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Correlation of Triclopyr and Rhodamine WT Dye Dissipation in the Pend Oreille River[1]

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INTRODUCTION

The US Environmental Protection Agency (USEPA) requires extensive field residue dissipation data for the registration of all aquatic herbicides. Typically, these dissipation studies are conducted by collecting large numbers of water samples from predetermined locations for a specified length of time, without knowing the direction(s) in which the herbicide will move (especially outside of the treated area) or for how long residues will persist. Samples may be collected and analyzed from areas where the herbicide is absent, or locations where the herbicide is present may not be sampled. In addition, samples may be collected and analyzed after the herbicide has dissipated from a particular station, or sample collection may be terminated prematurely.

An alternative approach to collecting aquatic herbicide dissipation data lies in the use of concurrent applications of herbicide and the fluorescent dye rhodamine WT. This dye was developed specifically for water tracing and can be monitored and quantified *in situ* using a fluorometer. Several studies have shown significant correlations between the dissipation patterns of this dye and those of the aquatic herbicides fluridone, bensulfuron methyl, and endothall, when applied concurrently in the field (Fox et al. 1991b, Fox et al. 1992 and 1993). Results from these studies indicated that aquatic herbicide dissipation can be predicted by monitoring dye movement and concentration, and by collecting only enough samples to establish the relationship between dye and herbicide values. However, correlations in dispersal patterns must first be established for each herbicide.

The triethylamine salt formulation (Garlon 3A[R]) of triclopyr ([(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid) is a herbicide currently in use in selected aquatic sites throughout the country under a USEPA Experimental Use Permit (EUP). This herbicide has been effective at controlling Eurasian watermilfoil (*Myriophyllum spicatum* L.) in both controlled-environment (Netherland and Getsinger 1992) and field studies (Getsinger et al. 1992). In conjunction with an effort to provide guidance for the most effective use of triclopyr in aquatic systems, a study was conducted to establish the relationship between triclopyr and rhodamine WT dye dissipation under field conditions.

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MATERIALS AND METHODS

Two sites on the Pend Oreille River, WA, were treated with triclopyr (as Garlon 3A) and rhodamine WT dye. The first site, designated as the River Plot, was located along the main channel of the river and was 6.1 ha in size with a mean water depth of 1.7 m. The surface area of this plot was divided into 6 equal quadrats with a sampling station located at the center of each quadrat. The second site, designated as the Cove Plot and located in a sheltered cove away from the main river current, was 4 ha in size with a mean water depth of 1.8 m. Three equally-spaced sampling stations were established along a center line in the Cove Plot.

The River Plot was treated on August 21, 1991, with triclopyr and dye at rates calculated to achieve aqueous concentrations of 2.5 mg/L acid equivalent (ae) triclopyr (maximum label rate) and 10 µg/L dye. The Cove Plot was treated on August 22, 1991, with a split application designed, on the basis of previous water exchange data, to provide good Eurasian watermilfoil control while using 30% less herbicide than the maximum label rate. Half of the Cove Plot was treated with the herbicide and dye at rates calculated to achieve 2.5 mg/L ae triclopyr and 10 µg/L dye, while the other half was treated at rates calculated to achieve 1 mg/L ae triclopyr and 4 µg/L dye. Due to initial problems encountered with mixing the two chemicals, the herbicide and dye were applied separately to the River Plot, within 0.5-1 hour of each other. This compatibility problem was later resolved, and the chemicals were applied concurrently to the Cove Plot.

Dye concentrations were monitored *in situ* using a Turner Designs field fluorometer equipped with a high-volume continuous-flow cuvette system. Water samples for triclopyr residue analysis were collected from the outflow of the fluorometer system at a third of the total depth below the surface and above the bottom of each sampling station. In addition, water samples were collected from outside of each plot in areas which dye was detected. Dye measurements and water samples were collected at 1, 5, 8, 12, 24, 48, 72, and 168 hours posttreatment for the River Plot and at 1.5, 8, 24, 48, 72, and 168 hours posttreatment for the Cove Plot. Samples were placed on ice and then frozen for later analysis. Triclopyr residue analyses were conducted by the Tennessee Valley Authority Environmental Chemistry Laboratory, Chattanooga, TN.

Correlations between triclopyr and dye concentrations were determined for each plot. Also, dissipation half-lives for each plot were calculated according to Fox et al. (1991a), and compared for any significant differences using a *t*-test.

