Herbicide Containment Study Protocol

Eagle Lake, NY

Introduction

When herbicides are applied in a lake system, many factors dictate the movement of the active ingredient, including the type of product applied (granular vs. liquid), water currents, wind action, and rainfall events. Turbidity curtains can be deployed to contain the active ingredient in target treatment areas, and restrict the movement into environmentally sensitive areas. The following protocol details the methodology to be used to perform a dye study on three treatment plots at Eagle Lake (Essex County, NY), in an effort to demonstrate that turbidity curtains can be used effectively to contain herbicides.

Containment Areas

For this study, three containment areas will be utilized, as depicted on the attached map. Prior to the study, the client needs to perform a bathymetry survey of all three sites to determine curtain depth. The measurements of the curtain are estimated. Actual curtain lengths will be determined based on the size of the Eurasian water milfoil bed in the target area. These sites are described as follows:

Containment Site 1: This site is located along the southern shoreline in the lower basin. Two 300 foot sections of the turbidity curtain will be deployed at this site anchored to the shoreline, and a fixed point in the water. The target Eurasian water milfoil bed is #47 on the Eagle Lake Eurasian Water Milfoil Location Map.

Containment Site 2: This site is located to the south of the island off the southeast shoreline in the upper basin, near the bridge where route 74 crosses the lake. Two sections of turbidity curtain will be deployed at this site. The south curtain will be attached to the southeast part of the island and the southern shore, approximately 300 feet long. The east curtain will be attached to the east point of the island to the west shore of the peninsula, approximately 450 feet long. The target Eurasian water milfoil beds are # 6 through #10 on the Eagle Lake Eurasian Water Milfoil Location Map.

Containment Site 3: This site is in the open water of the upper basin, west of the island. Four 300 foot sections of curtain will be attached to four fixed points, creating a square containment area. The target Eurasian water milfoil bed is #1 on the Eagle Lake Eurasian Water Milfoil Location Map.

Turbidity Curtain Specifications

The turbidity curtain used for this study is similar to those employed by Allied Biological, Inc. (2005, Lamoka Lake, NY using Sonar AS) and Getsinger, et. al. (1997, using triclopyr). The curtain is manufactured by Indian Valley Industries, located outside of Binghamton, NY. The curtain is classified as a Type I floating turbidity curtain constructed of 14 oz. impermeable PVC. The curtain is manufactured in 50 foot sections (for ease of deployment) that need to be attached by hand. It is assumed the curtain will be 15 foot high, although this height will be determined following the bathymetry survey. Floatation is provided by 12"x 12" EPS foam blocks, which provides 60 lbs. of buoyancy per LF. The top of the curtain is 5/16" vinyl-coated cable (9800# strength) that is attached to other sections via heavy duty clips and also serves as the anchoring points. The bottom of the curtain is ¼" ballast chain that keeps the curtain on the lake bottom. The seams of the curtain are heat-sealed. Each 50 foot section is attached to another section via hand tying ropes into #4 grommets spaced 12" apart along the seam. Velcro overlaps along the entire seam ensure a tighter seal.

Curtain Installation

Prior to installation, the individual sections of the curtain need to be attached by hand. This is accomplished by hand-tying short lengths of rope along all of the grommets of the seam, and then firmly pressing the Velcro flap over the seam. The cable at the top is attached to the next section via a heavy-duty clip. Likewise, the ballast chain is attached to the next section of chain via a heavy-duty clip. Next, the bottom of the curtain is bundled/folded up to the floatation top and secured with another length of rope. The assembly should be performed on the shore, and then the whole assembled curtain is towed into place on the lake by a boat.

The curtain cable needs to be attached to a solid object (a tree is best, or a 4" by 4" post sunk into the ground or lake bottom in the case of the apex of site # 1, or the corners of the containment at site 3) on each side. Once the cables are attached, and the curtain is in position, it should be inspected for twists. Following inspection, the top ropes are cut, and the curtain unfurls to the lake bottom. The curtain should be examined by divers, or an underwater camera to ensure it is lying flat on the bottom. In addition, the curtain is anchored to the bottom of the lake with 22 lb. danforth-style anchors, situated on each side of the curtain, every 100 feet apart. Containment site 3 might require additional anchors. Three feet of ½" chain will be attached to each anchor lead-line, which is affixed with a 1 foot diameter buoy.

It is estimated the installation of the curtains will take five field technicians two days to complete.

Dye Application

Rhodamine WT (Keystone Aniline Corp., Chicago, IL) is the dye of choice in water tracing applications. This liquid fluorescent dye is readily detected in the water with a fluorometer, simulates the movement of an herbicide in the water column, and is environmentally safe to use in aquatic systems. It's a bright red fluorescent dye (approximately 21% active dye) with exceptionally high tinctorial strength and a low tendency to stain silt, sediment, organic matter (plants) or suspended matter in fresh or salt water. Rhodamine WT dye liquid is certified by the National Sanitation Foundation International to ANSI/NSF Standard 60: Drinking Water Treatment Chemicals-Health Effects, for use in tracing drinking water under the following conditions, "Concentrations of Rhodamine WT Liquid in drinking water is not to exceed 0.01 PPB and exposure (end) use is to be infrequent." For more information on Rhodamine WT Liquid dye, see the MSDS sheet and technical bulletin 89 attached to this protocol.

A permit is required for its application in New York, which could take 12 to 16 weeks to apply for and be granted.

The rhodamine WT dye needs to be applied to each containment plot at a 10 ppb concentration. The bathymetry data collected by the client will be used to calculate the water volume of each plot, to determine the amount of dye needed to achieve a 10 ppb concentration. The dye will be applied via a tank and pump array in an airboat through weighted diffuser lines below the surface of the water. Since this is a dye that stains everything it comes into contact with, dedicated tanks and lines need to be purchased and used solely for this application.

It is estimated the treatments in all three containment plots will take four to six hours to complete with two field technicians.

Dye Monitoring

The crucial part of the study is the monitoring of the dye after applied in the water. A discreet sampler attached to a calibrated fluorometer will be used to measure the concentration of the dye throughout the lake. The fluorometer used will be an Aquafluor™ (Turner Designs, Sunnyvale, CA) dual channel mini-fluorometer. The instruction manual for this meter is attached to this protocol. The unit uses a single point and blank calibration, and has a Rhodamine dye detection limit of 0.4 ppb.

Below is a table listing the recommended sampling sites, including site name, GPS coordinates, and a description of the site location. These sample sites are also depicted on the containment study map included with this protocol. At each site, samples will be collected one foot under the surface of the water, at mid-depth, and one foot above the lake bottom. Samples shall be labeled

with the site number, and then an S, M, or B, for the surface, mid-depth, and near bottom depths, respectively. For example, the site 1 bottom sample would be labeled 1B, while the site 15 mid-depth would be labeled 15M. Samples will be collected at each site 4, 8, 24, 48, 72, and 144 hours (6 sampling events, total) after treatment to cover a wide range of concentration exposure models.

Table 1 Dye Sample Sites

Site #	GPS Coordinates	Description
1	43°52’26.02”N 73°36’14.07”W	Boat Launch
2	43°52’20.63”N 73°35’58.93”W	Site 1, Inside West
3	43°52’20.79”N 73°35’56.02”W	Site 1, Inside East
4	43°52’22.05”N 73°35’58.81”W	Site 1, Outside West
5	43°52’22.51”N 73°35’54.28”W	Site 1, Outside East
6	43°52’35.40”N 73°35’36.46”W	South of Bridge
7	43°52’42.64”N 73°35’18.74”W	Site 2, Inside North
8	43°52’38.88”N 73°35’24.44”W	Site 2, Inside South
9	43°52’40.55”N 73°35’30.01”W	Site 2, Outside West
10	43°52’46.16”N 73°35’19.96”W	Site 2, Outside North
11	43°52’55.12”N 73°34’49.13”W	Site 3, Inside Southwest
12	43°52’54.24”N 73°34’50.35”W	Site 3, Inside Northeast
13	43°52’56.62”N 73°34’49.17”W	Site 3 Outside North
14	43°52’51.85”N 73°34’49.01”W	Site 3, Outside South
15	43°52’53.82”N 73°34’51.74”W	Site 3, Outside West
16	43°52’53.99”N 73°34’45.29”W	Site 3, Outside East

The dye monitoring will require a crew of two field technicians, trained to use and calibrate the fluorometer, and a boat to be on site for 6 days. The boat used to collect the dye water samples must not be the application boat, to prevent cross contaminating the sites. A clean supply of water (not from the lake) needs to be on hand to rinse the equipment between each sample to prevent dye contamination. The fluorometer will be calibrated each day before use. Additional calibrations might be required, if drift is suspected during the sampling. On day one, the unit will be calibrated with a 10 ppb standard, but a 5 ppb standard will be used on day two and beyond.

Turbidity Curtain Removal and Storage

Following the dye study, the turbidity curtain sections need to be removed. It is estimated this process will take a crew of five field technicians two days to complete, using two boats. The curtain will be removed three to four sections at a time. Each section will be towed back to the boat launch and carefully removed from the water, scrubbed with brushes and rinsed with lake water (through a gas powered water pump), dried, and folded for storage. Following removal of the curtain, anchors will be removed as well as any posts used to secure the curtain.

The folded sections of the curtain will then be placed on a truck and shipped to an inside storage facility until the following year (approximately 9 months). Then, the same pieces of the turbidity curtain can be reused to perform the herbicide application, provided the results of this study are approved.

References

Getsinger, K.D., E.G. Turner, J. D. Madsen, M. D. Netherland. 1997. *Restoring Native Vegetation in a Eurasian Water Milfoil-Dominated Plant Community using the Herbicide Triclopyr*. Regulated Rivers: Research & Management, vol. 13, p. 357-375.

Keystone Aniline R&D Laboratories. 2002. *Technical Bulletin # 89: Keyacid Rhodamine WT Liquid*. Keystone Aniline Corporation, Chicago, IL.

Eagle Lake Herbicide Containment Study

Estimated Costs

1. Turbidity Curtain (Manufacturer-Indian Valley Industries, Inc.)

Specifications: Type I Turbidity Curtain: 50 foot sections, 15 feet deep.

Material: 14 oz. impermeable PVC

Floatation: 12”’x12’’ EPS foam blocks providing 60 lbs. per LF buoyancy

Cable/chain: 5/16” vinyl-coated cable (9800# strength), 5/16” ballast chain

Seams: Heat sealed with Velcro overlap closure and #4 grommets for connection

Anchors/buoys/rope/chain leader (35 sets): Cost: $3000.00

Price per section: $1037.50 per 50 foot section

51 Sections (2,550 feet) needed for all three containment areas (see map)

Total Cost: ($1037.50 x 51) = $52,912.50 plus $900.00 shipping to lake)

2. Curtain Installation (Allied Biological, Inc.)

Pre-installation Bathymetry Mapping (Client)

Five field technicians

Two boats

Two days installation

Travel (8 hours)

Total Cost: $9,000

3. Dye Application (Allied Biological, Inc.)

Rhodamine WT dye applied at 10 ppb in three contained areas (cost: $37.50/gallon)

Two field technicians (~ 6 hours)

One boat with dropper lines

Dedicated mixing tank and lines (cost: $500.00)

Permit Application (cost: $550.00)

Total Cost: $4,575.00

4. Dye Monitoring

Two field technicians

One boat (not the dye application boat)

16 sample sites; 3 depths/site (need pump array or Kemmerer sampler, and cleaning equipment)

6 sampling Events: 4 hours after treatment (AT), 8 hours AT, 1 day AT, 2 days AT, 3 days AT, and 6 days AT)

Fluorometer Rental: $200/day (x 8 days = $1600.00)

Total Cost: $10, 600.00

5. Turbidity Curtain Removal and Storage (Allied Biological, Inc.)

Five field technicians

Two boats

Two days

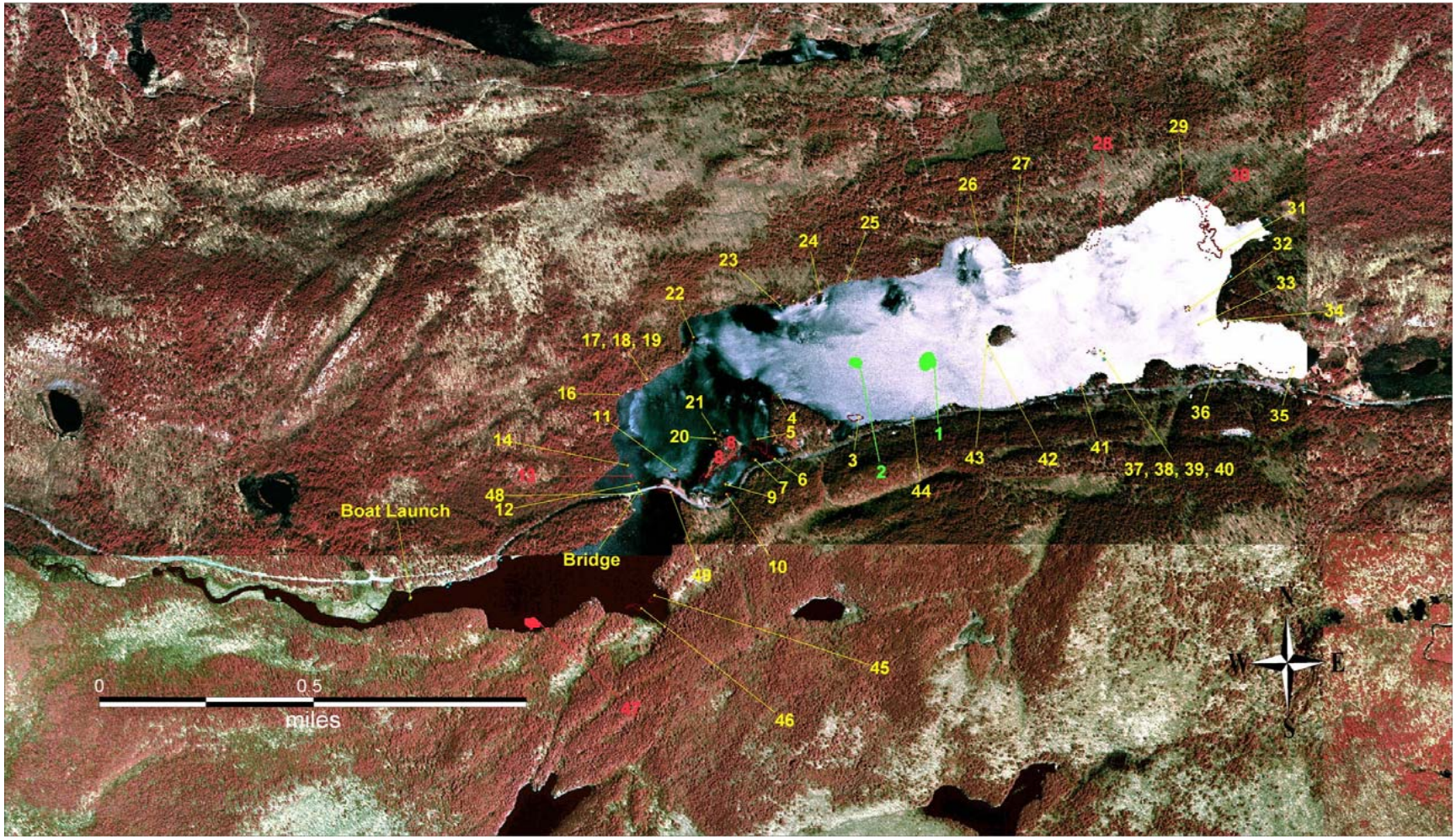
Travel (8 hours)

Transportation of Curtain to Indoor Storage (cost: $X)

Indoor Storage (from time of removal until herbicide treatment the following year; ~9 months)

Total Cost: $9,900.00 plus cost of the two 10’ by 20’ storage units.

