (SERA 2004a) and so represent concentrations at which chronic exposure is not expected to elicit an effect.

On the other hand, as cited by SERA (1997), hexazinone has been observed to affect photosynthesis in golden algae (*Chrysophyta* spp.) at concentrations as low as 3 $\mu g\ L^{-1}$ and in blue-green algae (*Anabaena* spp.) at concentrations as low as 30 $\mu g\ L^{-1}$, although multiple researchers have reported that these effects on photosynthesis are reversible (SERA 1997). Beyond this, Kreutzweiser et al. (1995) tested the effects of 12-h exposures to 2700 $\mu g\ L^{-1}$ hexazinone under actual field conditions and found no reductions in biomass in associated naturally occurring epilithic algal communities, and Mayack et al. (1982) reported no changes in macrophyte species composition or diversity after intermittent exposure to hexazinone concentrations ranging from 6 to 44 $\mu g\ L^{-1}$ over an 8-month period.

In the case of imazapyr, the most sensitive species are aquatic macrophytes (SERA 2004b). Seven-day exposures have been shown to have an impact on frond development in duckweed (*Lemna* spp.), with a reported NOEC of 13 $\mu g\ L^{-1}$ (SERA 2004b), and 14-day exposures resulted in reduced shoot and root growth in water milfoil (*Myriophillum* sp.), with EC_{25} (effect concentrations where 25% of test organisms are adversely effected) values ranging from 7.9 to 22 $\mu g\ L^{-1}$, depending on the endpoint (SERA 2004b).

Herbicide applications on most industrial forestlands occur as tank mixes, in which herbicides and surfactants are mixed together to minimize application cost and maximize control of competing vegetation. Although some toxicological studies on herbicide mixtures have been conducted (Tatum et al. 2011), there is a general paucity of studies on offsite movement and stream concentrations of herbicides after industrial tank mix applications on forestlands in the South. The Texas Intensive Silviculture Study was initiated to examine the effects of various intensive silvicultural practices on water quality, including commercial herbicide applications on forestlands. The purpose of this study was to quantify offsite movement of hexazinone, imazapyr, and sulfometuron methyl after applications to forestlands associated with different intensities of forest management (including chemical applications).

Materials and Methods

Site Description

Thirteen study watersheds were selected within the Neches River watershed in East Texas, about 16 km west of the town of Alto, Texas (Figure 1). Study watersheds range from 76 to 131 m above mean sea level and have dendritic drainage systems formed by random headward erosion. The

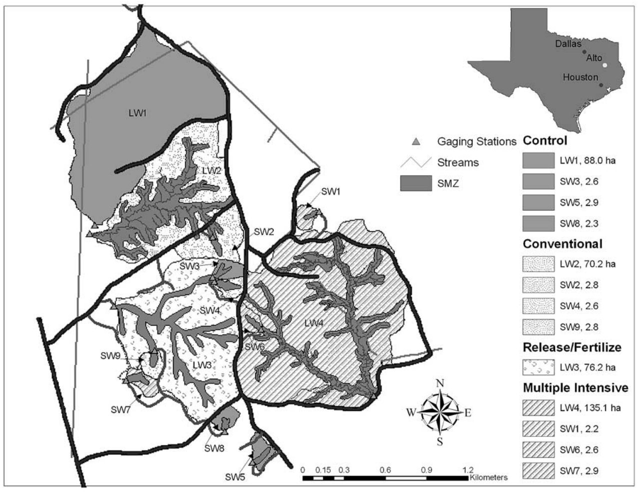

Figure 1. Texas Intensive Silviculture Study Alto experimental watersheds in East Texas, USA by treatment type and area (McBroom et al. 2008a).

topography is dominated by rolling hills, with flat floodplains associated with larger streams. Soils were historically overlain by mixed loblolly pine and hardwood forests, tend to be light-colored, and generally have low inherent fertility. Soils formed in marine sediments of Eocene strata, and dominant geological formations include the Sparta Sand and Cook Mountain formation in the Claiborne Group. Dominant soils include the Cuthbert and Kirvin series, which are classified as clayey, mixed, thermic Typic Hapludults with a fine-textured, sandy loam A-horizon up to 250-mm thick and a clay-textured B-horizon (Mowery 1959). Kirvin soils dominate on upper slopes and Cuthbert soils dominate on side slopes, with Kirvin soils being slightly deeper and Cuthbert soils having more ironstone in upper horizons. Other soil series found on the study watersheds include Lilbert, Teneha, Rentzel, Briley, and Darco, all Ultisols typified by deep, fine, sandy A-horizons.

The area has a humid subtropical climate with hot summers and cool winters. The mean annual rainfall of 117 cm is fairly evenly distributed throughout the year; April and May are the wettest months. Average annual temperature is 18.7° C, with summer averaging 27.2° C and winter averaging 9.5° C (Chang et al. 1996).

The virgin pine timber was harvested from this area in the 1920s and 1930s, and natural stands of mixed pine and upland hardwood regrew on the sites. This second growth timber was clearcut harvested in 1980 as part of an earlier study on the effects of different intensities of mechanical site preparation on water quality, and loblolly pine plantations were established on these watersheds at that time (Blackburn et al. 1986).

Study Design and Treatments

A replicated watershed approach was used to quantify the effects of site preparation intensity after clearcut harvesting on water quality and quantity (Table 1). Four large (70–135 ha, designated LW1–LW4) and nine small (2.5 ha, designated SW1–SW9) watersheds were instrumented in 1999. Streamflow monitoring started in 1999, and samples were collected to establish that there were no background levels of these herbicides. Watersheds LW1, SW3, SW5, and SW8 were not harvested or chemically treated during the study. Treatment watersheds were clearcut harvested in March through May 2002. Streamside management zones (SMZs) were retained in accordance with Texas BMP

Table 1. Silvicultural treatments implemented dates treatments were executed on study watersheds at the Alto Experimental Watersheds in East Texas.

Watershed	Treatment	Activities	Date
LW2, SW2, SW4, SW9	Conventional	Clearcut harvest	Mar.–May 2002
		Aerial herbicide site preparation*	Sept. 2002
		Machine planting 1,000 seedlings ha^{-1}	Dec. 2002
		Banded herbicide release†	Apr. 2003
LW4, SW1, SW6, SW7	Intensive	Clearcut harvest	Mar.–May 2002
		Aerial herbicide site preparation	Sept. 2002
		Subsoiling	Dec. 2002
		Hand planting 1,000 seedlings ha^{-1}	Dec. 2002
		Aerial broadcast fertilization‡	Dec. 2002
		Banded herbicide release†	Apr. 2003
		Aerial herbicide release§	Apr. 2004
LW3	Competition	Aerial herbicide release‖	Sept. 2002
	Control	Aerial broadcast fertilization‡	Aug. 2002
LW1, SW3, SW5, SW8	Control	No treatments	

* Aerial (helicopter) broadcast application of a tank mix of imazapyr and glyphosate (0.28 kg ha^{-1} [16 oz ac^{-1}] ai imazapyr as Arsenal, 2.24 kg ha^{-1} [2 qt ac^{-1}] ai glyphosate as Accord, and 1.17 L ha^{-1} [0.5 qt ac^{-1}] Rebound surfactant; 15 L ha^{-1} [6.4 qt ac^{-1}] spray volume).