RESULTS AND DISCUSSION

Correlations of dye and triclopyr concentrations were significant for both plots ($p < 0.001$), with r^2 values of 0.80 for the River Plot and 0.95 for the Cove Plot (Figure 1). Since the chemicals were applied separately in the River Plot, all values from the 1 hour posttreatment sampling period in this plot were excluded from the correlation to allow for sufficient time for complete mixing of the dye and herbicide. Otherwise, the correlation for the River Plot included surface and bottom samples collected from all stations within the plot and up to 900 m downstream of the plot. The correlation for the Cove Plot included all sampling times and stations (surface and bottom) with samples collected up to 400 m outside of the plot. It is likely that, had the two chemicals been applied concurrently to the River Plot, the correlation would have been similar to that of the Cove Plot.

Both chemicals dissipated from the plots in an exponential manner (River Plot: triclopyr, $r^2=0.92$; dye, $r^2=0.94$. Cove Plot: triclopyr, $r^2=0.85$; dye, $r^2=0.85$). Triclopyr and dye dissipation half-lives for the River Plot were 6.9 hours and 8.4 hours, respectively, and 51.2 hours and 52.2 hours for the Cove Plot. There was no significant difference between the dye and herbicide half-lives in either plot.

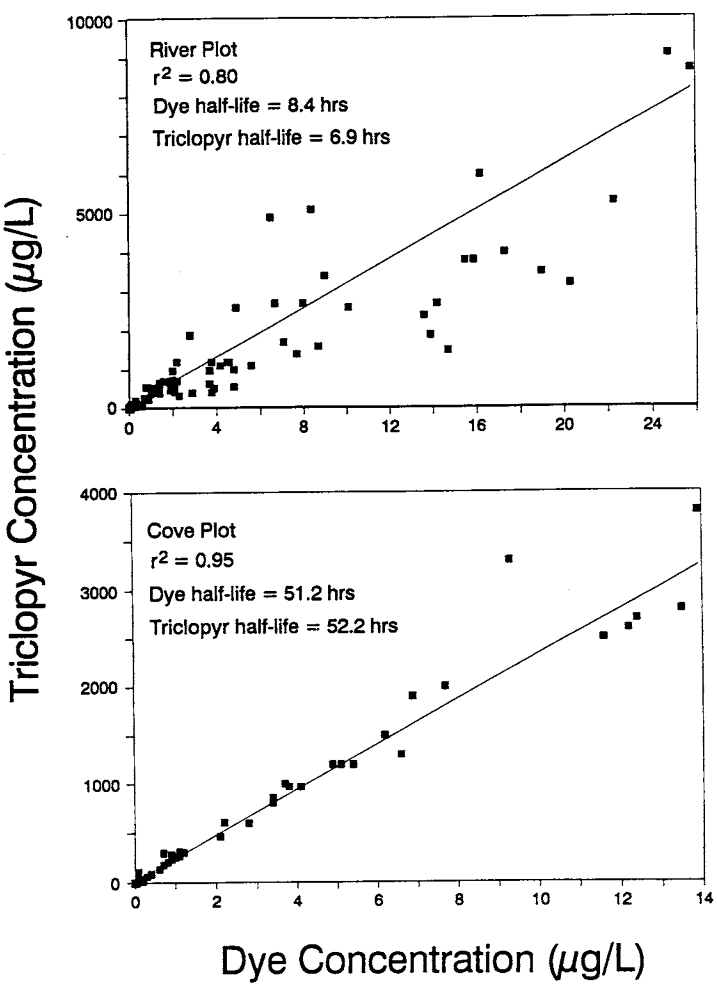

Figure 1. Correlations of rhodamine WT dye and triclopyr concentrations from 2 plots on the Pend Oreille River, WA, 1991.

These results indicate that rhodamine WT dye can be used to accurately simulate and predict triclopyr dissipation within areas of both high (River Plot) and low (Cove Plot) water exchange for up to 7 days posttreatment. In many water bodies such as rivers, large lakes, and reservoirs this should be sufficient time for triclopyr residues to diminish to below detectable levels.

In future triclopyr aquatic dissipation studies, similar in scope to the study reported here, the advantages of concurrent applications of rhodamine WT and triclopyr are clear. By monitoring the dye *in situ* it should be possible to determine: (1) where to position sampling stations outside of the target areas; (2) how often samples should be collected; and (3) when herbicide dissipation/dispersion from any specific station is complete. In this manner, the potential for collecting/analyzing too few or too many water samples can be minimized, thus ensuring that limited resources such as time, equipment, personnel, analytical budgets, etc. are used much more efficiently.

In static bodies of water, where water exchange is minimal, further triclopyr/rhodamine WT correlation studies should be conducted. Limited data suggests that in such systems, over extended periods, triclopyr loss from the water column proceeds at a greater rate than does rhodamine WT (Turner et al. 1991). Presumably, this accelerated dissipation of triclopyr is caused by photo/microbial degradation and plant uptake of the herbicide.

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