Total Project Cost (Sections 1 through 5, above): **$87,887.50**



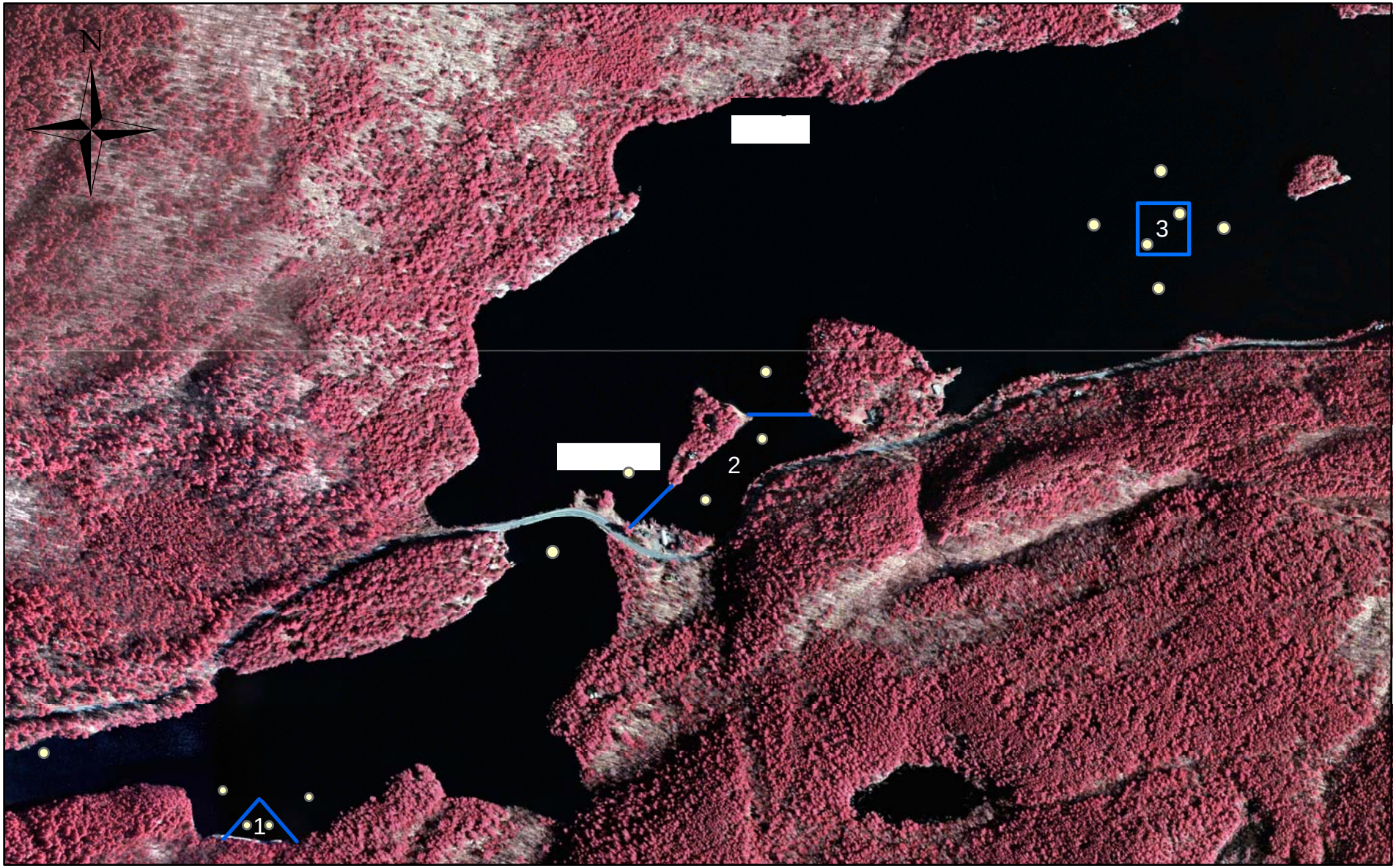
Eagle Lake
Essex County, NY

Eurasian Water Milfoil Bed Locations

Allied Biological

580 Rockport Road
Hackettstown, NJ 07840
(908) 850-0303
FAX 850-4994

Eagle Lake, NY
Herbicide Containment Study



0 300 600 1,200 Feet

Containment 1: Two 300 foot sections
Containment 2: One 300 foot and One 450 foot section
Containment 3: Four 300 foot sections

= Dye Sample Site

Allied Biological

KEYSTONE

SAFETY DATA SHEET

Keystone Aniline Corporation

www.dyes.com

Corporate Headquarters
2501 West Fulton Street
Chicago, IL 60612
Tel 312-666-2015
Fax 312-666-8530

Manufacturing Facility
2165 Highway 292
Inman, SC 29349
Tel 864-473-1601
Fax 864-473-2377

24 Hour Emergency Phones
In U.S. Call CHEMTEL 1-800-255-3924
Outside U.S. call CHEMTEL Collect at;
1-813-248-0585

HMIS RATINGS: **HEALTH:** 2 **FIRE:** 1 **REACTIVITY:** 0 **PERSONAL PROTECTION:** H

SECTION 1: PRODUCT IDENTIFICATION

Product I.D.: 70301027
Product Name: KEYACID RHODAMINE WT LIQUID
Product Description: Aqueous Acid Red Colorant Solution
Chemical Family: Confidential dye group
Effective Date: January 30, 2008

SECTION 2: HAZARD IDENTIFICATION AND EMERGENCY OVERVIEW

Emergency Overview:

Mild eye & skin irritant. Respiratory effects not established.

Eye Contact:

Depending on duration and personal sensitivity, unprotected contact may cause mild irritation, discomfort, redness, watering, itching or other effects. Heavy contact or for prolonged period may increase effects. Follow ALL supervisor and Personal Protection instructions in Section 8 of this SDS.

Skin Contact:

Depending on degree of unprotected contact with product and individual sensitivity, may cause mild irritation to skin, redness, rash, itching, and other effects. Constant/repeated long-term heavy contact with some powdered products may cause abrasion of skin. Some components may be absorbed through unprotected skin causing or adding to effects.

Inhalation:

Depending on duration of unprotected inhalation of product, vapors, mists, aerosols or dusts may cause mild irritation of the nose, throat, lungs and mucous membranes, shortness of breath, sneezing, cough, runny nose, nausea, headache and other effects. Prolonged or heavy exposure, or heating of liquid material may increase severity of symptoms.

Ingestion:

Depending on amount swallowed, product can cause mild irritation of mouth, throat, esophagus, stomach, and gastrointestinal tract, upset stomach, abdominal discomfort, nausea, vomiting, gastrointestinal disturbances, dizziness, diarrhea, and other effects. Aspiration into lungs during vomiting is an emergency and may cause lung injury and life-threatening conditions. Higher dose may increase irritation and severity of symptoms.

Medical Conditions Aggravated by Exposure:

The possibility of aggravation of existing medical conditions from inhalation of product dust, vapors, mists or aerosols , or from skin contact, eye contact or swallowing has not been determined. As a precaution against unknown effects on existing medical conditions, hypersensitivities, allergic reactions, or other unforeseen health effects, be sure to read, understand and follow all supervisor instructions, AND instructions for wearing Personal Protective Equipment and clothing in Section 8 of this MSDS. As a precaution, avoid inhalation of product in any form.

Skin Sensitization:

Skin sensitization from unprotected contact with this product has not been determined. Skin effects from repeated exposure may be unpredictable and may appear in sensitive individuals not previously known to be hypersensitive or allergic. As a precaution, avoid ALL exposures. Follow all supervisor instructions and all directions in Section 8 for personal health protection.

Respiratory Sensitization:

Respiratory sensitization caused by inhalation of product dust, vapors, mists or aerosols has not been determined. As a precaution against aggravating existing respiratory conditions, hypersensitivity, allergic reactions, or other unforeseen health effects, be sure to read, understand and follow all supervisor instructions, and instructions for wearing Personal Protective Equipment and clothing in Section 8 of this SDS. Avoid inhalation of product in any form. Allergic reactions and sensitivity depend on individuals and can be unpredictable.

Special Warnings:

None for this material

Unusual Health Hazards:

None for this material

Supplemental Hazard Information

No additional information is currently available

Notes to Physician

Treat Symptomatically based on Section 2 Hazard Warnings and Section 3 ingredients unless indicated otherwise

Cancer Information:

***** Not known to contain carcinogens *****

SECTION 3: OSHA HAZARDOUS INGREDIENTS

1 Component	CAS Number	Wt %	OSHA - PEL	ACGIH - TLV	Recommended PEL
Trimellitic acid	528-44-9	1 - 10%	Not established	Not established	Lowest achievable exposure or zero with best PPE
Sodium monochloride (Color standardizer)	7647-14-5	1 - 10%	15 mg/m3 TWA (Total dust/powder form)	10 mg/m3 TWA (Total dust/powder form)	Not applicable

Important Notice:

Unprotected contact with Section 3 ingredients may be hazardous based on OSHA 29 CFR 1910.1200 & related appendices. Components not listed are trade secrets, non-hazardous, or not reportable. This SDS is not intended to offer full disclosure, but all component information is available to medical or emergency personnel. All hazards are based on contact exposure. Reducing or eliminating contact can reduce or eliminate risk. Use protective equipment and clothing in Section 8 to minimize or eliminate contact. Effects may be unpredictable and may vary from person to person due to individual reactions. Users are responsible for hazard determination and communication. Unless indicated otherwise, non-carcinogenic components are indicated within a 1-10% range, and investigated or potential carcinogens within a 0.1-1% range. HMIS ratings are based on data interpretation, and vary from company to company. They are intended only for quick, general identification of the degree of potential hazards. Hazards range from 0 (Minimal) up to 4 (Severe). Consult the National Paint & Coatings Association HMIS Manual for detailed information on ratings. To handle material safely, consider all information in this SDS.

SECTION 4: FIRST AID INSTRUCTIONS

Eye Contact:

Immediately rinse with flowing water for at least 15 minutes while holding eyelids open. Get immediate medical attention, as a precaution.

Skin Contact:

Immediately remove contaminated clothing. Wash affected area with soap and rinse with plenty of water. Get medical attention, as a precaution.

Inhalation:

Immediately move person to fresh air. If breathing is difficult give oxygen, call 911, calm the individual. If not breathing, call 911, give artificial respiration (CPR) until medical help arrives. Have this Material Safety Data Sheet available.

Ingestion:

Do not induce vomiting unless directed to do so by a doctor or by other emergency medical personnel. Forced vomiting of certain chemicals may cause aspiration and lung damage. Have this Material Safety Data Sheet available.

SECTION 5: FIRE FIGHTING INSTRUCTIONS

Flash Point:
Not applicable or not established

Auto-ignition Temperature:
Not applicable

LEL:
Not applicable

UEL:
Not applicable

Unusual hazards:
None expected

Other Hazards:
None known

Types of Extinguishers:
CO2, dry chemical, foam, water fog or spray depending on type of fire

Fire Fighting Directions:
NA

SECTION 6: ACCIDENTAL SPILL OR RELEASE INSTRUCTIONS

Special Precautions:

None known. Follow general precautions shown below.

Reporting:

Check the RQ

Static Discharges:

Take precautionary measures against static discharges when cleaning up leaks or spills of powders, combustibles, or flammable liquids. Containers should be properly grounded with metal straps, cables or other appropriate means to relieve static electricity build-up or generation. .

Environmental Protection:

Immediately dike liquid spills with inert absorbent material (sand, "Oil Dry" or other commercially available spill absorbent) to contain and soak up liquid. Prevent material from entering floor drains, sewers, or any bodies of water. For powder spills, use sweeping compound, sawdust, or other appropriate material to contain dust. If possible, recover any uncontaminated materials to re-use.

Protective equipment and clothing:

Wear all proper personal protective equipment and clothing to care for spill situation. See section 8 of this MSDS.

Clean up:

After containing liquid spill by diking and soaking up with inert absorbent material, place in labeled container to be sealed for proper and regulated disposal. Only the slightest residue should remain. Try to save uncontaminated material for reuse whenever possible. For powders, use sweeping compound to minimize dust and pick up as much product as possible. Do not allow liquids to seep into drains, sewers, lakes, rivers, etc. Check Sections 1 and 2 for dye description or type. Solvent dye residue may be cleaned by scrubbing with detergent, depending on type. Do not add water to water-soluble dyes. Dye is concentrated. This will increase amount of color to remove. All cleaning or scrubbing liquids used should be absorbed and placed in labeled containers for correct disposal. Absorbent material containing solvents may release combustible or flammable vapors and should be handled accordingly, properly labeled and disposed. Check Sections 2, 5, 13 & 15 for applicable instructions and regulations.

SECTION 7: HANDLING AND STORAGE

Warnings and Precautions:

No special precautions anticipated. Wear all PPE in section 8 as a precaution, and avoid physical contact with material.

Personal Protection:

Wear ALL proper personal protective equipment as outlined in section 8 of this SDS.

Handling, Storage & Temperature Conditions:

Keep containers tightly sealed in cool & dry area, out of direct sunlight. FOR PRODUCTS LISTING FLAMMABLE/COMBUSTIBLE SOLVENTS or LOW FLASH POINTS: Store away from fire hazards and ignition sources, high heat, open flames, welding, hot plates, steam pipes, radiators, etc. Maintain good ventilation. Guard against static discharges. Ground all containers before mixing or filling. Use non-sparking tools to open, close or otherwise work with containers. Limit indoor storage to approved areas with automatic sprinklers. Vapors expected to be released when material is heated during process operations. At minimum, follow all Section 8 recommendations for Exposure Controls and Personal Protection. FOR WATER-BASED PRODUCTS: DO NOT FREEZE. Also ground containers when filling or mixing powders.

SECTION 8: EXPOSURE CONTROLS AND PERSONAL PROTECTION

Note: Selecting protective equipment & clothing:

When choosing personal protective equipment and clothing, consider each worker's environment, all chemicals being handled, temperature, ventilation, and all other conditions. Determination of the level of protection needed for the eyes, skin and respiratory system under working conditions is the responsibility of the product end-user or shift supervisor. SDS Sections 2, 3, 8 and 11 should be consulted.

Eye protection:

As a precaution, wear indirectly vented, splash-proof chemical safety goggles. When handling liquids, wear splash-proof goggles under a clear face-shield. Face shield is not to be used without these goggles. The type or extent of protection needed should be determined by the product end-user or shift supervisor.

Skin Protection:

Always wear impervious, chemical-resistant synthetic or rubber gloves. Check with manufacturer for best glove for the material being handled. Wear good quality long sleeved work shirt, coveralls, and a rubber or plastic apron. Wash hands after handling and before eating, drinking or using restroom. Shower after each shift. Clean contaminated but reusable protective equipment and clothing before reusing and wearing again. Discard contaminated disposable gloves and clothing. The type or extent of protection needed should be determined by the product end-user or shift supervisor.

Respiratory Protection:

Depending on type of material handled and processing conditions, it is recommended that an appropriate NIOSH approved organic vapor/mist respirator, or dust respirator (with proper filters as required) be worn when exposure to product is expected. After each shift or when equipment becomes contaminated, clean respirator and replace filters in compliance with 29 CFR 1910.134. The type or extent of protection needed should be determined by the product end-user or shift supervisor.

Eye Washes and Other Protection:

Eye wash stations and drench showers should be located within 100 feet or 10-second walk of the work area per ANSI standard Z358.1-1990.

Ventilation:

Local exhaust should be used to maintain exposure limits below specified amounts recommended by OSHA, NIOSH, or ACGIH and to draw spray, aerosol, vapors, or dusts away from workers and prevent routine inhalation. At least 10 air changes per hour are recommended for good room ventilation.