† Hand-applied backpack banded herbaceous weed control covering about 50% of the watershed, consisting of 0.81 L ha^{-1} (12.5 oz ac^{-1}) Oustar (0.55 kg ha^{-1} ai hexazinone, 0.10 kg ha^{-1} ai sulfometuron methyl in the applied strips, or 0.28 kg ha^{-1} ai hexazinone, and 0.05 kg ha^{-1} ai sulfometuron methyl across the entire treated area).

‡ Aerial (fixed-wing aircraft) broadcast application of 280 kg ha^{-1} (250 lb ac^{-1}) diammonium phosphate.

§ Aerial (helicopter) broadcast herbaceous weed control covering the entire treated area consisting of 0.81 L ha^{-1} (12.5 oz ac^{-1}) Oustar (0.55 kg ha^{-1} ai hexazinone and 0.10 kg ha^{-1} ai sulfometuron methyl).

‖ Aerial (helicopter) application of 0.17 kg ha^{-1} (10 oz ac^{-1}) ai imazapyr.

guidelines and were at least 15-m wide along all intermittent and well-defined ephemeral streams. SMZs on the small watersheds were thinned at the time of clearcut harvest also. Herbicide treatment was excluded from SMZs, and global positioning system data on spray lines supplied by contractors verified that no direct overspray occurred. No death of sensitive hardwood tree species in the SMZ was observed after application, further verifying that overspray did not occur.

After harvest, clearcut watersheds received one of two intensities of site preparation. The conventional treatment applied to watersheds LW2, SW2, SW4, and SW9 was considered to be the minimum treatment necessary for loblolly pine plantation establishment (Table 1). The intensive method applied to watersheds LW4, SW1, SW6, and SW7 was considered to be a treatment that would enhance loblolly pine growth on these sites (Table 1). One additional large watershed treatment (LW3) was a woody competition release and fertilization on a 5-year-old stand (Table 1). McBroom et al. (2008a) provided detailed results from these operations on streamflow and sediment, and McBroom et al. (2008b) presented results from the fertilization treatment.

Precipitation and Streamflow Measurements

Rainfall was measured with a series of recording and nonrecording precipitation gauges distributed across the watersheds. The stream monitoring system was designed to capture stormflow events, when offsite movement of herbicides may occur, as well as to gather baseflow samples on a less intense frequency. Streamflow on small watersheds was monitored with 0.9-m (3-ft) H-flumes and stage recorders. Stage was measured using a potentiometric float and pulley level recorder installed in the stilling well at the flume sidewall. The large watershed study used concrete control structures for flow measurements on LW1, LW2, and LW3. A 72-inch corrugated iron culvert was used as a control structure on LW4. Continuous flow-stage measurements, digitally recorded at each site, provided a basis for reproducing a storm hydrograph and for computing total discharge volume for each storm event. For a more detailed description of streamflow collection and analysis, see McBroom et al. (2008a).

Sample Collection and Analysis

Automatic pumping samplers (ISCO 3700; Teledyne Technologies, Inc., Lincoln, NE) were installed on all 13 watersheds to collect a series of discrete 1-L samples along the hydrographs of individual storm runoff events. The 1-L polypropylene bottles contained a phosphate buffer, preserving samples at pH 7 at the time of collection. Samples were retrieved as soon after each storm event as possible and always within 48 hours of collection. On return to the field laboratory (Stephen F. Austin State University), aliquots of each discrete sample were transferred directly to high-density polyethylene bottles and frozen. Some pH-preserved baseflow grab samples were also collected and immediately frozen.

As part of field quality assurance, representative sample splits were spiked (1–10 μg L^{-1}) with hexazinone, imazapyr, and sulfometuron methyl before freezing. Field blanks and blank spikes were also generated. Samples were analyzed for dissolved hexazinone, imazapyr, and sulfometuron methyl at the National Council for Air and Stream Improvement (NCASI), Inc., West Coast Regional Center (Corvallis, OR). The analytical method used for these analyses provided a limit of quantification (LOQ) of 1.0 μg L^{-1} for all three herbicides and was developed by NCASI in collaboration with Morse Laboratories (Sacramento, CA) using the basic approach reported by multiple researchers (Wells and Michael 1987, Powely and deBernard 1998, Rodriguez and Orescan 1998). A complete description of the analytical method has been published (NCASI 2007).

Testing for Quantitative Bias in Analytical Results

As noted, this study targeted determination of dissolved herbicides. However, samples were frozen whole and only filtered (0.45 μm) immediately before analysis. The primary assumption inherent in this approach is that herbicides native to a sample are at equilibrium with sample-specific total suspended solids (TSS) at the time of collection and preservation and that the freeze-thaw cycle does not have an impact on this equilibrium. This assumption is supported by the results summarized in Table 2, which show that 1,100 mg L^{-1} sample TSS had no effect on recovery of spiked herbicide over the freeze-thaw cycle. These results also support field spiking into whole samples (before freezing) followed by determination of dissolved herbicides as a valid means of characterizing herbicide stability from the point of spiking forward.

Separate experiments were performed to assess the potential for herbicide losses during the period of time between collection by the autosampler and freezing, i.e., before addition of the field spike. These experiments used unpreserved and pH-preserved (pH 7) filtered (0.45 μm) samples. Results (NCASI 2007) showed approximate 15% losses of nominal 1 μg L^{-1} spikes of the three herbicides over 30 hours at 10° C (in the dark) in unpreserved samples and no losses under the same conditions in pH-preserved samples. Although the use of filtered samples diminishes the authority of these results somewhat, Fischer et al. (2008) reported only minimal ($\leq$5%) losses of these three herbicides in an unfiltered sample collected from a stagnant forest stream in southern Alabama when the sample was preserved at pH 7 and held for 6 days under ambient

Table 2. Recovery of nominal 1 μg/L spikes into unfiltered (TSS = 1,100 mg L^{-1}) and filtered (0.45 μm) water after freeze-thaw (spikes added before freezing).

	Percent recoveries			
	Unfiltered		Filtered	
Herbicide	Mean*	SD	Mean*	SD
Hexazinone	99.5	6.69	98.0	2.00
Imazapyr	87.0	5.68	84.4	8.41
Sulfometuron methyl	82.2	4.25	85.0	2.45

* Mean result from triplicate treatments.

conditions (open containers at 22–25° C). All these data are consistent with reports of relatively slow microbial degradation of imazapyr (Sanders 1986, Sanders and Meyers 1988, Mangels 1991), hexazinone (US Environmental Protection Agency 1994), and sulfometuron methyl (Fallon 1989, Rhodes 1991). Thus, the period of time between collection and freezing is not considered to have had an effect on measured herbicide concentrations, and the recovery of field spikes added just before freezing is considered to be an accurate measure of overall recovery.

