

Water Chemistry of Ephemeral Streams¹

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ABSTRACT

Four individual, but related, studies are currently being conducted to determine the effects of clearcut and seed tree reproduction cutting methods on stream chemistry, sedimentation, and bedload movement by monitoring herbicide and nutrient movement in stemflow, overland flow, streamflow, and zonal subsurface flow. Sediment movement is being quantified for stormflow water samples. Comparative rates of movement are also being studied for imazapyr, hexazinone, and triclopyr. Analytical chemistry methods have been developed to permit detection of triclopyr at 0.5 micrograms per liter (parts per billion, ppb). Freezer storage studies are underway to demonstrate the suitability of frozen storage of water samples for herbicide analysis. Studies conducted on the epoxy paint, used throughout to protect wood and concrete surfaces during study installation, show a coeluting coextractable compound that interferes with triclopyr analysis. This compound does not appear after a 2-week curing period for the epoxy paint. Curing was complete long before triclopyr was applied to the site. Therefore, the coeluting coextractable compound will not confound any of the triclopyr analyses.

INTRODUCTION

The job of managing and protecting National Forest System land is constantly growing in complexity. Pressures are increasing for forest lands to produce greater amounts of goods and services while maintaining or enhancing water quality and site productivity. Accordingly, there is a continuing need to evaluate and monitor the effects of alternative silvicultural and forest management activities on the forest environment. Evaluating and monitoring the impacts of these activities on water yield, water quality, ecosystem functioning, and site productivity are essential to sound forest land management. Research has provided much information, which may be used to evaluate management activities, but there is little integrated research involving the myriad interactions in the environment.

Herbicides have been used in forest management with generally good results. The movement of forestry herbicides offsite and the potential impacts on nontarget organisms or ecosystems are a concern. Several studies have been summarized that report fate and movement of herbicides from forest sites (Michael and Neary 1990, 1993; Neary and others 1993). None of the reported studies monitored movement of triclopyr from injected sites. Where injection of other forestry herbicides was the mode of application, peak observed streamflow concentrations did not exceed 21 micrograms per liter (ppb) (table 1). A similar, low-intensity application method known as spot treatment resulted in a maximum observed concentration of 37 ppb in streamflow (table 1). Neary and others (1986) point out that sediment is the single greatest nonpoint source pollution problem created by forestry and that use of herbicides in forestry improves water quality by decreasing sediment loads to levels much lower than observed with other management tools. Thus, there is the question of ecosystem impacts and the relative impairment of water quality from herbicide use versus use of other tools in forest management.

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Table 1.—Maximum observed herbicide residues in streamflow from herbicide injection and spot treatments in the Southern United States

| Herbicide* | Location | Application | | Surface Source ¹ | Water ¹ |
|------------|-----------|---------------------|-------------------|-----------------------------|--------------------|
| | | Method [†] | Rate [‡] | | |
| Picloram | Georgia | INJ | 0.3 | M | ND |
| Picloram | Georgia | INJ | 0.3 | M | ND |
| Picloram | Georgia | INJ | 0.3 | M | 6 |
| Picloram | Kentucky | INJ | 1.3 | M | 21 |
| Picloram | Kentucky | INJ | 0.3 | M | 10 |
| Picloram | Tennessee | INJ | 0.6 | M | 4 |
| Hexazinone | Arkansas | SPOT | 2.0 | B | 8 |
| Hexazinone | Alabama | SPOT | 2.9 | M | 24 |
| Hexazinone | Alabama | SPOT | 2.9 | M | 37 |
| Hexazinone | Alabama | SPOT | 2.9 | M | 23 |
| Hexazinone | Georgia | SPOT | 1.6 | M | 6 |
| Hexazinone | Georgia | SPOT | 1.6 | M | 9 |

* Hexazinone - E.I. duPont deNemours & Company, Wilmington, DE; Picloram - DowElanco, Indianapolis, IN.

† Stem injection (INJ), application directly to the ground in a grid network (SPOT).

‡ Active ingredient (ai) applied in kg/ha.

¹ Bouchard and others 1985, Michael and Neary 1993.

¹ Expressed as $\mu\text{g/L}$, detection limits of analytical method are $1 \mu\text{g/L}$.

This study centers on the impacts that changes in ephemeral stream water quality may have on water quality and quantity at the landscape scale. Specifically, objectives are:

1. Investigate offsite movement of herbicides through water movement:
 - (a) to estimate total offsite movement of triclopyr injected for operational herbicide application,
 - (b) to estimate relative importance of different routes of offsite movement of triclopyr applied as single stem injection for vegetation management (stemflow, overland flow, and zonal subsurface flow); and
 - (c) to compare relative rate of movement of imazapyr, triclopyr, and hexazinone through subsurface routes following surface application.
2. Determine the effects of clearcut and seedtree reproduction cutting methods on stream chemistry, sedimentation, and bedload movement.