Airborne Exposure Limits:

Not referenced in literature

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

pH:	10.5 @ 1.0%
% Water Content:	70-80
% Total Solids / Non-Volatiles:	20-30
% Total VOC:	0
% Solvents:	0
% Other Components:	Undisclosed
Boiling Point:	>212 ºF (100 ºC)
Color:	Red
Form:	Liquid
Odor:	None
Freezing/Melting Point:	~ 32 ºF (0 ºC)
Lbs. per gallon:	9.41
Specific Gravity (Liquid):	1.13
Vapor Pressure:	Not established
Water Solubility:	Miscible @ 20 ºC
Solvent Solubility:	Not applicable
Other Properties:	Vapor density: Heavier than air Evap. rate: Slower than butyl acetate

All Data shown above are typical values, not specifications.

SECTION 10: STABILITY AND REACTIVITY

Stability:

Product is expected to be stable under normal, ambient (controlled) conditions concerning heat, moisture, pressure, fire and ignition hazards, and ventilation. Contact with incompatible or reactive materials may cause hazardous reactions in some products if indicated. Check information below.

Hazardous Polymerization:

Product will not undergo polymerization.

Conditions to Avoid:

None known

Incompatible Materials:

None known

Hazardous Decomposition Products:

In fire: Oxides of carbon, nitrogen, sulfur

Possible Hazard Reactions:

None known

SECTION 11: TOXICOLOGICAL INFORMATION

70301027
KEYACID RHODAMINE WT LIQUID

Oral LD50 (Rat):	No data currently available
Dermal LD50 (Rabbit):	No data currently available
Eye Effects (Rabbit):	No data currently available
Skin Effects (Rabbit):	No data currently available
Mutagenicity:	Positive in salmonella assay
Inhalation LC50 (Rat):	No data currently available
Skin Sensitization (Guinea Pig):	No data currently available
Respiratory Sensitization:	No data currently available
Additional Toxicity Data:	No data currently available
Supplemental Test Data:	No data currently available
Other Data:	No data currently available

SECTION 12: ECOLOGICAL DATA

BOD:	No data currently available
COD:	No data currently available
Aquatic Toxicity:	LC50 > 320 mg/l Rainbow trout 96 h LC50 170 mg/l Daphnia magna
Biodegradability:	No data currently available
Persistence:	No data currently available
Ecotoxicity:	No data currently available
Sewage Treatment:	No data currently available
Other Data:	No developmental abnormalities or toxicity to oyster larvae at 100 mg/l
Supplemental Test Data:	No data currently available

SECTION 13: DISPOSAL AND ENVIRONMENTAL CONSIDERATION

Reuse of materials:

Reclaim all uncontaminated material to reuse, recycle or otherwise rework whenever possible.

Contain - Do not release:

Do not release into sewers, water systems, ground systems or ecosystems without proper authorization.

Disposal Methods:

Incinerate, treat, or bury (landfill), after sampling and testing, at facility approved by applicable federal, state, and local authorities.

Empty Containers:

Empty containers may contain residue and/or vapors and should not be reused unless professionally cleaned and reconditioned. Crush if not cleaned, to prevent reuse.

Applicable Regulations:	See Section 15 if regulated
Special Instructions:	See Section 15 if regulated

SECTION 14: SHIPPING AND TRANSPORTATION INFORMATION

DOT Regulations (Ground):

DOT Notes: Not regulated. Protect from freezing. Attach PROTECT FROM FREEZING label.

IATA Regulations (Air):

IATA Notes: Not regulated. Protect from freezing. Attach PROTECT FROM FREEZING label.

IMDG / IMO Regulations (Water):

IMDG / IMO Notes: Not regulated. Protect from freezing. Attach PROTECT FROM FREEZING label.

SECTION 15: REGULATORY INFORMATION

Regulatory List Reference:

NOTE: When no components are shown in space above this note, no federal or state reporting requirements apply to this product. When components are listed above, list numbers shown below indicate applicable regulations.*

List numbers

1-Accidental Release Substance
2-CERCLA 304 Hazardous Substance (RQ)
3-Reserved
4-Clean Air Act-Sec. 111 Volatile Organic Compounds (VOC)
5-Clean Air Act-Sec. 112 Haz. Air Pollutant (HAP, HAP Code)
6-Clean Air Act-Ozone Depleting Chemical (ODC)
7-Clean Water Act-RQ
8-Clean Water Act-Priority Pollutant (PP) RQ
9-Marine Pollutant (MP)
10-PSM Highly Hazardous Chemical
11-RCRA Hazardous Waste (RCRA Code)
12-SARA 302 Extremely Hazardous Substance (EHS) (RQ)
13-SARA 313 Toxic Release Inventory (TRI) (TR Conc., TR Threshold)
14-SOCMI Chemical (CAA)
15-State Lists
CA-California Proposition 65, DE-Delaware, ID-Idaho, ME-Maine, MA-Massachusetts, MI-Michigan, MN-Minnesota, NJ-RTK New Jersey Hazardous Substance List, NJ-TCPA New Jersey Extremely Hazardous Substance List, NY-New York, PA-Pennsylvania, WA-Washington, WV-West Virginia, WI-Wisconsin
16-Supplemental regulatory information (SRI)

* Numbers shown immediately after a List Number indicate additional specific information. Examples: 2: 5000 (2 = CERCLA, 5000 = RQ), 11: D007 (11 = RCRA, D007 = Chromium)

Revised 011808 wln (Current list not applicable to previous Safety Data Sheets)

70301027
KEYACID RHODAMINE WT LIQUID

SARA 311/312 Hazard Categories:

Immediate / Acute Health Hazard:	YES
Chronic / Delayed Hazard:	NO
Fire Hazard:	NO
Sudden Release of Pressure Hazard:	NO
Reactivity Hazard:	NO

GLOBAL CHEMICAL REGISTRATION LISTINGS

AICS (Australia):	Status not determined
ASIA-PAC (Asia-Pacific):	Status not determined
DSL (Canada):	Status not determined
ECL (Korea):	Status not determined
EINECS (Europe):	Status not determined
ENCS (Japan):	Status not determined
IECSC (China):	Status not determined
PICCS (Philippines):	Status not determined
TSCA (US):	Components listed or exempt
OTHER:	

Supplemental Regulatory Information:
No additional information applies, or no supplemental information is available at this time.

Additional Info:

For additional international, federal or state regulatory compliance information not shown: Call 312-666-2015.

SECTION 16: OTHER INFORMATION

Reason for Revision:	New format 030306. Revised format. Added VOC % to section 9. 013008
Reviewed:	wln 013008

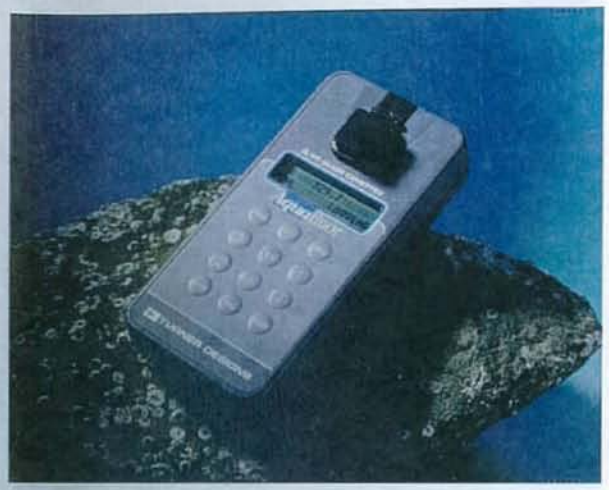
Disclaimer:

The information and recommendations contained herein are based upon data believed to be correct. However, no guarantee or warranty of any kind, expressed or implied, is made with respect to the information contained herein. This Material Safety Data Sheet was prepared to comply with the OSHA Hazard Communication Standard 29 CFR 1910.1200, and supersedes any previous information. Previously dated sheets are invalid and inapplicable.

END OF MSDS

*Aqua*fluor™

Handheld Fluorometer and Turbidimeter



User's Manual

Dated: 3/08/01
Version: 1.1
P/N 998-0851

TURNER DESIGNS
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Table of Contents

Appendices:

1. Introduction

1.1 Description

The *Aqua*fluor™ is a dual-channel mini fluorometer designed for quick, easy and accurate fluorescence and turbidity measurements. When properly calibrated with a standard of known concentration, the *Aqua*fluor™ displays the actual concentration of the compound.

1.2 Inspection and Setup

1.2.1 Inspection

Upon receiving your instrument, please inspect everything carefully and make sure all accessories are present. All shipments include:

- The *Aqua*fluor™
- The User's Manual
- 4 AAA batteries
- 4 Polystyrene cuvettes
- Storage Pouch

1.2.2 Setup

Before the *Aqua*fluor™ can be used, the supplied batteries must be installed.

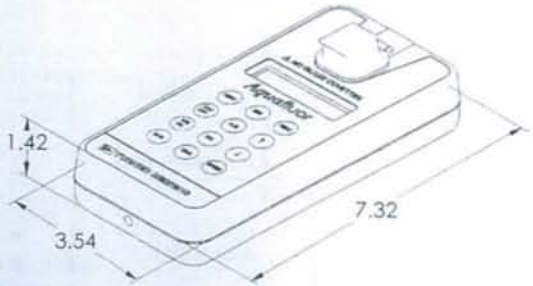
1. On the backside of the instrument, loosen the screw and remove the battery panel (see Section 2 for diagram).
2. Install the 4 AAA batteries into the appropriate spaces.
3. Replace the battery panel and tighten the screw. The panel has an o-ring, which creates a watertight seal. The battery panel may be difficult to install if there is no

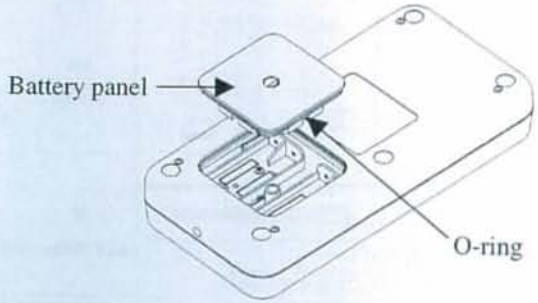
lubrication on the o-ring. Use a silicon based o-ring grease to lubricate the o-ring if necessary.

1.3 General Information and Precautions

- The sample compartment cannot accept glass or quartz cuvettes.
- A minimum volume of 2mls in a 10x10 cuvette is required for best results.
- Avoid having any air bubbles in your sample. They can significantly affect the fluorescent reading.
- For best results measuring low turbidities, use good polystyrene cuvettes (P/N 7000-957). See Section 4.4 for further information.

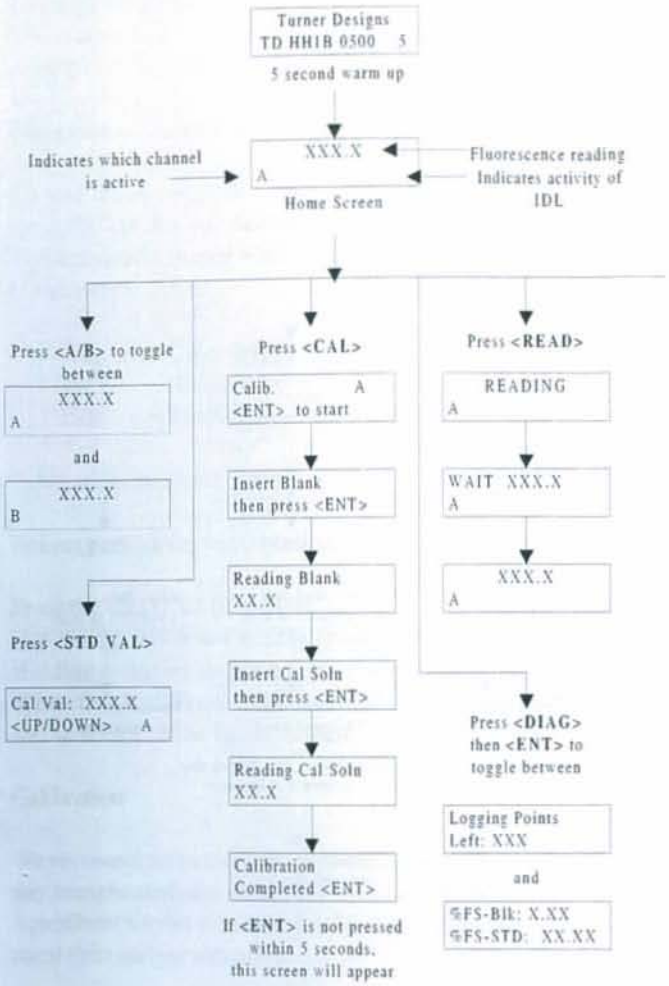
2. Quick View Diagrams

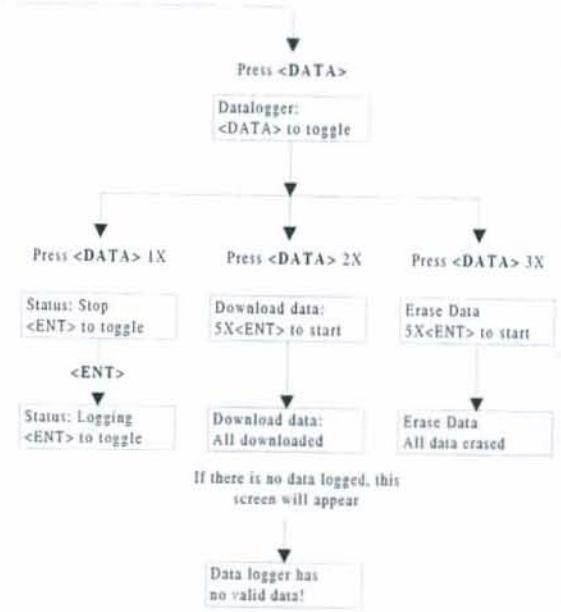




3. Instrument Parameters

3.1 Firmware Flowchart





3.2 Instrument Power Up

To turn on the *Aqua*fluor™, press the <ON/OFF> button. The instrument takes 5 seconds to warm up. After the warm up, the *Aqua*fluor™ is ready for operation.

3.3 Fluorescence or Turbidity Channel

Choose the appropriate channel for your analysis. To do this, press the <A/B> button to toggle between the 2 channels. The activated channel will be displayed in the lower left corner of the Home screen.

CHL	= Chlorophyll
RWT	= Rhodamine WT
TRB	= Turbidity

3.4 Calibration Standard Value

Before performing a calibration, set the value of your standard.

1. Press the <STD VAL> button.
2. Use the up and down arrows to adjust the standard value. Holding either arrow button down will activate faster scrolling.
3. When finished, Press <ESC> or <ENT> to accept the value and to return to the Home screen.

3.5 Calibration

We recommend that you always calibrate before performing any sample analysis. After the initial calibration, the *Aqua*fluor's solid standard can be used to check for instrument drift and recalibration.

1. Press the <CAL> button.
2. Press <ENT> to start the calibration.
3. Insert your blank and press <ENT>. The *Aqua*fluor™ will average the fluorescence for 10 seconds.
4. Insert the calibration standard and press <ENT>.
5. Press <ENT> when the calibration is complete to accept the calibration. If <ENT> is not pressed within 10 seconds, you will be asked if you want to abort the calibration. Press the up or down arrow to abort or accept the calibration respectively.

If at anytime during steps 1-4 you want to stop the calibration, press <ESC>. This will return you to the Home screen and will default the instrument to the previous calibration.

3.6 Sample Analysis

1. Insert your sample.
2. Press either <READ> button. The instrument will autorange, then measure and average the fluorescence signal over a 5-second interval.
3. The result will be displayed at the top and center of the Home screen.
4. The top left corner will display "WAIT" for 5 seconds. Once "WAIT" disappears, another sample reading can be performed.

3.7 Internal Data Logging (IDL)

This is an optional feature. If this feature has been purchased, your *Aqua*fluor™ can log up to 1000 data points. The DATA screens control logging, downloading and erasing the data. For further information, see Appendix B.