Field blank results show that background contamination was not an issue in this study, with mean concentrations of all three herbicides well below 1 $\mu g\ L^{-1}$ (Table 3). Imazapyr results from the sample field spikes showed a nominal 12% low bias regardless of spike level (nominally 1–9 $\mu g\ L^{-1}$), whereas recoveries of hexazinone and sulfometuron methyl showed some dependence on spike level; i.e., hexazinone results showed an approximate 35% low bias at spike concentrations $\leq 2\ \mu g\ L^{-1}$ and an approximate 10% low bias at concentrations between 5 and 9 $\mu g\ L^{-1}$, whereas sulfometuron methyl results showed an approximate 20% low bias at spike concentrations $\leq 2\ \mu g\ L^{-1}$ and an approximate 15% low bias at concentrations between 5 and 9 $\mu g\ L^{-1}$. This level of bias was not considered significant, and no corrections were made to any of the analytical results discussed below.

Analysis of field spiked samples was spread out over the entire period during which laboratory analyses were being performed, and results were examined for temporal trends to characterize the efficacy of freezing as a mode of preservation. No evidence of any loss of imazapyr or hexazinone over 850 days of storage was apparent, but results indicated a 3–5% loss of sulfometuron methyl over this same period (NCASI 2007). These losses are incorporated in the spike recoveries listed in Table 3.

Data Analysis

Mean herbicide concentrations and mass losses by treatment by watershed size (small watersheds were not compared with large watersheds) were analyzed for any statistical differences using an α level of 0.05. Data distributions were evaluated using the Shapiro-Wilk test, and data were found to violate normality assumptions. Therefore, the nonparametric Wilcoxon-Mann-Whitney test was used to test whether concentrations and losses were different among the three conventional small watersheds (SW2, SW4, and SW9) and the three intensive small watersheds (SW1, SW6, and SW7). This test was also used to evaluate differences in mass losses and concentrations among the three large watershed treatments, intensive (LW4), conventional (LW2), and release (LW3). Watersheds were sampled until the LOQ was reached for a minimum of two consecutive storms, resulting in unequal sample sizes. Mean differences by storm in herbicide concentrations and mass losses among treatments were analyzed using SAS statistical software, version 9.2.

Results and Discussion

Storm Events

Total flow in the headwater streams of the Neches River watershed is dominated by storm runoff, with baseflow making only a minor contribution to total annual water yield. Runoff occurs in winter and early spring during periods of low evapotranspiration demand and high antecedent soil moisture (McBroom et al. 2008a). After harvest and site preparation, storm runoff increased significantly on all six treatment small watersheds due to the reduction in evapotranspiration by harvested trees (McBroom et al. 2008a). On the clearcut large watersheds (LW2 and LW4), significantly greater growing season storm runoff was measured from treatment watersheds than from the control, but differences in watershed responses between the control and treatment watersheds were insignificant during the nongrowing season. This resulted in an annual change in volume of storm runoff that was not statistically significant. Differences in large versus small watershed flow responses were attributed to the small headwater watersheds generally having steeper channels, less storativity, and more circular basin shapes (McBroom et al. 2008a).

Herbicide Concentrations

Imazapyr Concentrations in Experimental Streams

Mean imazapyr concentrations varied greatly between watersheds, often in response to specific runoff patterns, but were not found to be statistically different ($P > 0.05$) between conventional and intensive treatment watersheds for either large or small watersheds (Tables 4–7). All herbicide concentrations on control watersheds were below the

Table 3. Summary of field quality assurance for herbicide samples collected at the Texas Intensive Silviculture Study Alto Watersheds.

				Sample spikes†					
	Field blanks*			Spikes at 1–2 $\mu g\ L^{-1}$			Spikes at 5–9 $\mu g\ L^{-1}$		
Herbicide	Mean	SD	n	Mean	SD	n	Mean	SD	n
	. . . .($\mu g\ L^{-1}$)			. . . . . .(%).			. . . . .(%)		
Hexazinone	0.028	0.060	22	67	10.6	13	88	8.7	39
Imazapyr	0.031	0.037	22	87	14.0	9	90	8.1	49
Sulfometuron methyl	0.030	0.023	22	78	6.9	13	86	4.6	51

* Blank results reported regardless of detection limit or limit of quantification.

† Only includes results from experiments in which the spike level was greater than twice the sample-specific native concentration; samples spiked before freezing.

LOQ (i.e., <1 μg L^{-1}). The highest in-stream concentrations were measured in the first events after each herbicide application. All streams were dry at the time of the Sept. 28, 2002, helicopter broadcast imazapyr application. The first runoff event after application was on Oct. 22, 2002 (24 days after treatment [DAT]; Tables 4 and 5), and was the first significant rain event after the long summer dry season. In this event, 3.33 cm of rainfall generated only a single (1 L) sample on two of the intensive treatment watersheds, LW4 (0.17-cm stage rise; 26.3 μg L^{-1} imazapyr) and SW6 (0.03-cm stage rise; 39.3 μg L^{-1} imazapyr). Six days later, on Oct. 28, 2002 (30 DAT), a 3.02-cm rainfall event resulted in greater flows but lower average concentrations for SW6 and LW4 than from the previous event. This small runoff event resulted in the highest concentrations on SW9 and SW2 (because these were the first runoff events from these watersheds). Five days later (35 DAT), 3.4 cm of rain fell, resulting in runoff on SW6, SW9, and LW4 and generating lower concentrations than the previous two events.

Two days later, on Nov. 4, 2002 (37 DAT), 10.9 cm of rain fell, resulting in runoff on all watersheds. On watersheds from which flow had been initiated by earlier events (SW2, SW6, SW9, and LW4), lower concentrations were measured than for earlier events, even though this event resulted in the highest runoff volumes for the year. Flow resumed on SW1, SW4, SW7, and LW2, and the highest mean imazapyr concentrations were measured from these watersheds for this event (7.9, 1.1, 11.7, and 6.1 μg L^{-1}, respectively; Figure 2). On the watershed that received the herbicide release operation (LW3), this event resulted in the only measurable imazapyr sample, with an average concentration of 2.3 μg L^{-1}.

Runoff again occurred on Dec. 4, 2002 (67 DAT), on all watersheds, but mean concentrations were much lower still, ranging from below the LOQ on SW4 and LW3 to 4.2 μg L^{-1} on SW7. By late February 2003, average imazapyr concentrations ranged from below the LOQ (LW2, LW3, SW2, and SW4) to just above it (all averages <2 μg L^{-1}). Subsequent events resulted in concentrations either just at or below the LOQ (Figure 2).

