

GREAT LAKES FISHERY COMMISSION

2021 Project Completion Report<sup>1</sup>

FIELD EVALUATION OF AN ALTERNATE SOLID TFM FORMULATION  
FOR USE IN TREATING SMALL TRIBUTARY STREAMS

Project ID – 2020\_LUO\_760150

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May 2021

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## **ABSTRACT**

A solid lampricide formulation containing 23% 3-trifluoromethyl-4-nitrophenol (TFM) as the active ingredient was developed in the mid-1980s for use in small tributaries of dendritic streams during routine treatments to kill larval sea lamprey. This TFM bar formulation was designed to use a matrix of commercially prepared surfactants that would dissolve and slowly release their TFM payload over an 8–10-hour period. Although this formulation has proven useful, several matrix surfactants have been discontinued, resulting in the need to reformulate the TFM bar multiple times. Maintaining acceptable performance of the TFM bars while reformulating has been challenging. As a result, an experimental surfactant-free tableted TFM formulation was developed as a potential TFM bar replacement. Release of TFM from the tablet formulation was evaluated in four independent experimental applications made over varied substrates in three small tributaries of the Ford River (Delta County, Michigan). For each tributary, TFM release from tablets was modeled using exponential decay curves and the time required to release 25, 50, 75 and 90% of the TFM tablets was calculated. Differences in water-quality properties were detected using one-way analysis of variance tests, and post-hoc Tukey Honest Significant Difference tests were used to determine which water-quality properties differed among the trials. The influences of water temperature

and water velocity on the release of TFM from the tablets has been previously reported; however, in this study substrate type also appeared to be an indicator of TFM release. In this study the performance of the TFM tablets appeared acceptable; however, it may be beneficial to conduct additional investigations to determine storage stability and handling durability as well as to identify potential challenges with mass production.

## INTRODUCTION

Invasion of the upper Great Lakes by the parasitic sea lamprey (*Petromyzon marinus*, Linnaeus, 1758) in the early 1900s resulted in the collapse of the commercial and recreational fisheries as well as devastating ecological and economic harm (Smith and Tibbles 1980, Siefkes 2017, Wilkie et al. 2019). Barriers and chemical control measures have been the primary means to control sea lamprey populations since the late 1950s (Christie and Goddard 2003, Wilkie et al. 2019). Cyclical treatments of larval sea lamprey nursery streams with the lampricide 3-trifluoromethyl-4-nitrophenol (TFM), with or without the additive lampricide Bayluscide, are the primary chemical control measures used to suppress sea lamprey populations in the Great Lakes. The combined use of these treatments and barriers effectively control sea lamprey populations, thereby preserving a fishery with an annual value of \$7B (GLFC 2014).

In the mid-1980s, a controlled-release solid formulation of TFM (i.e. the TFM bar) was developed to aid in the treatment of small streams by eliminating the need for labor-intensive applications of liquid TFM using metering pumps. The bar formulation was developed to contain 23% TFM as the active ingredient and a blend of commercially available surfactants that served as the release-controlling matrix for the TFM (Gilderhus 1985). Several matrix surfactants have subsequently become unavailable for use and required replacement. These multiple substitutions ultimately resulted in TFM bars with poor warm-weather performance characteristics (Solomon 2021). Unacceptable softening of the TFM bars during field storage and increased dissolution rates at mid-summer water temperatures provided the impetus to develop an alternative surfactant-free tableted TFM formulation using readily available inert ingredients (Luoma et

al. 2020). The tableted formulation is covered with a food-grade coating that controls the TFM release, and the formulation contains nearly three times the amount of active ingredient as the bar formulation (i.e., ~ 67% vs 23%; Luoma et al. 2020).

A comprehensive laboratory study of the tableted TFM formulation was completed to assess the release over a range of water temperatures and water velocities. Laboratory testing revealed that water temperature and water velocity both influenced release of TFM from tablets; however, the influences were not substantial and additional field testing was warranted (Luoma et al. 2020).