3.7.1 Activate Data Logging

1. Press the <DATA> button 2 times.
2. Press <ENT> to toggle between logging and stop statuses.
3. Press <ESC> when finished to return to the Home screen.

3.7.2 Download Data

1. Connect the *Aqua*fluor™ to the serial port of your computer.
2. Open the Turner Designs Interface Software. See Appendix B for computer requirements and installation.
3. Press the <DATA> button 3 times.
4. Press <ENT> 5 times to start the data download.
5. Press <ESC> when finished to return to the Home screen.

3.7.3 Erase Data

1. Press the <DATA> button 4 times.
2. Press <ENT> 5 times to erase all logged data.
3. Press <ESC> when finished to return to the Home screen.

3.8 Diagnostic Information

1. Press <DIAG> to access the diagnostic screens.
2. The first screen shows the number of data points available for internal data logging.
3. Press <ENT> to toggle to the %FS (Full Scale) values from the calibration blank and standard.
4. Press <ESC> when finished to return to the Home screen.

4. General Considerations for Analysis

4.1 Handling Samples

1. Take care not to spill samples into the sample chamber. Wipe up any spills promptly.

2. The *Aqua*fluor™ is very sensitive and even small amounts of material from a previous sample may result in errors. Use a clean cuvette for all readings. Thorough and proper cleaning of cuvettes between sample readings is essential, and is especially important if you are using the same cuvette for samples and blank.

3. Fill the cuvette at least 50% full (2mls). Significant error can result if the cuvette does not contain this minimum volume.

4. The cuvette MUST BE DRY on the outside when taking readings. Moisture and condensation on the outside can result in error.

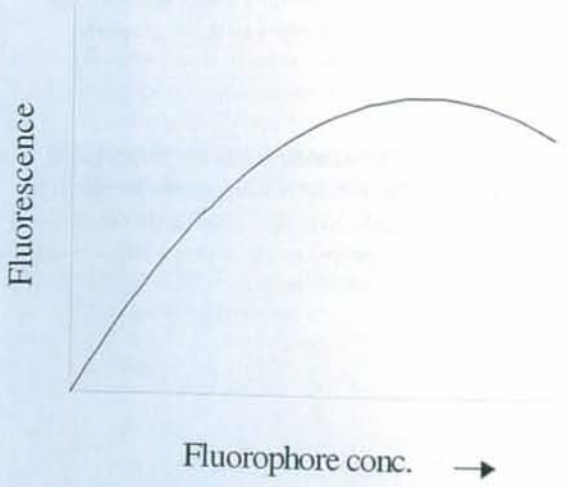
5. Minute bubbles in samples will cause drifting readings. Take care not to introduce bubbles into samples. Slight tapping with your finger on the outside cuvette wall will often help dissipate bubbles.

4.2 Linear Range and Quenching

The linear range is the concentration range in which the readout of the *Aqua*fluor™ is directly proportional to the concentration of the fluorophore. The linear range begins with the smallest detectable concentration and spans to an upper limit (concentration) that is dependent upon: the properties of the fluorescent material, the filters used, and the path length.

A nonlinear relationship is seen at very high concentrations where the fluorescence signal does not increase at a constant rate in comparison to the change in concentration. At even higher concentrations, fluorescence signal will decrease even though the sample concentrations are greater. This effect is known as "signal quenching".

Linearity may be checked by diluting a sample 1:1 or some other convenient ratio (be sure to use your matrix blank for the dilutions). If the sample is within the linear range, the reading will decrease in direct proportion to the dilution. If the reading does not decrease in direct proportion to the dilution or if the reading increases, the sample is beyond the linear range of your fluorophore.



4.3 Temperature Considerations

Fluorescence is temperature sensitive. As the temperature of the sample increases, the fluorescence decreases. For greatest accuracy, read blank, standard, and samples at the same temperature.

4.4 Positioning Samples

For low concentration samples, cuvettes often will give slightly different measurements depending upon their orientation in the sample compartment. This is due to defects in the shape of the cuvette that are not visible to the human eye. We recommend that the cuvette be marked at the top and positioned in the sample compartment the same way each time to minimize error.

We have found that turbidity is particularly sensitive to this factor. We recommend for best results, using high quality polystyrene cuvettes (P/N 7000-957) which showed little orientation and cuvette to cuvette variation in testing.

4.5 Data Quality

The *Aqua*fluor™ is only as accurate as the standards that are used to calibrate it. This is why it is important to take care when preparing standards, samples, and blank. One should follow good laboratory practices when preparing all solutions and reagents.

5. Warranty

5.1 Terms

Turner Designs warrants the *Aqua*fluor™ Fluorometer and accessories to be free from defects in materials and workmanship under normal use and service for a period of one year from the time of initial purchase, with the following restrictions:

1. The instrument and accessories must be installed, powered, and operated in compliance with the directions in this *Aqua*fluor™ User's Manual and directions accompanying the accessories.

2. Damage incurred in shipping is not covered.

3. Damage resulting from measurement of samples found to be incompatible with the materials used in the sample system is not covered.

4. Damage resulting from contact with corrosive materials or atmosphere is not covered.

5. Damage from seawater and other moderately corrosive materials that are not promptly removed from the instrument are not covered.

6. Damage caused by modification of the instrument by the customer is not covered.

5.2 Warranty Service

To obtain service during the warranty period, the owner shall take the following steps:

1. Write or call the Turner Designs service department and describe as precisely as possible the nature of the problem.

2. Carry out minor adjustments or tests as suggested by the Service Department.

3. If proper performance is not obtained, ship the instrument, prepaid, to Turner Designs, with a statement of shipping charges. The instrument will be repaired and returned free of charge, along with a check to cover shipping charges, for all customers in the contiguous continental United States.

For customers outside of the contiguous continental United States, and who have purchased our equipment from one of our authorized distributors, contact the distributor. If you have purchased direct, contact us. We will repair the instrument at no charge, but we will not pay for shipment, documentation, etc. These charges will be billed at cost.

NOTE! Under no conditions should the instrument or accessories be returned without notice. Prior correspondence is needed:

a. To ensure that the problem is not a trivial one, easily handled in your laboratory, with consequent savings to everyone.

b. To specifically determine the nature of the problem, so that repair can be rapid, with particular attention paid to the defect you have noted.

5.3 Out-of-Warranty Service

Proceed exactly as for Warranty Service, above. If our service department can assist you by phone or correspondence, we will be glad to, at no charge.

Repair service will be billed on a basis of time and materials. A complete statement of time spent and materials used will be supplied. Shipment to Turner Designs should be prepaid. Your bill will include return shipment freight charges.

Address for Shipment:
Turner Designs
845 W. Maude Ave.
Sunnyvale, CA 94085

Appendix A: Instrument Specifications

A1. General Specifications

Specification	Description
Size	1.75" x 3.5" x 7.25" (4.45cm x 8.9cm x 18.4cm)
Weight	13.9oz (0.4kg)
Dynamic range	3 orders of magnitude
Resolution	12 bits
LCD Display	2 x 16 characters
Case	Meets IP 67 Standard; dustproof and waterproof
Temperature	41-104 °F; 5-40 °C
Detector	Photodiodes: measurement capability from 300-1000nm
Calibration Type	Single-point and blank
Alarms	Low battery, circuit failure, High blank
Cuvette Type	10mm x 10mm plastic
Warm Up Time	5 seconds
Automatic Power Down	After 90 seconds of inactivity

A2. Optical and Application Specifications

	Chlorophyll Channel	Rhodamine Channel	Turbidity Channel
Light Source	Blue LED	Green LED	Green LED
Excitation Optics	460±20nm	540±20nm	515±10nm
Emission Optics	>665nm	>570nm	515±10nm
Limit of Detection	0.25ug/l	0.4ppb	0.5NTU
Max range	> 800 ppb	>300ppb	>150 NTU
Temperature coefficients	1.4%/°C Linear	0.026/°C Exponential	N/A

Appendix B: Internal Datalogging

B1. Shipping Checklist

Instruments with internal data logging purchased will also receive in their shipment:

- Interface cable
- Turner Designs Spreadsheet Interface Software (2 disks)

Both of these items are necessary for retrieving the stored data in the *Aqua*fluor™.

B2. Hardware Requirements

- PC with Windows 95 or later
- MS Excel 5.0 or later
- At least 1 available serial port

B3. Installation

1. Exit all Windows programs.
2. Insert Disk 1 and run the setup program.
3. The setup wizard will install the necessary files. You will be prompted for Disk 2 when necessary.
4. When the setup is complete, an icon named "_TD2" will be found in the "Programs" menu.
5. Restart your computer.

B4. Connecting

1. Using the provided cable, connect the 9 pin adapter of the cable into the available serial port of your computer.

1. Plug the opposite end of the cable into the base of the *Aqua*fluor™.
2. Open MS Excel 5.0 or later.
3. Open the TD2 spreadsheet interface software.
4. Click on the box to the right of the COM port icon to select the appropriate COM port. This is usually COM port 2.
5. Click on "Start". The program will open an Excel spreadsheet for data transfer. The boxes left of the COM port and MS Excel should both be green.
6. Follow the directions from Section 3.7 for collecting and downloading data from the *Aqua*fluor™. Data will automatically appear in the excel spreadsheet. BE SURE to save this data BEFORE closing the TD software.

B5. Real Time Data Transfer

Data can also be transferred directly to the computer after each reading. To do so:

1. Stop data logging (see 3.7.1)
2. Follow steps 1-6 of B4 to crate the connection between the *Aqua*fluor™ and your computer.
3. Insert a sample and press the <READ> button. The results will automatically transfer to the active Excel spreadsheet.

B.6 IDL Troubleshooting

Difficulties can arise when parameters are set incorrectly or connections with the cable are not tight enough. Here are some common problems.

1. Box to the left of the COM port is red. This means that the COM port is not available. Causes:
   a. Another instrument or program (such as palm pilot/ hot sync) could be occupying the port, making it unavailable. Make sure to close all programs of this type before downloading data
   b. The port selected is incorrect. Follow step 4 of connecting to choose another COM port.

2. All lights are green, but no data transferred, even though the instrument says "All data downloaded".
   a. The connection between the instrument and the computer is bad. Check and tighten the cable connections. Make sure both ends of the cable are plugged in tightly.

Appendix C: *In Vivo* Chlorophyll

The detection of *in vivo* chlorophyll *a* is by nature, a qualitative measurement. Physiological, environmental, morphological, and temporal factors all contribute to the variation between the *in vivo* signal and the actual chlorophyll *a* concentration of a sample. Physiological effects stem from the change in fluorescence per unit chlorophyll of cells at varying physiological states. On a basic level, an 'unhealthy' cell will fluoresce more than a 'healthy' cell due to the light energy absorbed is channeled into photosynthesis. However, in natural assemblages of phytoplankton, there is normally a mix of species at varying degrees of health, thus averaging out the physiological effect.

Environmental effects derive from mainly two factors: light and temperature. The light history of an algal population will affect fluorescence of living cells. Cells in a darker environment will fluoresce more per unit chlorophyll than cells in a well lit zone of the water column. One way of reducing the effects of light is to "dark adapt" your sample before analyzing it. Temperature effects are discussed in section 4.3 of the manual. For best sample analysis, all samples and calibration solutions should be measured at the same temperature.

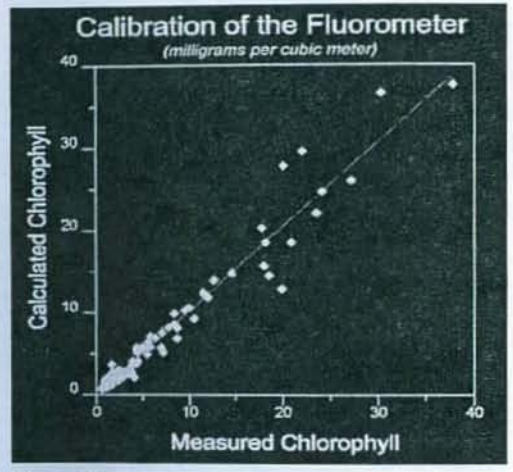
Temporal/Spatial effects are mainly due to differences in quantum efficiency and cell size between different species of phytoplankton and photosynthetic bacteria.

Interfering compounds in natural waters derive from several sources. The most common interfering compounds include pheophytins, chlorophyll *b* and *c*, dissolved organic matter and fluorometer. Optical filters with a wider bandpass will

be susceptible to more interference than filters with a narrower bandpass.

In spite of these concerns, this does not mean that actual chlorophyll concentrations cannot be extrapolated from the *in vivo* data. A simple way of correlating *in vivo* data to actual chlorophyll concentrations is accomplished by periodically collecting "grab" samples for chlorophyll extraction. Several samples should be collected within each niche or environment.

At the time of collection, the *in vivo* value must be noted. Once the chlorophyll concentration has been determined through extraction, the concentration should be correlated with the corresponding *in vivo* value (see Graph C1)



Graph C1

For detailed information on chlorophyll analysis, please see the reference list below or visit the Turner Designs webpage at www.fluorometer.com

REGULATED RIVERS: RESEARCH & MANAGEMENT, VOL. 13, 357–375 (1997)

RESTORING NATIVE VEGETATION IN A EURASIAN WATER MILFOIL-DOMINATED PLANT COMMUNITY USING THE HERBICIDE TRICLOPYR*

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ABSTRACT

In an effort to evaluate the selective control of the exotic weed Eurasian water milfoil (*Myriophyllum spicatum* L.) and to assess the recovery and restoration of the native submersed plant community, a 6-ha river and 4-ha cove plot were treated with the herbicide triclopyr at application rates of 2·5 and 1·75 mg/l, respectively, in the Pend Oreille River, WA, in August 1991. Water exchange half-lives within the plots were measured using rhodamine WT dye (river, $t_{1/2} = 20$ h; cove, $t_{1/2} = 52$ h), and triclopyr dissipation rates were also calculated (river, $t_{1/2} = 19$ h; cove, $t_{1/2} = 53$ h). Triclopyr concentrations were below the proposed potable water tolerance level (0·5 mg/l) within the river treatment plot by 3 days after treatment (< 0·01 to 0·41 mg/l), and 675 m downstream of that plot by 1 day after treatment (< 0·01 to 0·47 mg/l). Following the cove treatment, triclopyr residues ranged from 0·12 to 0·29 mg/l by 7 days after treatment, and from < 0·01 to 0·06 mg/l as close as 150 m downstream from the plot.

Eurasian water milfoil biomass was reduced by 99% in the treated plots at 4 weeks post-treatment, remained low one year later (river treatment, 28% of pretreat levels; cove treatment 1% of pre-treat levels) and was still at acceptable levels of control at two years post-treatment (river treatment, 47% of pre-treat levels; cove treatment, 24% of pre-treat levels). The four-week post-treatment efficacy results verified triclopyr concentration/exposure time relationships for controlling Eurasian water milfoil developed under laboratory conditions. Non-target native plant biomass increased 500–1000% by one year post-treatment, and remained significantly higher in the cove plot at two years after treatment. Native species diversity doubled following herbicide treatment, and the restoration of this robust community delayed the re-establishment and dominance of Eurasian water milfoil for three growing seasons. ©1997 by John Wiley & Sons, Ltd.

Regul. Rivers: Res. Mgmt, **13**: 357–375 (1997)

No. of Figures: 7. No. of Tables: 4. No. of References: 44.