Concentrations fell to below the LOQ within 2 months on the herbicide release watershed (LW3). Within 3 months, one conventional watershed (SW4) was below the LOQ. Five months after application, all watersheds were consistently at or below the LOQ, although there was one sample from SW6 that showed 1.1 μg L^{-1} from a runoff event in June 2003 (average concentration was 0.8 μg L^{-1}).

Hexazinone Concentrations in Experimental Streams

Mean hexazinone concentrations were not found to be statistically different ($P > 0.05$) between treatments for either large or small watersheds (Tables 4–7). The first runoff event after the banded application of hexazinone (Apr. 3–7, 2003) to all treated watersheds occurred on June 13, 2003 (71 DAT; Tables 6 and 7). This event resulted in collection of only one sample from LW4 (3.9 μg L^{-1}) and seven samples from SW6 (average concentration 7.7 μg L^{-1}). Three days later, on June 16, 2003 (74 DAT), another event resulted in runoff on all watersheds. Average hexazinone concentrations from this event ranged from below the LOQ on LW3 to 4.6 μg L^{-1} on SW6. As with imazapyr, the first runoff events resulted in the highest average concentrations even when subsequent rain events generated more runoff, and concentrations fell below the LOQ by November or December of that year (Figure 2).

An aerial broadcast application of hexazinone and sulfometuron methyl occurred on Apr. 1, 2004, only on intensive watersheds. The first runoff-generating event after this application occurred on Apr. 25, 2004, on all four intensive watersheds. Average storm event concentrations of these herbicides were much higher after this application, between 29.9 and 13.8 μg L^{-1}, than after the first application. Concentrations dropped in subsequent events and by Aug. 21, 2004 (143 DAT), levels at SW6 and LW4 were below

Table 4. Storm runoff and average imazapyr concentrations by storm for conventional treatment small (SW) and large (LW2) watersheds and the herbicide release treatment watershed (LW3) at the Texas Intensive Silviculture Study Alto Watersheds (imazapyr application Sept. 28, 2002).

	LW2		SW2		SW4		SW9		LW3	
Storm date	Runoff (cm)	Conc. (μg L^{-1})	Runoff (cm)	Conc. (μg L^{-1})	Runoff (cm)	Conc. (μg L^{-1})	Runoff (cm)	Conc. (μg L^{-1})	Runoff (cm)	Conc. (μg L^{-1})
Oct. 23, 2002	0.00		0.00		0.00		0.00		0.02	
Oct. 28, 2002	0.00		0.04	11.3	0.00		0.00	31.1	0.00	
Nov. 2, 2002	0.00		0.00		0.00		0.16	18.2	0.01	2.3
Nov. 4, 2002	3.00	6.1	4.43	5.5	1.00	1.2	6.04	9.9	1.78	<1.0
Dec. 4, 2002	1.76	2.3	3.15	2.2	0.96	<1.0	3.89	4.0	1.61	<1.0
Dec. 30, 2002	1.47	1.4	1.84	1.2	0.70	<1.0	2.61	2.0	1.44	<1.0
Feb. 20, 2003	1.36	1.0	2.07	<1.0	0.52	<1.0	2.86	1.8	1.49	<1.0
Feb. 21, 2003	4.12	<1.0	2.77	<1.0	1.47	<1.0	3.15	1.3	3.58	
Feb. 22, 2003	1.05		0.90		0.32		1.08	1.4	0.95	
Feb. 25, 2003	0.52		0.34		0.00		0.63	1.1	0.62	
Mar. 18, 2003	0.14		0.10		0.01		0.24	<1.0	0.10	
June 13, 2003	0.00	<1.0	0.00		0.00		0.00		0.00	
June 16, 2003	0.72		0.92		0.14		1.14		0.02	
June 24, 2003	1.98		1.62		0.53		1.36	<1.0	0.03	
Nov. 16, 2003	0.29		0.72		0.03		0.62		0.01	
Dec. 13, 2003	0.18		0.07		0.00		0.00		0.00	

Table 5. Storm runoff and average imazapyr concentrations by storm for intensive treatment small and large watersheds at the Texas Intensive Silviculture Study Alto Watersheds (imazapyr application Sept. 28, 2002).

	SW1		SW6		SW7		LW4	
Storm Date	Storm runoff (cm)	Imazapyr (μg L^{-1})	Storm runoff (cm)	Imazapyr (μg L^{-1})	Storm runoff (cm)	Imazapyr (μg L^{-1})	Storm runoff (cm)	Imazapyr (μg L^{-1})
Oct. 22, 2002	0.00		0.03	39.3	0.00		0.17	26.3
Oct. 28, 2002	0.00		0.18	17.7	0.00		0.38	10.7
Nov. 2, 2002	0.00		0.15	13.1	0.00		0.51	10.0
Nov. 4, 2002	4.44	7.9	4.59	7.7	3.02	11.7	8.22	8.8
Dec. 4, 2002	3.04	3.3	3.10	3.1	2.43	4.2	4.53	3.4
Dec. 30, 2002	1.63	1.8	2.62	1.4	1.71	2.4	3.54	1.8
Feb. 20, 2003	1.70	1.2	3.62	1.2	1.62	1.7	3.90	1.4
Feb. 21, 2003	2.16	1.2	2.90	1.5	2.65	1.6	4.34	1.1
Feb. 22, 2003	0.78		1.12	1.0	0.61		2.15	
Feb. 25, 2003	0.00		0.52	<1.0	0.32		1.31	
Mar. 18, 2003	0.02		0.61	<1.0	0.06		0.45	<1.0
June 13, 2003	0.00		0.27	<1.0	0.00		0.23	<1.0
June 16, 2003	0.26		2.28	1.1	0.56	<1.0	1.13	<1.0
June 24, 2003	0.66	<1.0	3.74	<1.0	0.79		1.53	
Nov. 16, 2003	0.08	<1.0	2.06	1.8	0.38	<1.0	0.20	
Dec. 13, 2003	0.00		0.20	<1.0	0.20		0.03	
Jan. 17, 2004	0.29	<1.0	1.63		0.42		0.18	
Jan. 24, 2004	3.51		4.03		2.72	<1.0	0.00	
Feb. 5, 2004	0.18		0.00		0.13	<1.0	0.29	
Feb. 9, 2004	1.25		1.26		0.69	<1.0	1.42	
Feb. 14, 2004	0.15		0.35		0.12	<1.0	0.39	
Apr. 25, 2004	0.37		1.47		0.41	<1.0	1.00	
May 1, 2004	1.05	<1.0	1.51		0.59		1.47	
June 8, 2004	0.00		0.24		0.00		0.23	
June 28, 2004	0.20		0.96		0.00		0.32	
Aug. 21, 2004	1.17		0.42		0.00		0.27	
Oct. 24, 2004	0.10		0.70	<1.0	0.19		0.25	
Nov. 17, 2004	0.01		1.28		0.51	<1.0	0.65	
Nov. 20, 2004	2.29		0.48	<1.0	0.38		0.47	

the LOQ. The storm on Aug. 21, 2004, did not produce runoff on SW7 and SW1; however, by the first runoff-producing storm after the summer dry season (Oct. 24, 2004), storm event concentrations at SW7 and SW1 were below the LOQ.