METHODS

Study Plans

This study is covered by four study plans. The need for multiple study plans arises from the complexity of each phase of the research:

- FS-SO-4351-92-1 Effects of reproduction cutting methods on streamflow, water quality, soil, and cultural resource characteristics (Clearcut Study or CCS)
- FS-SO-4105-1.25 (FS-SO-4351-93-1) Effects of seed tree cutting and site preparation on streamflow chemistry, sedimentation, and water yield in the Ouachita Mountains (Seed Tree Study or STS)
- FS-SO-4105-1.26 Development and validation of an analytical and freezer-storage method for triclopyr in water samples (Analytical Methods Study or AMS)
- FS-SO-4105-1.27 (FS-SO-4351-94-1) Subsurface flow of injected and ground-applied herbicides on a typical Ouachita National Forest mixed pine/hardwood site (Subsurface Flow Study or SFS)

Sites

A total of six study sites are divided among the four study plans. The sites are typical of the Ouachita National Forest shortleaf pine/hardwood mixed stands. Topographic relief is variable depending on the length of watershed under consideration, but slope is typically 10 to 25 percent with loamy surface soils ranging from moderate to well drained.

The CCS includes four ephemeral watersheds located on the clearcut stands in Compartment (Cpt) 1658 Stand (St) 05 (Womble Ranger District) and Cpt 458 St 16 (Fourche Ranger District). Each stand includes two small watersheds. These watersheds were clearcut in July and August 1993.

The STS site is a 32.5-acre watershed on the Alum Creek Experimental Forest. It was harvested in August 1993 by removal of all merchantable stems except 10 to 15 seed trees per acre and approximately 5 ft²/acre of hardwood basal area.

The SFS site is also located on the Alum Creek Experimental Forest. Soils here are shallow to moderately deep (6 ft), well drained, with slow to moderate permeability. Existing mature pines will not be harvested from this site, which includes several very small drainages of which two are instrumented. The small drainage to be used in this study is approximately 0.25 acres.

Instrumentation

All sites include H-flumes of the appropriate size. The CCS sites were instrumented in the fall/winter of 1992. Control sections are constructed from plywood and protected from the elements with a coat of epoxy paint. The output from control sections passes through 2-ft H-flumes. Each control section is covered with a fiberglass roof extending over the H-flume output. Instrument huts are also constructed of plywood and contain all sampling instrumentation. Sampling instruments for collection of water samples are Isco® automatic samplers connected to Isco flow meters and plotters. Control sections for the STS site and below the SFS site are constructed of concrete coated with epoxy paint for 4.5-ft and 3-ft H-flumes, respectively.

All sites are fitted with tipping bucket and weighing bucket rain gauges. The tipping bucket rain gauges are connected to electronic data loggers, which store precipitation data until it is downloaded and processed by the Oxford Laboratory.

Sample Handling

All samples are removed on a per-storm basis from the Isco samplers, double labeled with preprinted, stick-on labels, and stored in freezers at the appropriate work centers. Chest-type freezers are located at each work center and are for the exclusive storage of these samples. When freezers approach full capacity, a team from the Auburn Laboratory travels to the work centers in Arkansas carrying empty freezers. Samples are transferred to the empty freezers and returned to the Auburn Laboratory in a frozen state. All personnel involved in the study have received training in the collection, labeling, handling, and logging-in of samples, in the programming of Isco sampling device, and in the maintenance of samplers and rain gauges.

Chemical Analysis

Triclopyr

An analytical method for triclopyr has been developed at the Auburn Laboratory. It is an HPLC method utilizing UV detection. This method is undergoing final validation. Triclopyr is first extracted and concentrated using solid phase extraction technology, then cleaned-up and eluted for HPLC analysis. The method is capable of quantitation at the 0.5 to 1 part per billion level, depending on the initial sample size. A second method for more rapid analysis is being tested. Utilizing enzyme-linked immunosorbent assay technology, this method (ELISA) permits analysis of approximately 80 to 100 samples in a day with very good reliability. Some problems with interfering substances (a problem with all analytical methods) still exist, and solutions are being investigated.