KEY WORDS: aquatic plant control; aquatic weeds; Garlon® 3A; *Myriophyllum spicatum*; pesticide dissipation; rhodamine WT

INTRODUCTION

The submersed plant Eurasian water milfoil (*Myriophyllum spicatum* L.), hereafter called milfoil, has spread throughout many rivers and reservoirs since its introduction into the United States prior to the 1940s (Reed, 1977; Couch and Nelson, 1985). Once established, growth and physiological characteristics of milfoil enable it to form a surface canopy and develop into immense stands of weedy vegetation, outcompeting most submersed species and displacing the native plant community (Grace and Wetzel, 1978; Aiken *et al.*, 1979; Madsen *et al.*, 1988, 1991a; Smith and Barko, 1990). These surface mats can severely impair many of the functional aspects of regulated rivers such as maintenance of water quality for wildlife habitat and public health, water storage capacity, navigation and recreation (Hansen *et al.*, 1983; Newroth, 1985; Ross and Lembi, 1985; Nichols and

*This article is a US Government work and, as such, is in the public domain in the USA.
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Shaw, 1986). Furthermore, a milfoil-dominated submersed plant community can greatly reduce the biodiversity of an aquatic system (Smith and Barko, 1990; Madsen *et al.*, 1991b).

To develop methods for controlling the growth and spread of milfoil in public waters, our research group has been evaluating the herbicide triclopyr (3,5,6-trichloro-2-pyridinyl-oxyacetic acid) for restoring aquatic habitats dominated and degraded by this non-indigenous species. Triclopyr is a pyridine-based systemic compound registered since the mid-1970s in the US for control of broadleaf weeds and woody plants on rights-of-way, rangeland, industrial sites and other non-crop areas. Furthermore, in 1995 triclopyr received US registration for controlling weeds in rice grown for food production. Since the chemical has demonstrated potential for selectively controlling several aquatic weeds, including milfoil (Getsinger and Westerdahl, 1984; Langeland, 1986; Green *et al.*, 1989; Wujek, 1990), DowElanco Chemical Company is pursuing an aquatic registration for the triethylamine salt formulation of triclopyr (presently labelled as Garlon® 3A) under an experimental use permit (EUP) issued by the US Environmental Protection Agency (US EPA).

Previous aquatic testing has shown that triclopyr is susceptible to photolytic degradation and has a low toxicity to non-target organisms (Gersich *et al.*, 1984; Mayes *et al.*, 1984; McCall and Gavit, 1986; Dow Chemical Co., 1988; Woodburn *et al.*, 1993a,b). Field dissipation studies have indicated that triclopyr accumulation in sediment, shellfish and fish is negligible (Getsinger and Westerdahl, 1984; Woodburn *et al.*, 1993b). Laboratory studies have clearly shown that triclopyr efficacy is dependent upon the concentration and length of time milfoil remains exposed to the herbicide (Netherland and Getsinger, 1992). However, this compound can be subject to rapid dilution and dispersion from treatment areas through gravity flow, tides, thermal- and wind-induced water circulation patterns, etc. (Fox *et al.*, 1991a; Getsinger *et al.*, 1992). Although rapid dissipation may be environmentally desirable, this process can reduce the degree of plant control owing to insufficient herbicide exposure. Therefore, successful triclopyr treatment of milfoil in rivers and reservoirs requires knowledge of herbicide concentration and exposure time requirements for this species, as well as site-specific water exchange characteristics.

The Pend Oreille River, a regulated system located in north-eastern Washington, is a major tributary of the Columbia River and has been infested with milfoil for over a decade (Rawson, 1985, 1987; WATER Environmental Sciences, 1986, 1987). Milfoil control practices in the past have included herbicides such as 2,4-D (2,4-dichlorophenoxy acetic acid) and fluridone {1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl-4(1H)-pyridinone]}, and have been only moderately successful (Durando-Boehm, 1983; WATER Environmental Sciences, 1986, 1987). Recent water exchange studies conducted in selected sites on this river suggested that triclopyr contact times sufficient to provide acceptable levels of milfoil control could be achieved in these areas (Getsinger *et al.*, 1993). Moreover, the presence of a multispecies submersed plant community (albeit dominated by milfoil) provided the opportunity to assess the selective properties of this herbicide under field conditions. A large-scale study was conducted to evaluate triclopyr applications as a technique for restoring native submersed plant communities in a regulated river previously dominated by milfoil. In addition, dissipation rates of triclopyr from treated areas were determined and laboratory-derived triclopyr dosage rate relationships for controlling milfoil were verified.

MATERIALS AND METHODS

Study site and plot description

The study was conducted along a stretch of the Pend Oreille River (48° N, 117° W) between Albeni Falls and Box Canyon dams (Figure 1). River levels in this region are controlled by water inflowing from Albeni Falls Dam on Lake Pend Oreille, Idaho, and outflowing at Box Canyon and Boundary Dams in Washington, and at two dams in British Columbia, Canada. River discharge, measured at the Albeni Falls Dam, averages 565 cm per year, with a maximum of 1500 cm in May or June, and a minimum of 165 cm in January and February, or in August and September.

In mid-August 1991, two milfoil-dominated submersed plant stands were selected for the study. The first was in the main stem of the river approximately 0·5 km upstream from river mile (RM) marker 62, and the second in a protected cove approximately 0·3 km downstream from RM marker 48. In shallow areas of these stands (< 1 m

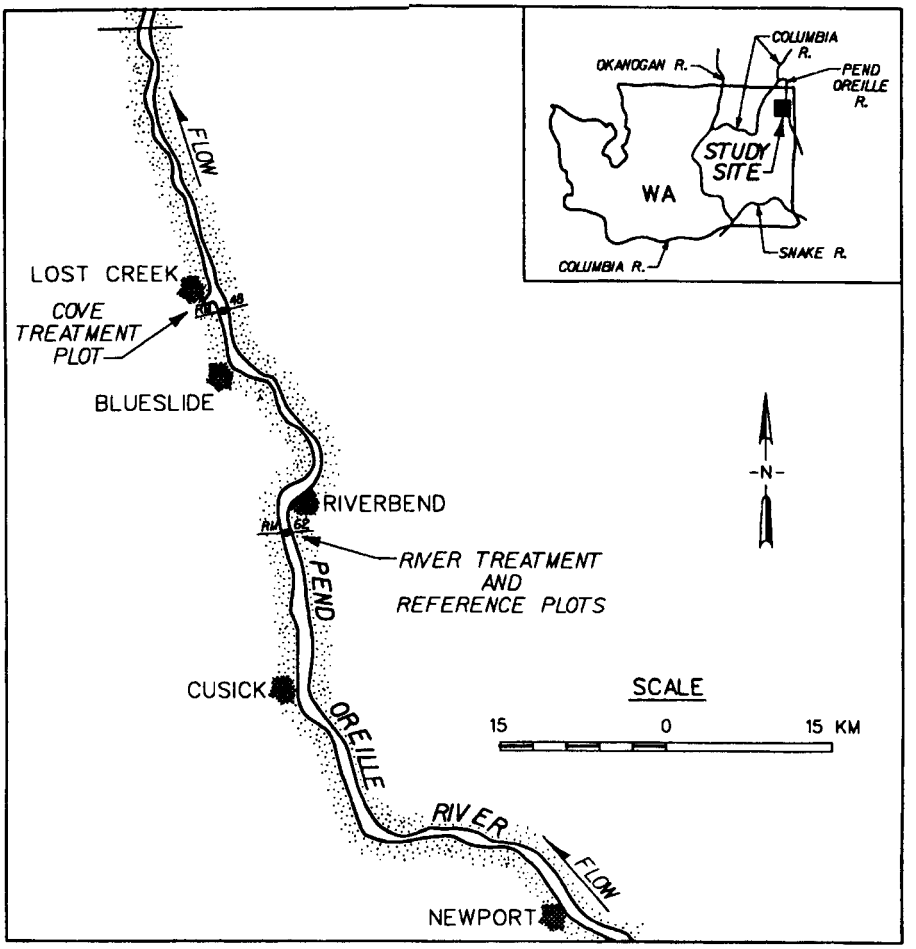

Figure 1. Location of study site for triclopyr herbicide treatment on the Pend Oreille River, WA

deep), entangled shoots of milfoil covered the surface of the water forming a dense mat. In deeper regions of the stands milfoil shoots formed a dense submersed canopy 15–20 cm below the surface of the water. Although milfoil was the dominant species in the plots, an understorey comprising 13 other submersed plants (one exotic and 12 natives) was encountered during the pretreatment evaluation (Table I). The other exotic plant was the monocotyledonous (monocot) species curlyleaf pondweed (*Potamogeton crispus* L.). Principal natives included the monocots elodea (*Elodea canadensis* L.), flatstem pondweed (*Potamogeton zosteriformis* Fernald) and water stargrass (*Heteranthera dubia* (Jacq.) MacM.), and the dicotyledonous (dicot) species coontail (*Ceratophyllum demersum* L.) and white water crowfoot (*Ranunculus longirostris* Godron).

The submersed plant communities selected for the study represented milfoil-dominated stands typical of those targeted for operational herbicide treatments. However, water-exchange characteristics of the two sites were dissimilar ($t_{1/2} < 20$ h in the river and > 50 h in the cove), thus providing the opportunity to compare the efficacy, selectivity and dissipation of triclopyr under different flow, concentration and exposure time conditions.

Two river plots were established in submersed plant stands in the River Bend area near RM 62. A 6-ha river treatment plot was located 250 m downstream from the 2-ha river reference plot (Figure 2). Both plots were situated in a parallel arm of the main river channel, bounded on the west by a narrow island, and bordered on the north, south and east by submersed plant stands or open water. These plots ranged in depth from 0·3 m (west side) to 2·5 m (east side), with a mean depth (±SE) of $1{\cdot}62 \pm 0{\cdot}07$ m ($n = 60$). Six water sampling stations (1–6) were established inside the RT (river treatment) plot representing three flow zones: Stations 1 and 2, upstream zone;

Table 1. Frequency of plant species in study plots in Pend Oreille River, WA (1991–1993), for all transects per plot and year: monocot (M), dicot (D), native (N), exotic (E).

		RR* Plot			RT† Plot			CT‡ Plot		
Species	Year	1991	92	93	91	92	93	91	92	93
coontail (DN)		2	5	10	9	28	28	20	59	61
Ceratophyllum demersum L.										
elodea (MN)		21	9	20	7	50	33	28	93	79
Elodea canadensis L.										
water stargrass (MN)		3	1	8	8	8	18	0	1	3
Heteranthera dubia (Jacq.) MacM.										
northern water milfoil (DN)		0	0	0	7	< 1	0	0	0	0
Myriophyllum sibiricum Komarov										
Eurasian water milfoil (DE)		100	98	95	94	56	78	89	25	59
M. spicatum L.										
whorled water milfoil (DN)		0	0	1	< 1	< 1	5	0	0	0
M. verticillatum L.										
curlyleaf pondweed (ME)		17	27	87	4	27	12	7	15	30
Potamogeton crispus L.										
American pondweed (MN)		8	5	5	< 1	< 1	0	0	0	0
P. nodosus Poiret										
blunt-leaf pondweed (MN)		0	0	< 1	0	39	0	6	7	< 1
P. obtusifolius Mert. & Koch										
sago pondweed (MN)		12	0	8	5	9	7	11	1	2
P. pectinatus L.										
redhead grass (MN)		2	0	< 1	2	6	3	< 1	1	1
P. perfoliatus L.										
whitestem pondweed (MN)		0	0	0	0	0	< 1	0	0	< 1
P. praelongus Wulfen										
small pondweed (MN)		0	0	< 1	0	0	32	0	0	1
P. pusillus L.										
Vasey's pondweed (MN)		0	0	0	10	0	< 1	8	1	0
P. vaseyii Robbins										
flatstem pondweed (MN)		15	11	16	28	64	77	40	36	53
P. zosteriformis Fernald										
white water crowfoot (DN)		5	8	21	12	50	16	3	19	1
Ranunculus longirostris Godron										

* River reference plot
† River treatment plot
‡ Cove treatment plot

Stations 3 and 4, mid stream zone; Stations 5 and 6, downstream zone. One water sampling station was established in the centre of the river reference plot.

A 4-ha cove treatment plot was established in the submersed plant stand in Lost Creek Cove, located on the west shore of the river (Figure 3), approximately 21 km downstream from the river plots. Water depth in this plot ranged from 0·75–2·8 m, with a mean depth of $1{\cdot}72 \pm 0{\cdot}04$ m ($n = 80$). Three water sampling stations were established inside the cove treatment plot, with Station 1 located in the southern half of the plot, Station 2 in the centre of the plot and Station 3 in the northern half of the plot.

In addition, several water sampling stations were established outside and downstream of the two treated plots. The locations of each of these stations were based on the presence and quantity of a fluorescent dye applied concurrently with the herbicide (described below). Downstream stations were used to monitor movement of triclopyr out of the treated plots. This dissipation information can be used to establish any label restrictions for potable water tolerance set-back distances in relation to triclopyr treatment sites and water intake structures. Potable water tolerance set-back distances ranging between 400 m (0·25 mi) and 800 m (0·50 mi) are currently being considered for the triclopyr aquatic label. In the river application, five water sampling stations were

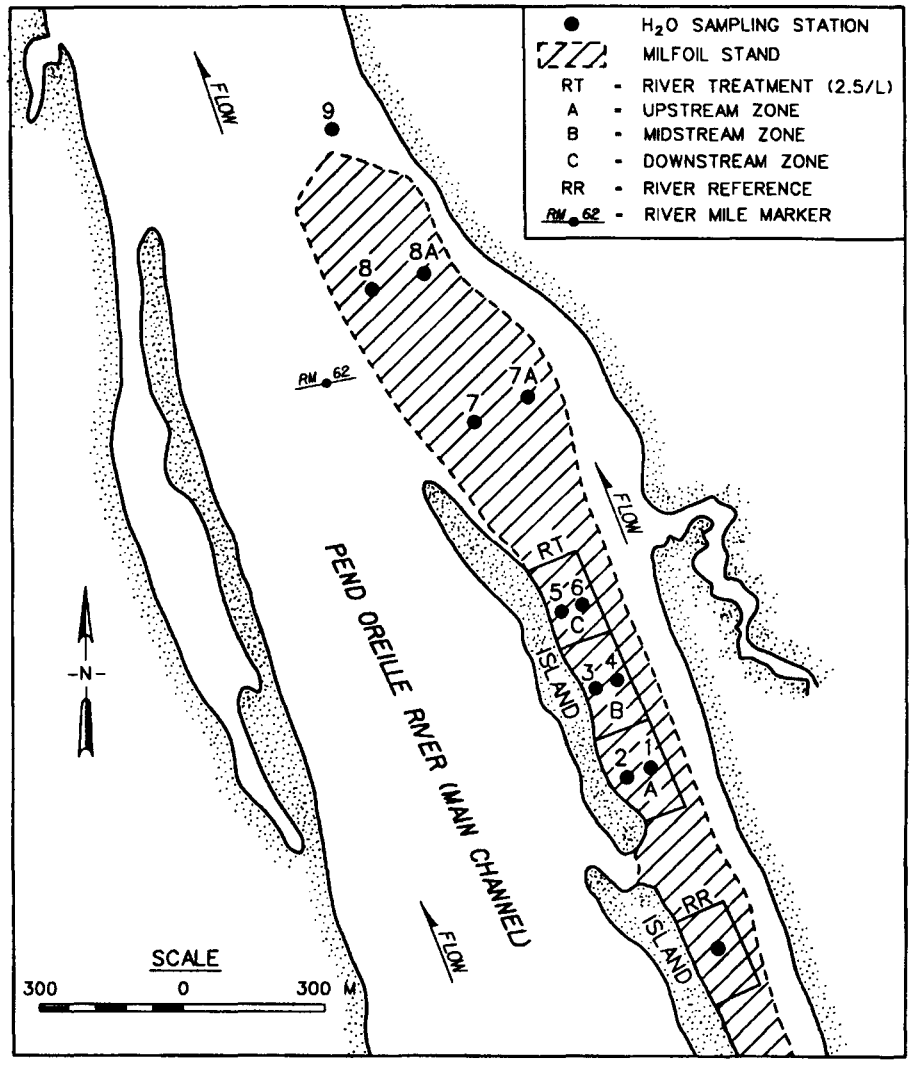

Figure 2. River treatment (RT) and river reference (RR) plots and water sampling stations on the Pend Oreille River, WA

established downstream of the northern edge of the plot (Figure 2): Stations 7 and 7a, 300 m downstream; Stations 8 and 8a, 675 m downstream; Station 9, 975 m downstream. In the cove application, two water sampling stations (4 and 5) were established at 150 m and 395 m, respectively, downstream of the plot (Figure 3).