The higher concentrations found after aerial broadcast application of hexazinone may be attributed to multiple factors. First, twice as much active ingredient (ai) was applied with the broadcast application. In addition, only 24 days (less than 1 half-life) passed between broadcast application and the first runoff-producing storm, whereas 71 days (more than 2 half-lives) passed between application and first runoff for the banded application. Greater time for photolysis and degradation means less available ai for transport. Furthermore, the first runoff-producing storm after the banded application on June 13, 2003, had about 1 cm less runoff volume (depth of runoff if distributed over the entire watershed area) than the first event following the broadcast application on Apr. 25, 2004.

Sulfometuron Methyl Concentrations in Experimental Streams

Mean sulfometuron methyl concentrations were not found to be statistically different ($P > 0.05$) between treatments using the Wilcoxon test for either small or large watersheds. The banded sulfometuron methyl application did not result in any concentrations above the LOQ (and only a handful above the detection limit). Sulfometuron methyl has a half-life of 10 days and is photodegraded and easily hydrolyzed. Seven half-lives passed between application of sulfometuron methyl and the first runoff-producing event, so very little of the applied ai would have been available for transport (Tables 6 and 7).

After aerial broadcast application on the intensive watersheds, the pattern was similar to that observed for hexazinone, with the highest concentrations for the first storms after application ranging from below the LOQ to 3.7 μg L^{-1}. Concentrations then fell below the LOQ by June 8, 2004 (69 DAT), on SW6. Runoff did not occur on the other three intensive watersheds on June 8, 2004, but did occur by June 28, 2004, on SW1 and LW4, with concentrations below the LOQ. The first storm after the summer dry season (Oct. 24, 2004) resulted in the first runoff from SW7 since April, and concentrations were below the LOQ. Higher sulfometuron methyl concentrations were recorded from the broadcast than from the banded application for the same reasons as discussed for hexazinone.

Concentrations within Storm

Imazapyr and hexazinone concentrations typically peaked within 3–5 hours after the onset of storm runoff, meaning that peak herbicide concentrations were typically

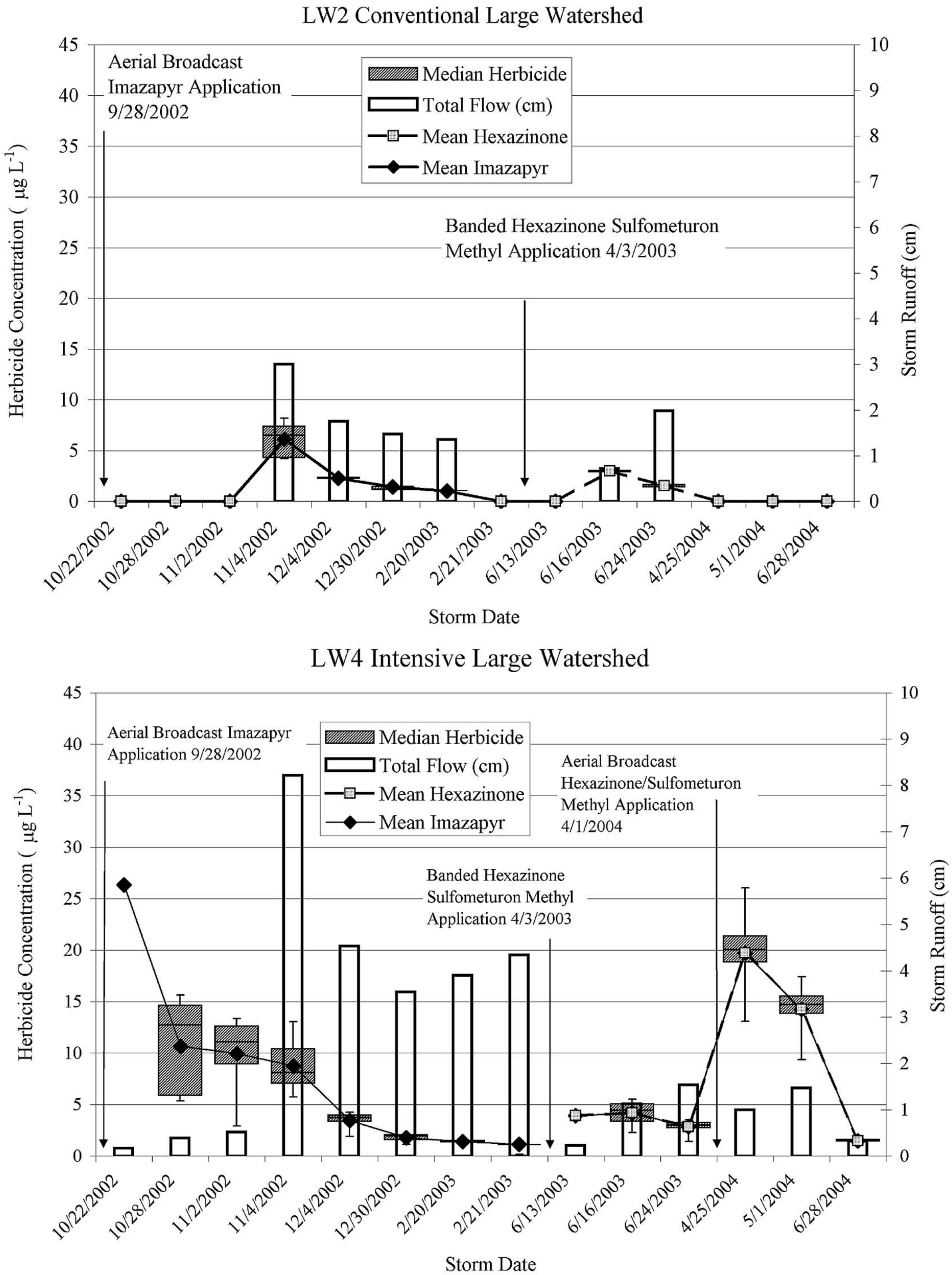

Figure 2. Mean and median box (25th and 75th percentile) and whisker (maximum and minimum) plot for conventional (SW9) and intensive (SW6) small watershed imazapyr and hexazinone concentrations and total storm runoff at the Texas Intensive Silviculture Study Alto Watersheds.

observed after peak discharge, because peak discharge occurred in <3–5 hours after onset of storm runoff (Figure 3). However, for events with longer durations, in which peak runoff occurred several hours after storm runoff initiation, as was the case on Nov. 4, 2002 (37 DAT), peak imazapyr concentration occurred well before peak discharge (Figure 4). Similar trends were observed on other watersheds for this event. The maximum concentration of herbicides in streamflow was not related directly to peak runoff, except when higher flow rates may have diluted herbicide concentrations.