## OBJECTIVES

The objectives of this Technical Assistance Project to evaluate the field performance of the TFM tablets were met within the constraints of the field conditions and within the limitations imposed by our experimental use permit waiver. The specific objectives included the following:

- (1) Evaluation of TFM release under various flow and substrate conditions.

Summary result: A total of four TFM tablet applications were made on three small tributaries of the Ford River (Delta County, Michigan). Two independent applications, with different application points, were made in Don Creek, and single applications were made in Chuckies and Jackstraw Creeks. All applications targeted 1.0 mg/L of TFM to reduce confounding variables. The mean water velocity and discharge of the creeks ranged from 0.082 to 0.239 m/s and 0.016 to 0.066 m<sup>3</sup>/s, respectively. Applications were completed on various substrates including primarily gravel and sand (Don Creek, trial one), cobble and rock (Chuckies Creek), detritus and sand (Don Creek, trial two), and detritus/woody debris and sand (Jackstraw Creek).

- (2) Evaluation of TFM tablet formulation mobility under various flow and substrate conditions.

Summary result: A catch screen was placed downstream from the application points and observations for TFM tablet dislodgement and screen impingement were completed hourly for the first 12 hours after application and then a final observation was made 24 hours after application.

The tablets disintegrated upon removal, precluding enumeration. Tablet movement from the application site was only observed during Don Creek trial one.

- (2) Determination if formulation modifications are warranted based on field performance.

Summary result: The TFM tablets performed well with regard to conditions under which they were tested as demonstrated by similar TFM release among trials. Although formulation modifications do not appear warranted based on field test results, additional data would be beneficial to verify product storage stability and handling durability as well as to determine if there are any issues associated with production-scale manufacturing.

## **METHODS**

TFM tablets were produced at Northland College (Ashland, Wisconsin) using concentrated TFM prepared by U.S. Geological Survey (USGS) staff. A representative sample of the tablets was analyzed to determine active ingredient concentration prior to use in four independent experimental applications that were made in three small tributaries of the Ford River (Delta County, Michigan). Water samples were collected every 30 minutes during the 24-hour application and analyzed for TFM content to evaluate the performance (i.e. TFM release) of the tablets under field conditions. TFM release profiles were examined and visual observations (e.g. tablet mobility) were assessed to determine the potential for the TFM tablet formulation to serve as a replacement for the TFM bar.

### *TFM Extraction*

High-purity TFM used in the production of the tablets was prepared at the Upper Midwest Environmental Sciences Center (La Crosse, Wisconsin) using the methods described by Luoma et al. (2020) to extract and concentrate the TFM from the end-use liquid formulation (U.S. Environmental Protection Agency registration No. 6704-45). TFM was extracted from 32 individual 1-L batches of liquid end-use lampricide, resulting in 11.6 kg of concentrated TFM. Individual batches of TFM concentrate were

comingled, thoroughly mixed, and then analyzed by high performance liquid chromatography (HPLC) to confirm the purity exceeded 99% before it was used for TFM tablet production.

### *TFM Tablet Production and Coating*

TFM tablets were produced at Northland College in Ashland, Wisconsin, using a multi-step process that used high purity TFM and low regulatory concern inert ingredients. To prepare the formulation for tableting, batches of TFM (300.0 g) and calcium hydroxide (53.7 g, Acros Organics, Fair Lawn, New Jersey) were mixed and allowed to stand for a minimum of 5 hours (mildly exothermic on mixing). The



TFM mixture was then blended with magnesium stearate (2.23 g, Alfa Aesar, Haverhill, Massachusetts) and sand (90.0 g, Badger Mining Corporation, Berlin, Wisconsin) to create a homogeneous flowable powder that was then pressed into 14-mm tablets and covered with a TFM release-control coating according the procedures described by Luoma et al. (2020). After the coating was applied and cured, the tablets were approximately 1.1 g, 14-mm diameter, and 4-mm thick. The tablets were stored at room temperature in plastic bags in quantities of approximately 300 g until used in the applications (Figure 1).