Chemical applications and sampling regimes

On 21 and 22 August 1991, the river and cove treatment plots, respectively, were treated with a liquid formulation of the herbicide Garlon® 3A [31·8% triclopyr acid equivalent (ae)] using a conventional submersed application technique. The herbicide was injected 30–60 cm below the surface of the water using a pressurized diaphragm pump, fitted with a 208-litre (55 gallon) holding tank and a manifold with six hoses (60 cm length) attached at 30-cm intervals. Tee jet #6 nozzles affixed to the ends of the hoses provided an average nozzle output of 2·3 l/min at a pressure of 206 kPa (30 psi). The manifold was stern-mounted on an airboat, allowing the nozzles to penetrate the water column to a depth of 20–30 cm, and providing a 2·4-m application swath width.

The river treatment plot was treated as four subplots (1·5 ha each), with the application beginning in the downstream subplot (0800 hours) and, once completed, proceeding upstream until the entire 6-ha plot was treated

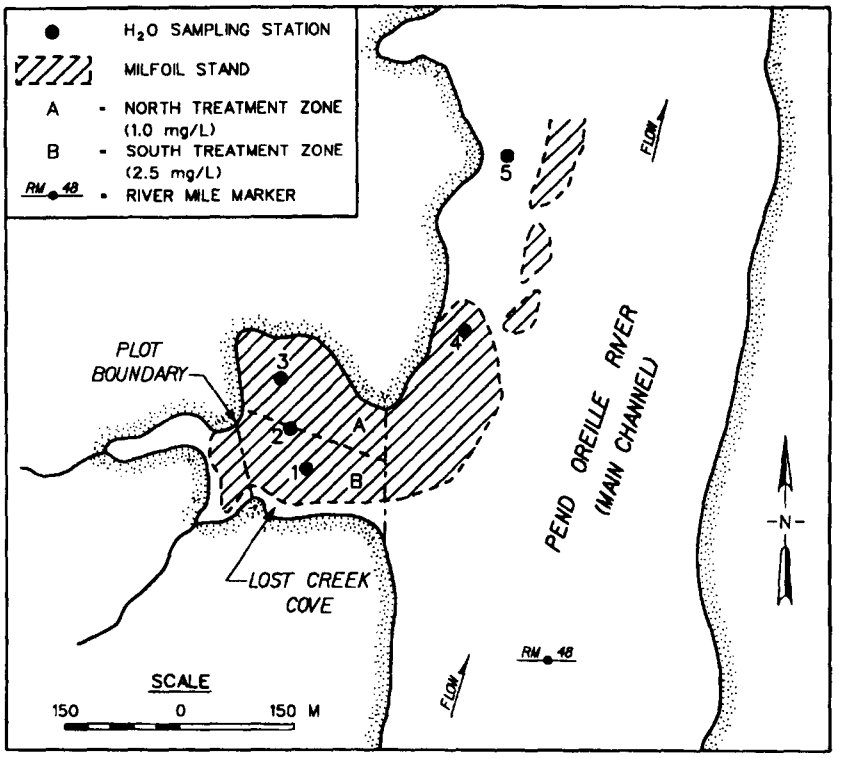

Figure 3. Cove treatment (CT) plot and water sampling stations on the Pend Oreille River, WA

(1130 hours). This subsurface application technique provided a nominal concentration of 2·5 mg/l triclopyr in the plot (the maximum EUP label concentration). At the time of treatment, skies were clear, water column temperature was essentially isothermal (25°C), and wind velocity was < 2 km/h from the east.

The cove treatment plot was treated as two subplots of 2 ha each, with the northern subplot treated first (0950–1020 hours), at a nominal triclopyr application rate of 1·0 mg/l, and the southern subplot receiving a nominal triclopyr application rate of 2·5 mg/l at 1035–1135 hours. The nominal triclopyr application rate for the entire plot was 1·75 mg/l. At treatment time, skies were partly cloudy, water column temperature was isothermal (24°C), and wind was south-east at approximately 10 km/h.

While treating each subplot, the airboat travelled at 5 km/h in an alternating east–west pattern that provided an even areal distribution of the herbicide throughout the plots. Application rates selected for both plots were based on results of previous water exchange studies in those sites, and on laboratory-derived triclopyr concentration and exposure time requirements (Netherland and Getsinger, 1992; Getsinger *et al.* 1993).

The inert fluorescent dye, rhodamine WT, was used to characterize water exchange and movement during the study, and to aid in the selection of water sampling stations outside the treated areas. This dye (US EPA approved for use in potable water at concentrations up to 100 μg/l) can be quantified *in situ* and is routinely used for water tracing and exchange studies (Johnson, 1984; Kilpatrick and Wilson, 1989). The dye has also been used to successfully simulate aqueous dissipation of several herbicides, including triclopyr, used for aquatic plant control (Fox *et al.*, 1991b, 1992, 1993; Turner *et al.*, 1994).

Rhodamine WT was applied immediately following the triclopyr treatment in the RT plot using identical application techniques to achieve a nominal aqueous concentration of 10 μg/l. In the cove treatment plot, the dye was tank mixed with the herbicide to achieve a nominal concentration of 4 and 10 μg/l in the north and south portions of the plot, respectively. The different initial dye concentrations in the cove treatment plot reflected the initial triclopyr application rates, and ensured that the empirical relationship between triclopyr and dye quantities would remain consistent throughout the plot. Dye concentrations were measured at 25-cm depth intervals at each

sampling station using Turner Designs Model 10-005 field fluorometers equipped with high-volume continuous flow cuvette systems. Water was circulated through the fluorometers with submersible pumps attached to the end of weighted opaque hoses. All dye values were temperature corrected according to Smart and Laidlaw (1977) using Cole–Parmer thermistors attached to the exhaust hoses of the fluorometers.

Water samples were collected for triclopyr residues concurrently with dye measurements, using fluorometers and pump systems described above, from each station inside the plots at one-third total depth below the surface (upper sample) and one-third total depth above the bottom (lower sample). Water was collected at a depth of 1 m at the river treatment plot downstream stations, and at 0·5 and 0·75 m at the CT plot downstream stations. Water was pumped into 500-ml amber polyethylene bottles, stored on ice in the field, and frozen when returned to the field station, within 6 h. Dye levels were recorded and triclopyr water samples were collected from all river treatment plot stations at pretreatment, 1, 5, 8 and 12 hours after treatment, and at 1, 2, 3 and 7 days after treatment. Dye levels were recorded and triclopyr water samples were collected from all cove treatment plot stations at pretreatment, 1.5 and 8 hours after treatment, and at 1, 2, 3 and 7 days after treatment. Additional triclopyr water samples were collected from all stations at 14 and 21 days after treatment. In the untreated upstream river reference plot, triclopyr water samples were collected at mid-depth at pretreatment, and 8 and 24 hours after treatment. Dye measurements were recorded on the downstream edge and at selected locations in the river reference plot from 1 hour after treatment to 7 days after treatment.

Water samples were analysed for triclopyr residues (detection limit $< 0{\cdot}01$ mg/l) using a high performance liquid chromatography method (DOW Chemical Co., Midland, MI) by the Tennessee Valley Authority Water Chemistry Laboratory, Chattanooga, TN. Mean percentage recovery of all triclopyr-spiked samples ($n = 38$) was $98{\cdot}12 \pm 0{\cdot}69$ SE.

Dye and triclopyr data were subjected to statistical analysis to obtain dissipation curves using Statgraphics 3·0 (Statistical Graphics Corp). Mean dye and triclopyr values were regressed against time using the exponential model:

$$y = \exp(a + bt),$$

where:

y = chemical concentration at time t, a = intercept of regression line, b = slope of regression line (dilution factor).

Dissipation half-lives were then calculated according to:

$$t_{1/2} = \frac{\text{natural logarithm of } 0{\cdot}5}{\text{slope of regression line}}$$

River discharge and flow rates

River discharge, as measured from the Albeni Falls Dam, ranged from 360 to 405 cm on the triclopyr application dates. River discharge slowly declined to a level of 245 cm by 4 days after treatment, and stabilized to a level of 170 cm by 7 days after treatment. Flow rates were measured using a Montedora–Whitney electronic flow meter in the open channel adjacent to the plant stands, and ranged from 2 to 3 cm/s. Flow rates were generally below the detection limits of the meter ($< 0{\cdot}1$ cm/s) 1–2 m inside the plant stands·

Plant biomass and diversity

At each plot, four 100-m long transects were established at equally spaced intervals (40 m, river reference plot; 75 m, cove treatment plot; 120 m, river treatment plot) in an east to west direction to quantify the amount of submersed vegetation. At each transect, three biomass samples were collected by a scuba diver from stratified random locations using a $0{\cdot}1\ m^2$ quadrat (Madsen, 1993), for a total of 12 biomass samples per plot. Samples were sorted to species, separated into roots and shoots, and dried at 50°C. Biomass samples were collected pretreatment (18–20 August, 1991) and 4 weeks (18–20 September, 1991), 1 year (10–14 August, 1992), and 2 years (16–20 August, 1993) after treatment. Biomass levels between years at given plots were compared statistically using a one-way analysis of variance (ANOVA), with significant differences between means calculated using a Bonferroni test at the $p = 0{\cdot}05$ level.

Transects were also used to quantify the distribution and diversity of aquatic plants. Each 100-m transect was divided into 1-m intervals, and species present under each interval were recorded by a diver (Madsen *et al.*, 1994). Transects were examined concurrently with biomass collection at pretreatment, and one and two years after treatment. Frequency of species or community classes (i.e. native or exotic monocots or dicots) were compared for all transects at a given plot between years using χ^2 analyses of two-by-two comparisons between means of actual number of transect intervals with and without that species or community class. Average number of species or species classes per interval were compared for all transects at a given plot between years using a one-way ANOVA, with significant differences between means calculated using a Bonferroni test at the $p = 0{\cdot}05$ level. Voucher specimens of plants were collected and archived at the USAEWES Lewisville Aquatic Ecosystem Research Facility, Lewisville, TX.

RESULTS AND DISCUSSION

Triclopyr dissipation from river treatment plot

Inside river treatment plot. At 1 h after treatment, the whole-plot aqueous triclopyr residue (mean ± SE of all stations, all depths) was $4{\cdot}59 \pm 1{\cdot}46$ mg/l (Table II). This greater than predicted whole-plot triclopyr concentration was primarily caused by high residue levels found at station 2 (14 mg/l, discrete station data not shown) which was located in a shallow area ($z = 0{\cdot}5$ m) of the plot. Elevated herbicide residues are not uncommon in site-specific regions of a treatment area immediately following a submersed application, which typically occurs in the upper levels of the water column. In addition, water column mixing of herbicides can be inhibited by factors such as linear flow, thermal stratification and wind-driven circulation patterns (Fox *et al.*, 1991a; Getsinger *et al.*, 1992). Although measured triclopyr residues were initially greater than the nominal application rate, concentrations were well below acute and chronic toxicity levels established for non-target aquatic organisms, and were present for only short periods of time. Conversely, some locations within the treated area received below the intended dose of triclopyr in the first few hours following application. If data from the shallow sampling station are excluded, the whole-plot triclopyr concentration was $2{\cdot}71 \pm 0{\cdot}88$ mg/l, very close to the nominal application rate of 2·5 mg/l.

Whole-plot triclopyr concentrations remained $\geqslant 2$ mg/l through 12 h after treatment and were > 1 mg/l at 1 day after treatment. Based on laboratory-derived concentration and exposure time relationships, a triclopyr dose of $\geqslant 1$ mg/l for 24 h should provide up to 85% milfoil control, with some regrowth potential likely by five weeks posttreatment (Netherland and Getsinger, 1992). Although the whole-plot aqueous triclopyr value was still relatively high at 1 day after treatment ($1{\cdot}27 \pm 0{\cdot}43$ mg/l), residues were below the proposed potable water tolerance level of 0·5 mg/l by 2 days after treatment, when herbicide concentrations were measured at $0{\cdot}27 \pm 0{\cdot}13$ mg/l. By 3 days after treatment, triclopyr concentration in the plot was $0{\cdot}17 \pm 0{\cdot}1$ mg/l, and was near or below detection ($< 0{\cdot}01$ mg/l) in the upstream (Stations 1,2) and midstream (Stations 3,4) zones. Triclopyr concentrations were below detection in all sampling zones by 7 days after treatment.

Whole-plot aqueous half-life of triclopyr (Table III) was calculated to be 19·4 h ($r^2 = 93{\cdot}9$), which was very similar to the calculated half-life of the dye (20·1 h, $r^2 = 96{\cdot}5$). Correlation of dye and triclopyr concentrations was significant ($p < 0{\cdot}001$), with an r^2 value of 0·80 (Turner *et al.*, 1994). When analysed by flow zones, actual mean triclopyr concentrations and calculated half-lives (Tables II and III) showed that the minimum herbicide contact time occurred in the upstream zone ($t_{1/2} = 2{\cdot}7$ h, near detection limit by 1 day after treatment). While triclopyr exposure times in the midstream ($t_{1/2} = 15{\cdot}9$ h, near detection limit by 3 days after treatment) and downstream ($t_{1/2} = 24$ h, near detection limit by 7 days after treatment) zones were much longer. The relatively constant gravity flow in the river would be expected to produce this type of progressive herbicide dissipation pattern through the zones of the plot. Also, a small channel allowing water to flow from the main river channel into the south-west, upstream corner of the plot may have contributed to the accelerated dilution of the herbicide in the upstream zone. The extended triclopyr contact times in the mid- and downstream zones would be expected to provide a greater degree of milfoil control in those regions of the plot. Aqueous triclopyr dissipation varied between the upper ($t_{1/2} = 14{\cdot}9$ h) and lower ($t_{1/2} = 26{\cdot}4$ h) water sampling locations in the plot (Table III),

Table II. Mean triclopyr residues (mg/l ± SE) in water column inside treatment plots following Garlon® 3A applications, Pend Oreille River, WA, August 1991.