Hysteresis loop analysis has commonly been used to examine sediment and storm discharge relationships (Williams 1989, Seeger et al. 2004). Plotting the relationship between storm discharge and herbicide concentration as a hysteresis loop can be an effective means of examining

Table 6. Average hexazinone and sulfometuron methyl concentrations by storm for conventional treatment small and large watersheds at the Texas Intensive Silviculture Study Alto Watersheds.

Storm date	LW2		SW2		SW4		SW9	
	Hex	SM	Hex	SM	Hex	SM	Hex	SM
	(μg L^{-1})							
Banded application, Apr. 3, 2003								
June 13, 2003			1.3					
June 16, 2003	3.0	<1.0		<1.0	1.9	<1.0	3.5	<1.0
June 24, 2003	1.5	<1.0	1.1	<1.0	1.1	<1.0	2.9	<1.0
Nov. 16, 2003	<1.0	<1.0	<1.0	<1.0		<1.0	1.2	<1.0
Dec. 13, 2003	<1.0	<1.0	<1.0	<1.0		<1.0		
Jan. 17, 2004							<1.0	<1.0
Jan. 24, 2004					<1.0	<1.0	<1.0	<1.0
Feb. 5, 2004			<1.0	<1.0			<1.0	<1.0
Feb. 9, 2004			<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Feb. 14, 2004	<1.0	<1.0						

Hex, hexazinone; sm, sulfometuron methyl.

Table 7. Average hexazinone and sulfometuron methyl concentrations by storm for intensive treatment small and large watersheds at the Texas Intensive Silviculture Study Alto Watersheds.

Storm date	SW1		SW6		SW7		LW4	
	Hex	SM	Hex	SM	Hex	SM	Hex	SM
	(μg L^{-1})							
Banded application, Apr. 3, 2003								
June 13, 2003			7.7	<1.0			3.9	<1.0
June 16, 2003	3.4	<1.0	4.6	<1.0	1.9	<1.0	4.2	<1.0
June 24, 2003	2.8	<1.0	3.0	<1.0	1.3	<1.0	2.9	<1.0
Nov. 16, 2003	<1.0	<1.0	1.6	<1.0	<1.0	<1.0		
Dec. 13, 2003			<1.0	<1.0				
Jan. 17, 2004	<1.0		<1.0	<1.0				
Jan. 24, 2004			<1.0	<1.0		<1.0		
Feb. 5, 2004			<1.0	<1.0	<1.0	<1.0		
Feb. 9, 2004			<1.0	<1.0	<1.0	<1.0		
Feb. 14, 2004			<1.0	<1.0	<1.0	<1.0		
Broadcast application, Apr. 1, 2004								
Apr. 25, 2004	29.9	2.5	21.3	2.0	13.8	1.0	19.7	1.8
May 1, 2004	20.6	1.3	14.7	1.1			14.3	1.0
June 8, 2004			6.5	<1.0				
June 28, 2004	4.5	<1.0	3.6	<1.0			1.5	<1.0
Aug. 21, 2004			<1.0	<1.0			<1.0	<1.0
Oct. 24, 2004	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Nov. 17, 2004	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0		
Nov. 20, 2004	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0		

Hex, hexazinone; SM, sulfometuron methyl.

these relationships. In general, a counterclockwise loop indicates that peak concentration occurred after peak discharge, whereas a clockwise loop indicates the opposite relationship. Counterclockwise loops are often associated with the concentration flux lagging behind the flood wave at the gauging station with fairly constant inputs of the analyte from all over the watershed (Williams 1989). This is characteristic of most observed runoff events, especially Oct. 28, 2002, Nov. 2, 2002, Dec. 4, 2002, June 16, 2003, and June 24, 2003, and the first peaks on Apr. 25, 2004 and May 1, 2004. Herbicides are traveling from outside the riparian area because application did not occur in SMZs; thus, there are longer lag times. For these events, herbicides are not coming from near source areas, but from areas further away from the stream (Figure 3). Stormflow probably resulted first from riparian source areas (McDonnell 1990) that were protected by an untreated SMZ, whereas herbicides had a longer transit time from upland source areas.

The exception to this trend was the Nov. 4, 2002 (37 DAT) event, which resulted in a clockwise hysteresis loop (Figure 4). Clockwise loops occur when there is a depletion of available analyte before water discharge has peaked and are usually associated with long duration and/or very intense storm events (Williams 1989). Such loops may also be associated with the earlier part of the storm runoff season or early-period analyte availability from preceding flows (Williams 1989). This was the case for the Nov. 4, 2002 (37 DAT) event that, as noted above, had a long duration and occurred shortly after the Nov. 2, 2002 (35 DAT) event; the concentration of imazapyr in runoff peaked before the peak in runoff (Figure 4). Imazapyr that was mobilized in the

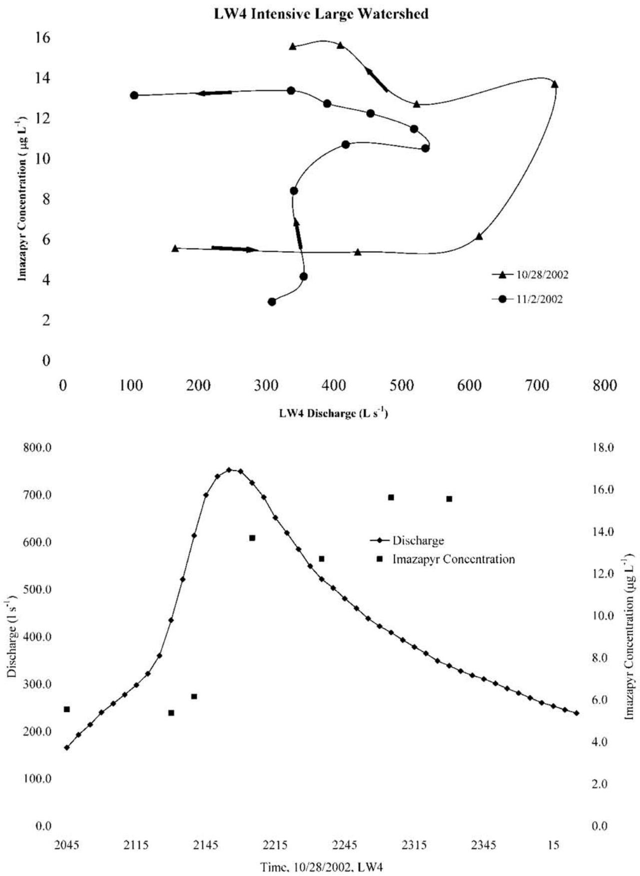

Figure 3. Hysteresis loop for LW4 on Oct. 28, 2002 and Nov. 2, 2002, storm runoff events, and discharge hydrograph (L s^{-1}) with imazapyr concentrations (μg L^{-1}) on Oct. 28, 2002 at the Texas Intensive Silviculture Study Alto Watersheds.