**Figure 1.** TFM tablets packaged in quantities of approximately 300 grams (equivalent to approximately one TFM bar).

### *TFM Tablet Active Ingredient Content*

The mean active ingredient concentration of the TFM tablets was computed from the sample TFM concentration ( $c_s$ ) measured in 25 indiscriminately selected tablets and was determined to be  $66.5 \pm 1.4\%$ . Each tablet was weighed and bisected prior to eluting the TFM with methanol in a 100-mL volumetric

flask. The eluate was diluted 1,000-fold with 18 MΩ-cm water and the resulting solution was analyzed for TFM content using HPLC. The percentage of TFM in each tablet was determined with equation 1.

$$\text{Percent active ingredient} = c_s \times \frac{1}{m} \times 10,000 \quad (1)$$

where

$c_s$                     sample TFM concentration (mg/L), and  
 $m$                     tablet mass (mg).

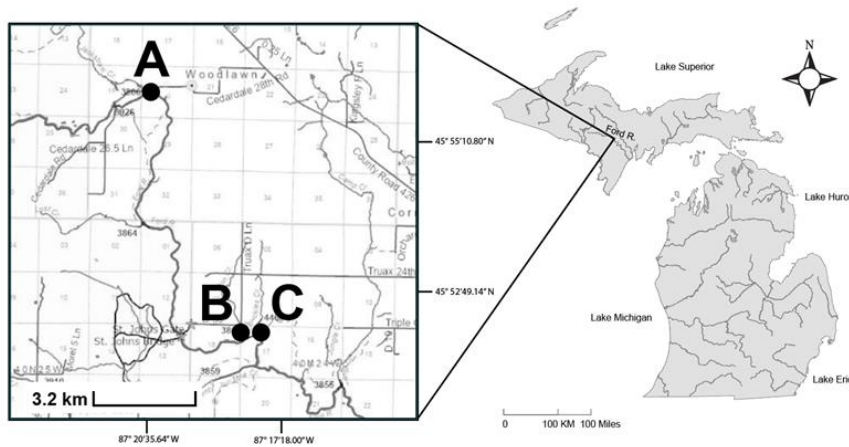
### *Water quality*

Standard water-quality properties (temperature, hardness, alkalinity, specific conductance, and pH) were measured hourly in each creek for the first 12 hours after application and then again 24 hours after application. Temperature was measured with a digital thermometer (Thermopen model Mk4, ThermoWorks Company, American Fork, Utah), and pH was measured using a water-quality meter equipped with a digital pH probe (models HQ40d and PHC 70501, respectively; Hach Company, Loveland, Colorado). Specific conductance was measured using a hand-held conductivity meter (Accumet model AP75, Fisher Scientific Company, Pittsburg, Pennsylvania). Grab water samples were collected from each creek prior to application as well as at 12 and 24 hours after application and analyzed for total hardness and alkalinity using the ethylenediaminetetraacetic acid titrimetric method (method 2340C; American Public Health Association, 2012) and by titrating to an endpoint of pH 4.5 (method 2320B; American Public Health Association, 2012), respectively.

### *Field applications*

Four experimental applications of the TFM tablet were made during the timeframe approved for a regularly scheduled Sea Lamprey Control Program (SLCP) lampricide treatment of the Ford River (Delta

County, Michigan). The applications were conducted in tributaries of the Ford River from October 15-19, 2020 (Figure 2).



**Figure 2.** Location of Jackstraw Creek (A), Don Creek (B), and Chuckies Creek (C) of the Ford River system (Delta County, Michigan) where experimental TFM tablets were applied.