	Hours after treatment					Days after Treatment					
Station	1	1·5	5	8	12	1	2	3	7	14	21
RT*											
1–6	4·59 ± 1·46	NS†	2·72 ± 0·92	2·00 ± 0·48	2·23 ± 0·52	1·27 ± 0·43	0·27 ± 0·13	0·17 ± 0·10	BD‡	NS	NS
1–2	8·15 ± 3·44	NS	4·69 ± 2·43	2·53 ± 0·75	1·98 ± 1·19	0·02 ± 0·01	BD	BD	BD	NS	NS
3–4	1·86 ± 0·92	NS	1·18 ± 0·48	1·21 ± 0·32	2·08 ± 0·55	1·66 ± 0·57	0·06 ± 0·02	BD	BD	NS	NS
5–6	3·75 ± 1·97	NS	2·31 ± 0·98	2·27 ± 124	2·63 ± 1·09	2·14 ± 0·96	0·81 ± 0·22	0·41 ± 028	BD	NS	NS
CT§											
1–3	NS	2·32 ± 0·56	NS	2·03 ± 0·41	NS	0·78 ± 0·22	0·68 ± 0·23	0·47 ± 0·16	0·22 ± 0·03	BD	BD
1	NS	1·95 ± 0·05	NS	2·55 ± 0·05	NS	0·12 ± 0·09	0·07 ± 0·06	0·06 ± 0·05	0·12 ± 0·06	BD	BD
2	NS	3·55 ± 0·25	NS	2·75 ± 0·05	NS	1·03 ± 0·17	1·25 ± 0·25	0·45 ± 0·16	0·29 ± 0·02	BD	BD
3	NS	0·90 ± 0·30	NS	0·80 ± 0·50	NS	1·20 ± 0·0	0·72 ± 0·25	0·89 ± 0·08	0·25 ± 0·01	BD	BD

* River treatment; nominal triclopyr concentration = 2·5 mg/l
† No sample collected
‡ Below detection (< 0·01mg/l)
§ Cove treatment; nominal triclopyr concentration = 1·75 mg/l

Table III. Half-lives and regression equations for dissipation of triclopyr and dye for plots treated with Garlon® 3A and rhodamine WT, Pend Oreille River, WA, 1991. Unless noted, regression correlations (r^2) are significant at $p \leq 0.01$

Station	Depth	Regression equation $y = \exp(a + bt)$*	r^2	Half-life (h)
		River Plot		
1–6	all	[triclopyr] = exp(8·1335 − 0.0357t)	93·9	19·4
		[dye] = exp(2·3845 − 0·0344t)	96·5	20.1
1 + 2	all	[triclopyr] = exp(9·7465 − 0·2514t)	96·3	2·7
		[dye] = exp(4·8482 − 0·4429t)	88·6†	1·6
3 + 4	all	[triclopyr] = exp(7·6267 − 0·0434t)	68·6‡	15·9
		[dye] = exp(2·4227 − 0·0518t)	82·4	13·4
5 + 6	all	[triclopyr] = exp(8·1225 − 0·0288t)	95·4	24·0
		[dye] = [dye] = exp(2·0113 − 0·0206t)	52·3§	34·2
1–6	upper	[triclopyr] = exp(8·4471 − 0·0478t)	98·4	14·9
		[dye] = exp(2·7603 − 0·0466t)	99·5	14·5
1–6	lower	[triclopyr] = exp(7·8012 − 0·0262t)	84·7	26·4
		[dye] = exp(1·8864 − 0·0222t)	77·1	31·3
		Cove Plot		
1–3	all	[triclopyr] = exp(7·4469 − 0·0131t)	87·6	52·7
		[dye] = exp(1·9417 − 0·0133t)	87·4	52·0
1–3	all	[triclopyr] = exp(7·5279 − 0·0144t)	87·6	52·7
		[dye] = exp(2·0490 − 0·0148t)	87·4	52·0
1–3	all	[triclopyr] = exp(7·3881 − 0·0121t)	89·1	57·3
		[dye] = exp(1·8391 − 0·0120t)	88·1	57·7

* Chemical concentration (μg/l) at time (t) = exp ((intercept − slope(t))
† $p = 0.017$
‡ $p = 0.021$
§ $p = 0.066$

suggesting that laminar flow patterns (and perhaps triclopyr degradation rates) were dissimilar in these different layers of the water column.

Downstream river treatment plot. Aqueous triclopyr residues peaked at Stations 7 and 7a, located 300 m downstream from the northern edge of the river treatment plot, at 1·20 mg/l (1 day after treatment) and 0·42 mg/l (8 h after treatment), respectively (Table IV). Based on these residues, some off-target injury and/or milfoil control was expected downstream of the river treatment plot. At Stations 8 and 8a, located 675 m downstream from the plot, triclopyr residues peaked at 0·47 mg/l (1 day after treatment) and 0·12 mg/l (8 h after treatment), respectively. Residues at the 975 m downstream station (Station 9), were near or below detection throughout the post-treatment sampling regime. These low downstream triclopyr concentrations indicate that the potable water tolerance level (0·5 mg/l) set-back distances of 400–800 m (0·25–0·50 mile) being considered for the triclopyr aquatic label are appropriate for applications made along shorelines of slow-flowing rivers.

Triclopyr dissipation from cove treatment plot

Inside cove treatment plot. At 1·5 h after treatment, the whole-plot aqueous triclopyr residue (mean ± SE, all stations, all depths) was 2·32 ± 0·56 mg/l (Table II), somewhat greater than the nominal application rate of 1·75 mg/l. However, triclopyr concentration in the plot was 2·03 ± 0·41 mg/l at 8 h after treatment, and by 1 day after treatment a level of 0·78 ± 0·22 mg/l was measured. Triclopyr concentrations were below the proposed potable water tolerance level of 0·5 mg/l by 3 days after treatment, when triclopyr was measured at 0·47 ± 0·16 mg/l. By 7 days after treatment, the mean triclopyr concentration in the plot was 0·22 ± 0·03 mg/l, and was below detection at all stations and all depths by 14 days after treatment. Based on laboratory-derived concentration and exposure time requirements, a triclopyr dose of > 0·25 mg/l for ≥ 72 hours should provide excellent milfoil control with little or no regrowth (Netherland and Getsinger, 1992).

Table IV. Triclopyr residues in water downstream from treatment plots following Garlon® 3A application, Pend Oreille River, WA, August 1991

	Hours after treatment					Days after treatment					
Station	1	1·5	5	8	12	1	2	3	7	14	21
RT*											
7 300 m†	BD‡	NS§	0·23	0·55	0·97	1·20	0·57	0·57	0·06	NS	NS
7a 300 m	0·10	NS	0·21	0·42	0·03	0·02	0·02	BD	BD	NS	NS
8 675 m	NS	NS	BD	0·07	0·13	0·47	0·02	0·15	BD	NS	NS
8a 675 m	NS	NS	BD	0·12	0·09	BD	BD	BD	BD	NS	NS
9 975 m	NS	NS	BD	0·02	BD	BD	BD	BD	BD	NS	NS
CT¶											
4 150 m	NS	0·30	NS	0·28	NS	0·02	BD	BD	BD	BD	BD
5 395 m	NS	0·09	NS	0·32	NS	0·04	BD	BD	BD	BD	BD

* River treatment, samples collected at 1 m depth
† Distance downstream from plot
‡ Below detection
§ No sample collected
¶ Cove treatment, samples collected at 0·5 m (station 4) and 0·75 m (station 5) depths

Whole-plot aqueous half-life of triclopyr in the cove treatment plot (Table III) was calculated to be 52·7 h ($r^2 = 87·6$) which was nearly identical to the calculated half-life of the dye (52 h, $r^2 = 87·4$). Correlation of dye and triclopyr concentrations was significant ($p < 0·001$), with an r^2 value of 0·95 (Turner *et al.*, 1994). This high correlation coefficient indicates that a tank mix, rather than sequential (river treatment plot, $r^2 = 0·80$), application of triclopyr and rhodamine WT can improve the herbicide simulation characteristics of the dye.

When analysed by individual sampling stations, mean triclopyr concentrations were near target levels for both north and south subplots up to 8 hours after treatment (Table II). Residue levels declined most quickly at Station 1 in the higher water exchange subplot, diminishing to levels of approximately 0·10 mg/l or less by 1 day after treatment. The proximity of this southern portion of the plot to the main river channel and a tributary stream undoubtedly increased the degree of water exchange in that region of the plot. In contrast, triclopyr water residues at Stations 2 (mid-plot) and 3 (low water-exchange, northern subplot) remained at levels $\geqslant 0·25$ mg/l up to 7 days after treatment. These data suggested that optimum milfoil control could be expected in the mid and northern sections of the plot. Triclopyr dissipation half-lives in the upper ($t_{1/2} = 47·9$ h) and lower ($t_{1/2} = 57·3$ h) portions of the water column were more comparable in the cove treatment plot (Table III) than in the river treatment plot. Consequently, laminar flow was probably not a key component in the dissipation of triclopyr in the cove treatment.

Downstream cove treatment plot. Aqueous triclopyr residues peaked at 1·5 h after treatment at Station 4 (150 m downstream) and at 8 h after treatment at Station 5 (395 downstream) at 0·30 mg/l and 0·32 mg/l, respectively (Table IV). Residues at both of these stations were near or below detection by 1 day after treatment. Based on these triclopyr levels, little off-target injury and/or milfoil control was expected. As shown in the river treatment, these low downstream triclopyr residues indicate that the proposed potable water tolerance level (0·5 mg/l) set-back distances of 400–800 m are appropriate for triclopyr applications in relatively quiescent coves of slow-flowing rivers.

River reference plot

No triclopyr residues were detected in the untreated, upstream river reference plot at pretreatment, 8 and 24 hours after treatment. In addition, dye was never detected at the downstream edge of the river reference plot, nor anywhere inside the plot during the seven-day post-treatment sampling period. These results showed that there was no upstream migration of the chemicals from the river treatment plot, and no milfoil injury and/or control was anticipated.

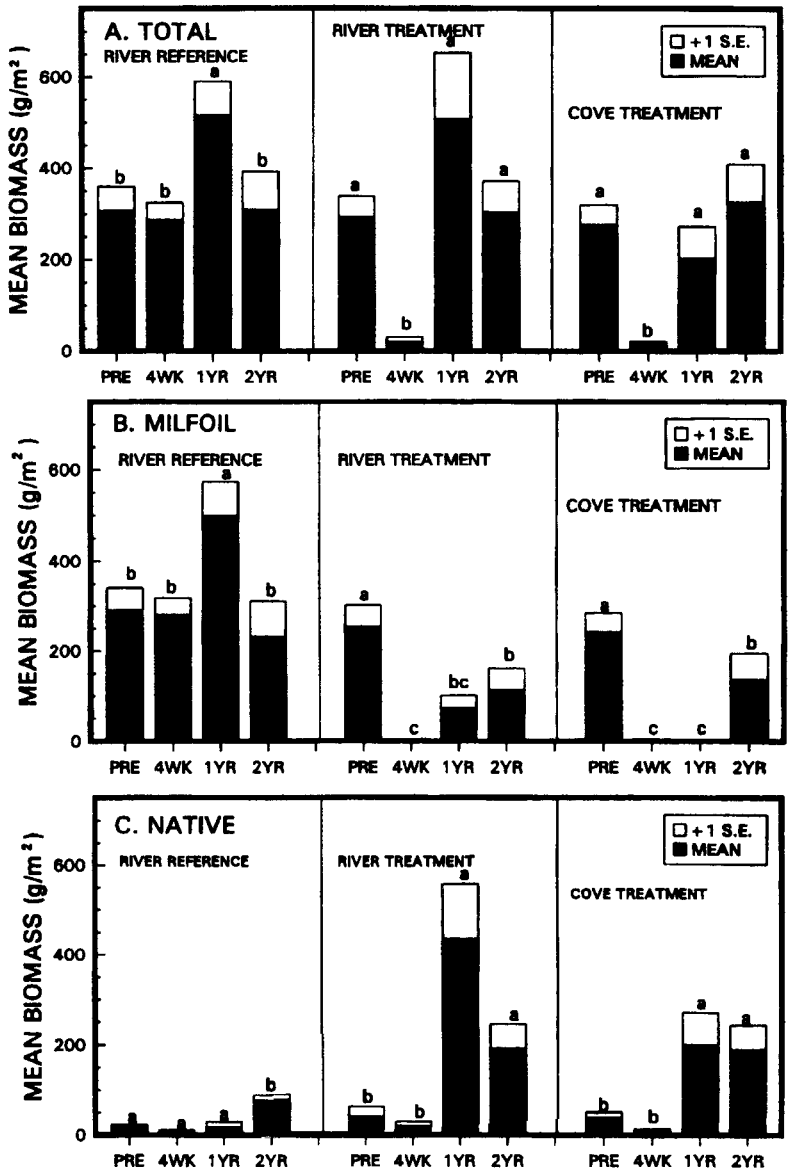

Figure 4. Plant community biomass at three study plots in the Pend Oreille River: (A) total community biomass, (B) Eurasian water milfoil biomass, (C) native community biomass. Letters indicate significant difference at the $p = 0{\cdot}05$ level using ANOVA Bonferroni LSD

Treatment efficacy: plant biomass

Total biomass. An examination of total biomass alone (Figure 4A) indicates that although the triclopyr treatment significantly reduced the amount of plants present in both plots four weeks after application, there was no effect on total community biomass one and two years post-treatment. In this respect, the triclopyr treatment had no long-term effect on plant productivity. However, closer inspection shows that the composition of biomass within the triclopyr-treated submersed plant community was significantly effected over the long term.

Milfoil biomass. Milfoil biomass in the untreated river reference plot maintained constant levels, with the exception of higher biomass during the first year after treatment (Figure 4B). In contrast, milfoil biomass was considerably reduced in both the river and cove treatment plots up to two years post-treatment. The amount of

milfoil at four weeks post-treatment was 1% of pretreatment levels in both treatment plots, indicating excellent triclopyr efficacy on the target plant. One year post-treatment, milfoil biomass in the RT plot was 28% of pretreatment and 1% of pretreatment in the cove treatment plot, and was still significantly lower (47–66%) in both plots two years post-treatment. Close examination of milfoil root crowns, an important source of new plant growth, revealed that most of these perennating structures were severely damaged or completely destroyed in both treated plots by four weeks post-treatment. These observations indicate that current-borne transport of healthy milfoil stem fragments, which is the species' primary reproductive strategy (Madsen *et al.*, 1988), from plants growing outside the treatment areas were primarily responsible for regrowth that occurred in the plots. Despite this reinvasion, duration of acceptable milfoil control at these sites using triclopyr was at least one year longer than reported from previous 2,4-D and fluridone applications in identical or similar locations in the river (Durando-Boehm, 1983; WATER Environmental Sciences, 1986, 1987).

Based on laboratory-derived concentration and exposure time relationships (Netherland and Getsinger, 1992), triclopyr levels in the river treatment plot should have at least 85% milfoil control, with some regrowth occurring by five weeks post-treatment; while milfoil control in the cove treatment plot should have been > 85%, with little to no regrowth occurring by five weeks post-treatment. In fact, field efficacy was better than the laboratory prediction, with triclopyr applications providing excellent control (99% milfoil biomass reduction) for the remainder of the growing season in both plots. Moreover, excellent (99% milfoil biomass reduction) and acceptable (72% milfoil biomass reduction) control were still being maintained in the cove and river treatment plots, respectively, at one year post-treatment. This enhanced field efficacy has been observed with other aquatic herbicides (Getsinger, 1993; Langeland, 1993; Netherland *et al.*, 1993; Nelson *et al.*, 1995) and may be related to levels of environmental stress (e.g. wave action, currents, water turbidity, microbes and pathogens, etc.) that are lacking or minimized in evaluations conducted under laboratory conditions.

Although water exchange and triclopyr half-lives in the river treatment plot suggested that milfoil control in the upstream zone might be less than that in the mid- and downstream zones, this was not the case. The four-week post-treatment efficacy evaluation showed excellent milfoil control throughout the plot, even along the upstream (southern) treatment boundary. High triclopyr concentrations (4·69 to 8·15 mg/l) measured in the upstream zone up to 5 h post-treatment, and concentrations in that zone of 2–2·5 mg/ through 12 h post-treatment, probably accounted for the good milfoil control in the upstream regions of the plot. Observations confirmed that milfoil was partially controlled at distances of up to 250 m directly downstream from the northern boundary of the river treatment plot, with more complete control occurring < 100 m downstream. This level of off-target control was not surprising, since triclopyr residues at Station 7 (300 m downstream) peaked at 1·2 mg/l at 1 day after treatment. As expected, no milfoil control was observed > 10 m upstream of the southern boundary or more than 10 to 20 m beyond the eastern boundary of the plot. Triclopyr injury symptoms were not observed on milfoil growing > 400 m downstream of the river treatment plot; this was expected from the low herbicide residues measured at those distances.

In contrast to the presence of off-target triclopyr efficacy in the river application, no collateral damage was observed on milfoil growing a few metres past the eastern boundary of the cove application. Dye measurements taken during previous water exchange studies (Getsinger *et al.*, 1993) and during this treatment demonstrated that water exchange between the cove and river was relatively low; therefore, efficacious levels of triclopyr extending beyond the confines of the cove were unlikely. The quiescent nature of the cove waters would restrict rapid transport of triclopyr into the river, and would enhance the photolytic and microbial degradation of the herbicide. Lack of off-target injury symptoms and/or milfoil control observed at the CT (cove treatment) plot was supported by the low triclopyr residues measured at the downstream water sampling Stations 4 and 5.