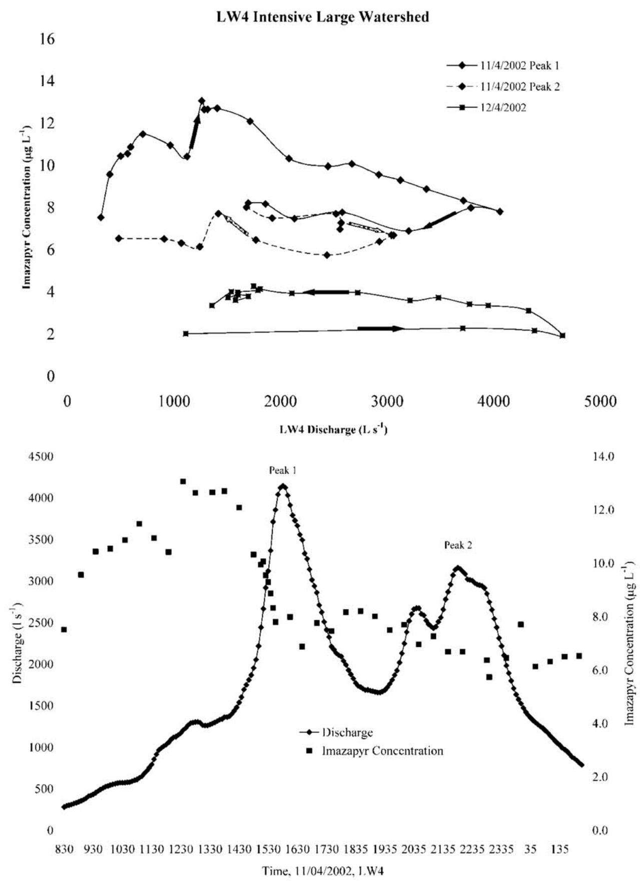

Figure 4. Hysteresis loop for LW4 on Nov. 4, 2002 and Dec. 4, 2002, storm runoff events, and discharge hydrograph (L s^{-1}) with imazapyr concentrations (μg L^{-1}) on Nov. 4, 2002 at the Texas Intensive Silviculture Study Alto Watersheds.

earlier event was immediately available for transport and was stored in runoff source areas, with insufficient time for significant degrade in herbicide to occur.

Baseflow Concentrations

After the imazapyr application of Sept. 28–29, 2002, baseflow samples were collected from LW3, LW4, SW1, SW2, and SW6 on Oct. 23, 2002 (25 DAT). This was the first time these watersheds had any postapplication baseflow and was the only baseflow sampling giving any sample(s) having concentrations above the LOQ. On LW4 and SW6, imazapyr concentrations of 15.2 and 12.6 μg L^{-1}, respectively, were recorded. This is probably due to the fact that while the streams had returned to baseflow levels, some recession flow remained in the streams from the previous day's runoff event. As noted, the highest imazapyr concentrations ($\approx$40 μg L^{-1}) occurred during the Oct. 22, 2002 event, and it is likely that all of the herbicide had not purged from the stream system after this "first flush." Later baseflow sampling events did not show concentrations greater than the LOQ for any herbicide.

Biological/Toxicological Implications

Although total herbicide (dissolved plus particulate) is the best metric for characterizing net export of herbicide(s) from a site into receiving waters, the dissolved chemical poses the most immediate risk to aquatic organisms. Even with allowance for excessive (e.g., ×2) low bias in the experimental results, the peak dissolved concentrations found in this study were orders of magnitude below levels that have been observed to have any effects on fish in standard laboratory testing (SERA 1997, 2004a, 2004b, NCASI 2004). Because these assays involve exposing fish to *dissolved* chemicals for periods ranging from 48 to 96 hours or longer, the potential for any effects is further mitigated by the relatively short-term (<24 hours) "pulsed" exposures to these peak concentrations resulting from these storm runoff events. Similarly, short-term exposures to the concentrations found in this study are not expected to pose a threat to aquatic invertebrates (Kreutzweiser et al. 1995, SERA 1997, 2004a, 2004b, NCASI 2004).

However, as noted, aquatic plants and algae are the organisms that are most sensitive to the herbicides applied at these sites (SERA 1997, 2004a, 2004b). In this study, the peak concentrations of sulfometuron methyl found in storm runoff were nominally equivalent to the USDA Forest Service (SERA 2004a) NOECs for sensitive algae (2.5 μg L^{-1} for *Selenastrum* sp.), but a nominal order of magnitude greater than the NOECs for plants (0.21 μg L^{-1} for *Lemna* sp.). These results suggest some potential for effects on aquatic plants specifically. However, the relatively short

(<24-hour) pulses in sulfometuron methyl concentration observed in this study would tend to mitigate this potential.

For hexazinone, peak concentrations measured in this study are within the range reported by SERA (1997) to affect photosynthesis in golden algae (3 μg L^{-1} for *Chrysophyta* spp.) and in blue-green algae (30 μg L^{-1} for *Anabaena* spp.). Again, however, the exposure periods in these bioassays (3–21 days) were much greater than the duration of peak concentrations observed in streams monitored as part of the current study. For imazapyr, peak concentrations measured in this study were within the ranges of NOECs and EC_{25} concentrations (7.9–22 μg L^{-1}) reported by SERA (2004b) for aquatic macrophytes. However, as with sulfometuron methyl and hexazinone, the exposure periods for these toxicity tests were in all cases much longer than the durations of the concentration pulses observed in the experimental streams.

Although additional testing of possible effects of herbicides on various biota under different exposure regimens, including pulsed exposure, may be warranted, the results from this study strongly suggest that modern forestry practices can effectively preclude chronic exposures to silvicultural herbicides at relevant concentrations.

Herbicide Export

With use of the Wilcoxon test, no statistical differences ($P > 0.05$) were observed between treatments for mean mass losses of imazapyr, hexazinone, or sulfometuron methyl for either the intensive or conventional treatments. This result was due in part to the relatively low number of storm events sampled, the large dispersions about the mean concentrations, and the relatively low absolute difference between treatments. In addition, storm runoff did not increase significantly between treatments, limiting the likelihood that differences in mass losses would be statistically significant.

Although a measure of total (particulate plus dissolved) herbicide is required to calculate the total mass of herbicide exported from a site with storm water runoff, results (Table 2) indicate that the TSS in samples collected as part of this study had very low affinity for hexazinone, imazapyr, and sulfometuron methyl. This result is generally consistent with the literature on these chemicals (SERA 1997, 2004a, 2004b). Thus, export of dissolved herbicide appears to be a reasonable surrogate for export of total herbicide. Average dissolved concentrations were multiplied by the total volume of runoff to determine mass exported, and this total mass exported was then divided by watershed area to obtain a measure of loss per unit area.