Freezer storage stability studies are being conducted to determine the recovery of triclopyr from samples fortified with known amounts of triclopyr and stored in the frozen state for up to 1 year. Triclopyr has a water solubility of 430 parts per million (ppm) at 77 °F. Frozen samples thawed for analysis will be at room temperature when extracted (approximately 72 °F) and are not expected to contain more than about 0.04 ppm, so solubility should not be a concern in this study. Any decreased recovery would be attributable to surface sorption on the container wall or due to hydrolysis.

Studies have been conducted to determine whether any coextractable coeluting substances elute from the epoxy paint (used throughout these studies), which might interfere with triclopyr analysis. Prior to complete curing, a single compound appears to elute from the paint, but use of a two-stage gradient mobile phase elution technique completely separates this compound from triclopyr. Subsequent to curing, which takes about a week, no additional compounds elute to interfere with the triclopyr analysis. In addition, studies were conducted to determine whether triclopyr would preferentially sorb onto the epoxy paint surface. No triclopyr sorption was detected.

Sediment

Aliquots (500 ml) of the water samples collected by Isco automatic samplers are filtered through prewashed, dried, and weighed Whatman® GF/B glass fiber filters to remove all suspended sediment. Subsequent to filtration, each filter is again dried to constant weight at 105 °C and then weighed. The difference in weight-suspended sediment-is related to flow measured with the Isco flow meters to calculate total suspended sediment transported offsite.

Nutrients

Anions and cations are analyzed using a Dionex® ion chromatograph. Concentrations will be related to storm flow and treatment. The pH of all samples is also checked and recorded.

Stem Injection

Injection of hardwood stems began during the week of 18 October 1993. Auburn and Oxford Laboratories, as well as National Forest System personnel, were on site to record the exact amount of triclopyr used on each watershed. The two watersheds on the Womble were treated 21 October 1993; site 1 received a total of 3,885 ml undiluted Garlon® 3A with blue dye added to this mixture; site 2 received 3,610 ml with blue dye added to this mixture. The Fourche watersheds were treated 22 October 1993; site 3 received 6,630 ml with no dye added, and site 4 received 5,330 ml with no dye added. And the Alum Creek watershed was treated 23 October 1993; the total area received 30,530 ml whereas the watershed drainage monitored by the H-flume received 26,280 ml. Monitoring of offsite movement began with the first precipitation event following the application.

The application method was not a classical injection treatment. Classical injection is application via some instrument like a tubular type injector (e.g., Jim-Gem® or Cran-jector®). This type of injection equipment ensures insertion of the herbicide into cuts usually at the rate of 1 or 2 ml per cut. A modification of the injection technique, which reduces the back strain common with tubular injectors, is the Hypo-Hatchet®. Hypo-hatchets are hatchets with narrow bits specially hollowed to allow delivery of the herbicide on impact with the injected stem. The method used in this study is more aptly described as a hack-and-squirt method. In hack-and-squirt, as it was used on the Fourche, Womble, and Alum Creek watersheds, a machete, hatchet, or other cutting device was used to essentially girdle each stem and remove bark, often down to the xylem. A spray bottle was then used to spray either a steady stream or a spray mist onto each tree around the girdle. During this process, some splashing was observed, which frequently went directly onto the ground. Because of this, values of offsite movement will likely be intermediate between the values observed in spot and injection treatments (table 1).

RESULTS AND DISCUSSION

All sites have been completely instrumented except the SFS site. Sampling equipment is present on the SFS site, but stem collars for the monitoring of stemflow from injected sites have not been installed.

Some baseline sampling has been conducted on these sites. Precipitation data and stream stage data have been correlated to produce hydrographs indicating stream response to precipitation events of different magnitudes. Early results produced atypical hydrographs in which flow began and then appeared to remain constant for a long time, instead of decreasing in an orderly and predictable fashion. The problem was identified and determined to be the result of incident precipitation received in the flumes. Because H-flumes are designed to have a small dip at the gauging point, incident precipitation pooled over the pressure transducers used to record stream stage. Identification of this problem led to covering the entire length of control section and the H-flume to preclude interception by the control section and the resulting false flow. Subsequent hydrographs have been more typical. Flow from the Fourche watersheds typically lasts much longer (3 to 5 days) than that observed for the Womble (1 to 3 days). The STS site on Alum Creek may flow for weeks after a rain event.

Preliminary surveys indicate the Fourche watersheds are approximately 8 and 13 acres while the Womble watersheds are approximately 3 acres (2.8 and 2.7). The Alum Creek STS is approximately 32.5 acres. The Alum Creek SFS is approximately 14 acres, with 0.25 acres instrumented for subsurface flow sampling. Additional surveys will be conducted to more completely identify the area of the treated watersheds.

LITERATURE CITATIONS

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