In addition to verifying laboratory-derived dosage rates, the CT plot treatment demonstrated the value of matching herbicide application rates with site-specific water exchange information. Knowledge of the water exchange characteristics of Lost Creek Cove, allowed for 30% less herbicide to be used (1·75 mg/l, versus maximum rate of 2·5 mg/l) with a high degree of confidence to achieve excellent milfoil control. Most importantly, this technique of coupling herbicide dosage rate and water exchange data can aid in reducing the amount of herbicide used in operational treatments, lowering environmental loading of chemicals and costs associated with herbicide applications, without sacrificing efficacy. In regulated rivers, herbicide contact might be maximized by appropriately modifying discharge rates during and after chemical applications, or by scheduling

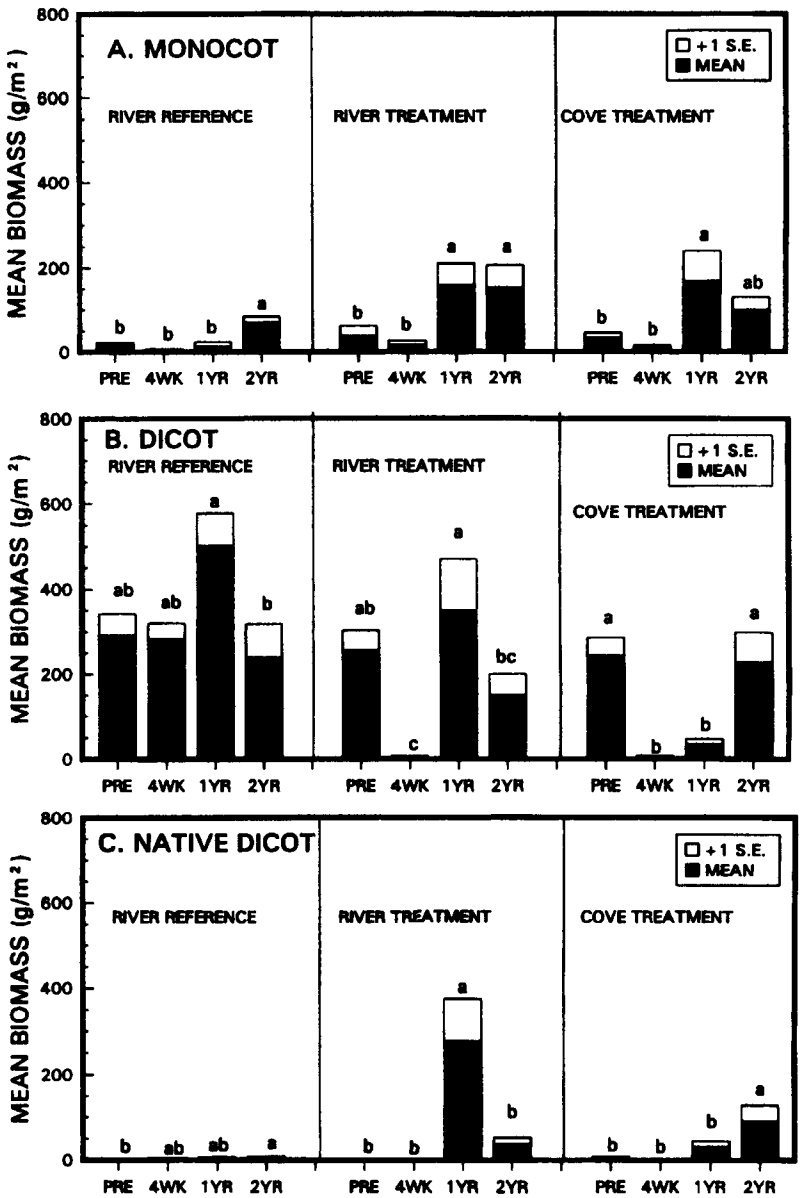

Figure 5. Submersed plant biomass (g/m^2 dry weight) categorized by taxonomic class (see Table I) at three study plots in the Pend Oreille River, (A) monocots, (B) dicots, (C) native dicots. Letters indicate significant difference at the $p = 0{\cdot}05$ level using ANOVA Bonferroni LSD

herbicide applications to take advantage of normal dam/spillway operations. While contact time is of primary importance, laboratory studies have shown that a relatively moderate increase in triclopyr exposure (i.e. from 12 to 24 hours) can provide acceptable control of milfoil at rates as low as 0·25 mg/l, 10 times below the maximum EUP label rate (Netherland and Getsinger, 1992).

Native plant biomass. Native plant biomass levels responded dramatically to the removal of milfoil (Figure 4C). At the untreated river reference plot, native plant biomass remained mostly unchanged, with a slight increase two years post-treatment. Although native plant biomass remained low four weeks after triclopyr application in the river and cove treatment plots, in part owing to the lateness of the growing season, it had increased dramatically (500–1000%) in both treatment plots one year post-treatment (Figure 4C). Native plant biomass remained significantly higher in both plots two years post-treatment. Thus, selective control of milfoil resulted in

higher abundance of native plants up to two years after treatment and suggests that a timely restoration of a diverse native plant community can delay the reinvasion and dominance of an aggressive and opportunistic weed. In fact, this reinfestation was delayed for at least two years in the treated plots, even though milfoil was selectively removed from only small areas (4–6 ha) surrounded by hundreds of untreated hectares infested with milfoil.

As expected from a product having an activity spectrum similar to 2,4-D and other auxin-type growth regulators that are non-toxic to most dicots, monocot species were not adversely affected by the triclopyr application. Rather, monocots significantly increased in abundance in post-treatment years one and two (Figure 5A). The dense milfoil canopy had apparently inhibited native monocot growth, and once this canopy was removed by triclopyr, monocots were able to flourish.

Response of dicots as a group to triclopyr includes the response of the target plant (Figure 5B), and although milfoil was significantly reduced, overall dicot biomass was not consistently different in the treated plots one and two years after treatment. Native dicots (Figure 5C) increased significantly in the river treatment plot one year after treatment, and in the cove treatment plot two years after treatment, largely owing to regrowth of white water crowfoot.

Treatment efficacy: Community diversity

Species frequency. A total of 17 submersed plant species were encountered during the one- and two-year post-treatment evaluations; two were non-native (exotic) species, 15 were native species, 12 were monocots and 5 were dicots (Table I). Transect data provided an assessment of the distribution of plants throughout each plot, and as such are a measure of eveness. Milfoil was observed in virtually all transect intervals in the untreated RR (river reference) plot in all three years (Figure 6A). Before triclopyr treatment, more than 90% of transect intervals had milfoil in both the river and cove treatment plots. These high pretreatment frequency values, coupled with biomass levels and observations by scuba divers, showed that mature milfoil plants were evenly distributed throughout the plots.

Following triclopyr application, milfoil frequency in the river treatment plot dropped to 60% one year after treatment, and remained less than 80% at two years post-treatment. Cove treatment plot milfoil was more affected, with less than 30% frequency one year post-treatment, and 60% two years post-treatment. When these frequency values are coupled with corresponding biomass levels and observations by divers, a clear depiction of

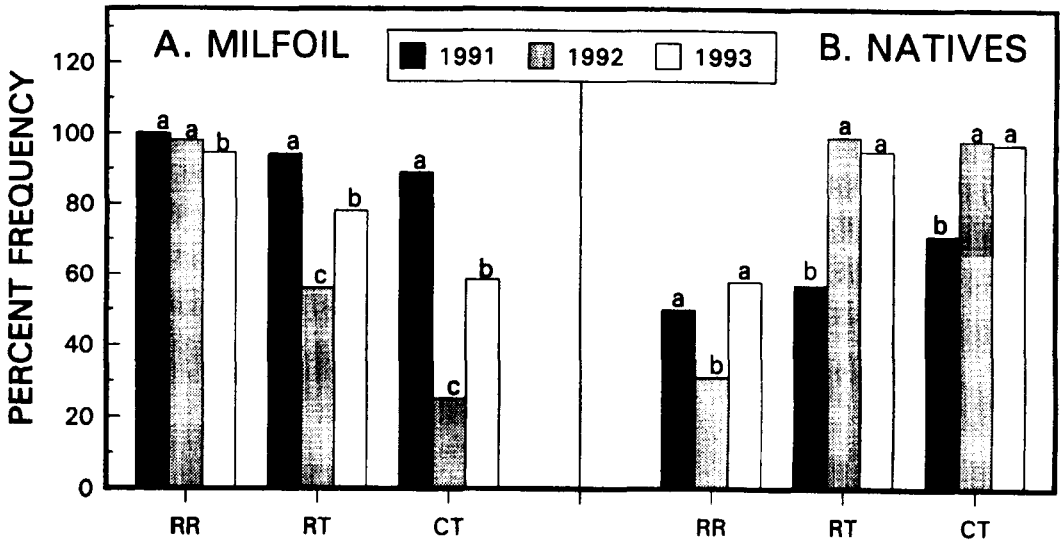

Figure 6. Frequency of plants along transects at three study plots in the Pend Oreille River over the three study years; (A) Eurasian water milfoil, (B) native plant species (all). RR, river reference; RT, river treatment; CT, cove treatment. Letters indicate significant difference at the $p = 0.05$ level using χ^2 analysis

triclopyr efficacy emerges: young shoots of milfoil (initiating from imported stem fragments) unevenly distributed within the treated plots, particularly at one year post-treatment.

Frequency of native species (non-milfoil, non-curlyleaf pondweed) was approximately 50–70% in the treatment plots before triclopyr treatment (Figure 6B). The untreated river reference plot had native plant frequency values from 40% to 60% (Figure 6B). Once treated however, natives increased to nearly 100% frequency two years after treatment. Thus, the seed/propagule bank was sufficient in these submersed plant communities to provide sources for re-establishing native plants; removal of the dense milfoil canopy was all that was required to restore the native plant community.

Species richness. The diversity measure used in this study was average number of species per transect interval, or average species richness. When all species are included, the three plots were at approximately two species per interval prior to triclopyr treatment (Figure 7A). Species richness remained low in the untreated river reference plot one year post-treatment, but increased to over 2·5 at two years post-treatment owing to the increased distribution of the exotic monocot, curlyleaf pondweed. Richness increased to over three species per interval in both treated plots two years post-treatment. When only native species are considered, all three plots were at

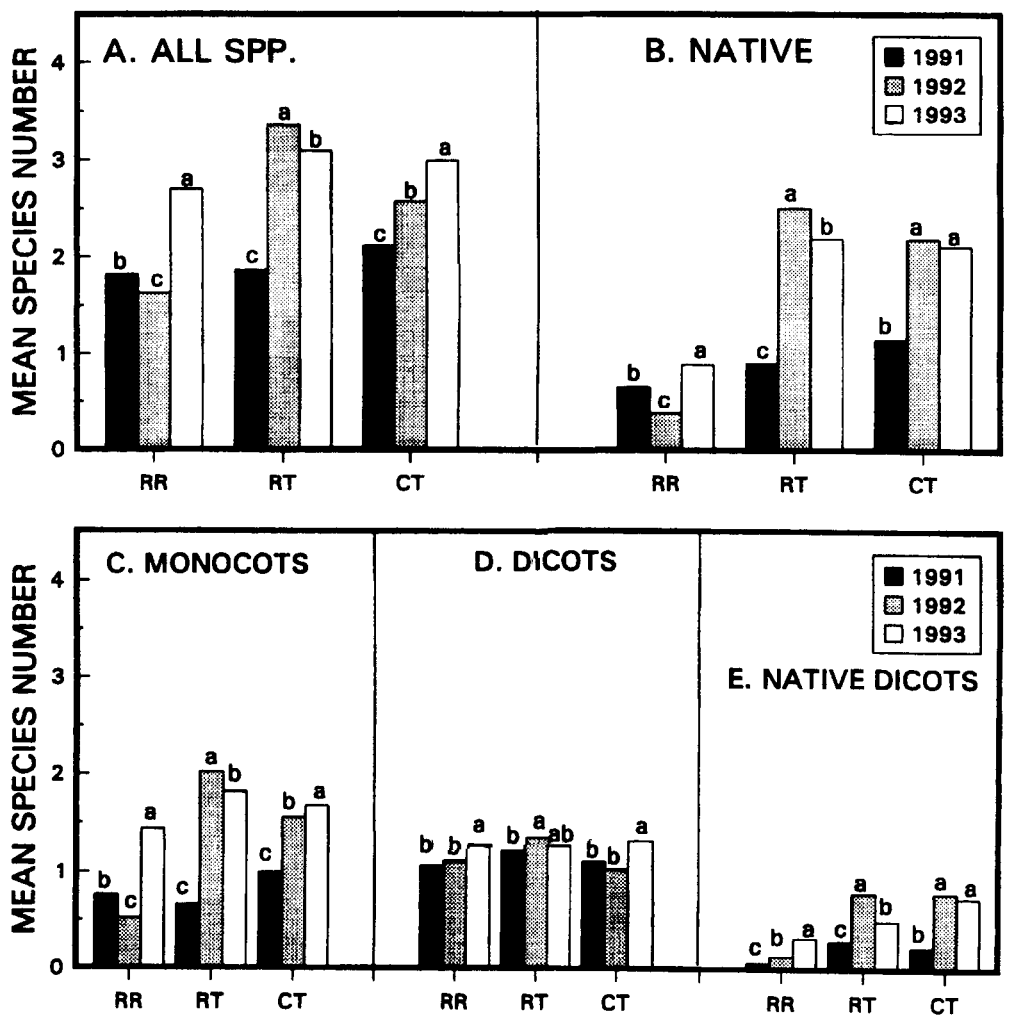

Figure 7. Average number of species per transect interval at three study plots in the Pend Oreille River over three study years; (A) all species; (B) native species only; (C) monocots; (D) all dicots; (E) native dicots only. RR, river reference; RT, river treatment; CT, cove treatment. Letters indicate significant difference at the $p = 0{\cdot}05$ level using ANOVA Bonferroni LSD

approximately one species per interval before treatment, and the untreated river reference plot remained near this level throughout the study (Figure 7B). Following herbicide treatment, richness of native species increased to over two species per interval, more than doubling the diversity of native species in both treatment plots. Higher plant diversity remained in both the river and cove treatment plots two years post-treatment.

The main component in this restoration of plant diversity was the monocot species, which more than doubled in average diversity along transects in the treated plots, both one and two years after treatment (Figure 7C). These were predominantly the native pondweeds (*Potamogeton* spp.). Dicot diversity as a whole was unchanged, owing to the substantial decrease in milfoil distribution (Figure 7D). As with the monocot community, native dicot diversity increased substantially in the rive and cove treatment plots, more than doubling after triclopyr treatment (Figure 7E). It is apparent that the triclopyr treatment did not have a prolonged negative affect on the native dicot community, and in fact allowed these dicots to flourish by removing the dense monoculture of milfoil that had been suppressing their growth.

CONCLUSIONS

This study has demonstrated that the herbicide triclopyr can be used to control selectively the exotic weed Eurasian water milfoil in coves and along shorelines in regulated rivers, while restoring diverse native submersed plant communities in these sites. Such native communities can delay the re-establishment of problematic levels of milfoil for up to three growing seasons. Within a similar areal scale and under comparable hydrodynamic and environmental conditions, triclopyr residues in treated water can be expected to dissipate and/or degrade to very low levels in a short period of time. In addition, this study shows that judicious planning and application can maintain triclopyr concentrations outside treated areas at levels that are extremely low or below detection, and that proposed potable water tolerance set-back distances of 400–800 m are adequate. Finally, we have seen that a knowledge of site-specific water exchange characteristics, coupled with well-established herbicide concentration and exposure time relationships, can be used to prescribe applications that will minimize herbicide dosage rates while maximizing effectiveness against a target plant.

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