As expected, the greatest herbicide losses occurred with storm events that occurred soon after application, with losses tapering off with time (Table 8). The greatest loss rates for imazapyr occurred on LW4, which also had high runoff rates (McBroom et al. 2008a). Herbicide losses from these watersheds were found to be sensitive to soil type, and soil differences between watersheds partially account for differences in response (Wang et al. 2007). Overall, the 11.6 g ha^{-1} recorded from LW4 represents approximately 4% of the 280 g ha^{-1} ai of imazapyr applied (Figure 5). On average, approximately 1–2% of applied imazapyr moved offsite in storm runoff (Table 8). The highest hexazinone loss (14.3 g ha^{-1}) was recorded on SW6 and represented approximately 1.7% of the 825 g ha^{-1} ai applied in two applications (275 g ha^{-1} in banded application and 550 g ha^{-1} in broadcast application). Average percent hexazinone losses in storm runoff ranged from 0.2% on conventional watersheds to 0.6% on intensive watersheds (Table 8). Losses of sulfometuron methyl in runoff were even lower than those observed for hexazinone (Table 8).

Although not statistically significant, the slightly higher loss rate for imazapyr than for hexazinone may be somewhat counterintuitive, given the relatively higher solubility of hexazinone. However, runoff quantity and timing can account for this. The first hexazinone application in 2003 was banded, with less potential for movement and storm runoff was relatively low after application compared with that during the months of November through February (Figures 2 and 5). On the second broadcast application of hexazinone in 2004 on the four intensive watersheds only, two significant runoff events occurred after application, 25

Table 8. Herbicide mass losses and percent herbicide loss by treatment type and watershed at the Texas Intensive Silviculture Study Alto Watersheds.

Treatment	Mass loss			% Loss		
	Imazapyr	Hexazinone	Sulfometuron methyl	Imazapyr	Hexazinone	Sulfometuron methyl
	(g ha^{-1})			(%)		
Intensive						
LW4	11.6	5.0	0.3	4.14	0.60	0.22
SW1	5.1	1.1	0.1	1.80	0.13	0.06
SW6	6.0	14.3	0.7	2.13	1.73	0.49
SW7	3.4	0.8	0.0	1.23	0.10	0.01
Mean intensive	6.5	5.3	0.3	2.33	0.64	0.19
Conventional						
LW2	1.9	0.5	0.0	0.68	0.19	0.00
SW2	0.9	0.3	0.0	0.33	0.12	0.00
SW4	0.2	0.1	0.0	0.07	0.03	0.00
SW9	8.4	0.8	0.0	3.00	0.28	0.00
Mean conventional	2.9	0.4	0.0	1.02	0.15	0.00
Herbicide release						
LW3	0.4			0.15		

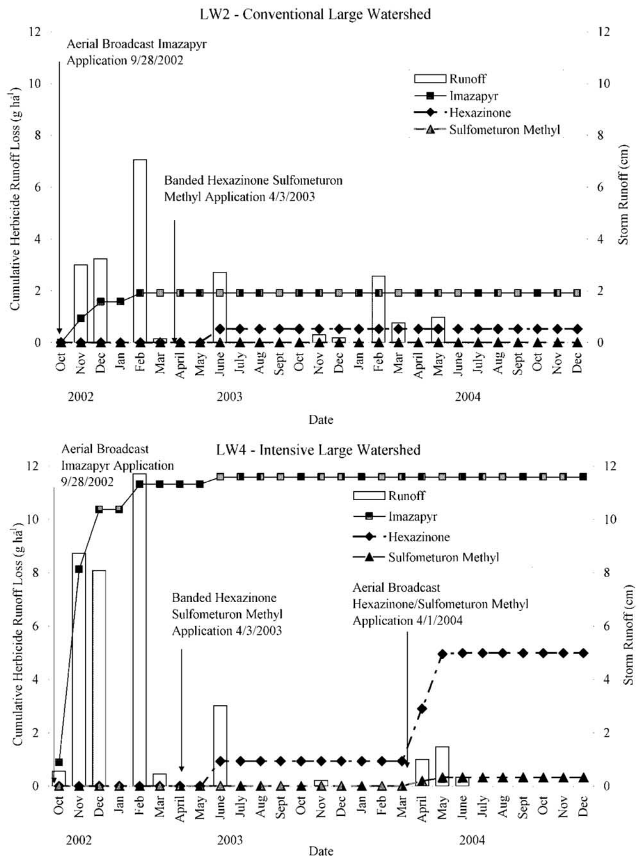

Figure 5. Cumulative mass losses of imazapyr, hexazinone, and sulfometuron methyl (g ha^{-1}) and storm runoff (cm) for the large intensive (LW4) and conventional (LW2) watersheds.

and 31 DAT (Tables 5 and 7), and these two runoff events had much lower total volumes than storms after the imazapyr broadcast application the previous year (Figures 2 and 5). After the broadcast hexazinone application, runoff declined dramatically owing to the high evapotranspiration demand and low rainfall in summer. By the runoff event in late August 2004, hexazinone concentrations were below the LOQ. These results indicate that although herbicide chemical properties are important for determining fate and dispersal in the environment, runoff characteristics after application govern loss rates to a large extent.

Conclusions

In-stream (dissolved) herbicide concentrations were highest during the first storm event immediately after application regardless of the size of subsequent events and were below the LOQ (i.e., <1 μg L^{-1}) within 150 DAT. A review of the relevant literature indicates that the concentrations found in this study were not likely have a negative impact on aquatic biota. The relatively short-lived peak concentrations (<1 day) are a key factor mitigating any potential for effects on aquatic organisms.

The highest concentrations during a given storm event tended to occur after peak discharge on these watersheds. The time required for herbicide movement through untreated riparian buffers versus storm runoff originating from riparian variable source areas could account for this. The exceptions to this pattern were long-duration or multiple-peaked events or events that occurred within a few days of each other. In those cases, herbicides mobilized and transported in earlier events were immediately available for transport.

Overall, a relatively small percentage (1–2% imazapyr and <1% hexazinone and sulfometuron methyl) of applied herbicide moved off site in runoff. Slightly larger amounts of imazapyr moved off site because larger runoff events occurred after the imazapyr application. Only 0.15% of applied imazapyr ran off as dissolved chemical from the 5-year-old plantation that received herbicide release (LW3). Aerial broadcast applications resulted in higher concentrations in runoff, probably because twice as much active ingredient was applied compared with that for banded applications. In addition, there was 1½ months less time between application and the first runoff-producing storm for the broadcast application compared with banded applications.

No significant differences in herbicide concentrations or mass losses were observed between treatments for either the small or large watersheds. Thus, intensive silviculture with BMPs did not increase the potential for herbicides to negatively affect water quality relative to conventional forest stand establishment. Use of untreated streamside management zones in particular prevents direct application into streams and provides a terrestrial herbicide degradation buffer around the stream channel, effectively reducing potential stormwater herbicide losses. Additional variables such as time between application and the first runoff-producing event also govern potential herbicide losses. Overall, herbicide site preparation with BMPs appears to have little potential to degrade water quality due to runoff of herbicide(s) applied in tank mixes.

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