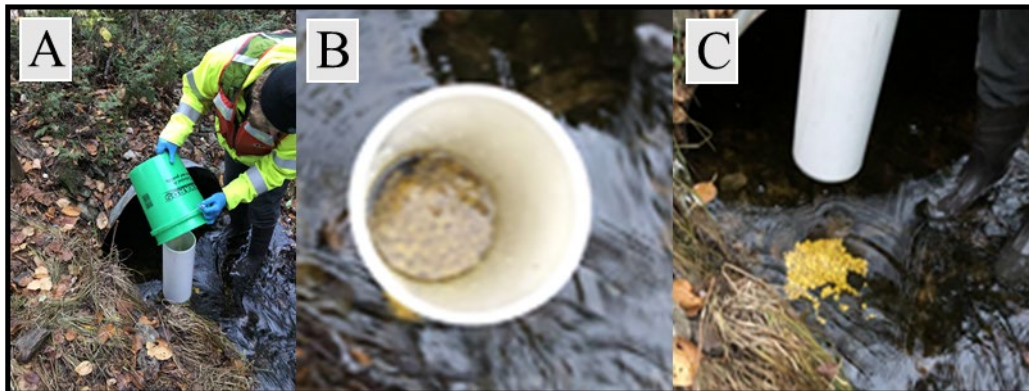
Two independent applications were made at different locations in Don Creek and single applications were made in Chuckies and Jackstraw Creeks after consultation with SLCP personnel. Treated tributaries had (1) varied, but low discharge, (2) variable application point substrates, (3) varied, but cold water temperatures, (4) varied water-quality properties, and (5) reaches that were both accessible and suitable to promote uniform mixing. TFM tablets were applied according to procedures described in the SLCP Technical Operating Procedure (TOP) 015, Procedures for the Supplemental Application of TFM Bar Formulation (Solomon 2021), with the following exceptions: (1) TFM tablets were substituted for the TFM bars on an active ingredient equivalent basis, and (2) the TFM tablets were placed in piles on the creek bed by pouring them down a guide tube (Figure 3). To reduce confounding effects, a concentration of 1.0 mg/L of TFM was targeted for all applications. The SLCP TOP 015 calculation assumes a consistent amount of TFM will be released, resulting in concentration of 1.0 mg/L for 10 hours. The mass of tablets applied to each creek was calculated using the discharge measured immediately prior to application and was as follows: Don Creek trial one – 2,809 grams, Chuckies Creek – 1,006 grams, Don Creek trial two – 2,080 grams, and Jackstraw Creek – 3,909 grams. The 1.0 mg/L TFM target concentration was



approximately three orders of magnitude above the detection limit and below a level that would cause concern for nontarget species. The TFM tablets were placed in a single pile on the creek bed for all applications except in Jackstraw Creek, where tablets were placed in two separate piles because of the higher amount of TFM required and the low turbulence (i.e. low mixing) observed in the vicinity immediately downstream from the application point. Locations for application points, water velocity and discharge measurements, and water sample collection sites were selected in consultation with SLCP personnel that had previous experience applying lampricides in these creeks.

Discharge calculation procedures were consistent with SLCP Technical Operating Procedure 001 (Solomon 2021). A FlowTracker 2<sup>®</sup> acoustic doppler velocimeter (SonTek – a Xylem brand, San Diego, California) fitted with a top mounting wading rod was used to obtain velocity data and calculate discharge prior to application as well as at 12 and 24 hours after application. The automated FlowTracker 2 velocimeter calculated discharge using the mean-section method with the water velocities measured at 60% of water depth (from the substrate) because creeks were < 30 cm deep.

A cross section of each creek was divided into a minimum of 15 stations (i.e. measurement points)



**Figure 3.** Placing TFM tablets in guide tube (A), TFM tablets after placement (B), and TFM tablets after guide tube removal (C).

and panels were created between stations across the section. The mean velocity of each panel was calculated by averaging the velocity of adjacent stations, and no more than 10% of the total discharge was measured within a single panel. Mean-section discharges were calculated using equation 2 (Xylem 2019).

$$\begin{aligned}
Discharge = \sum (b_1 - b_0) \left( \frac{d_1 + d_2}{2} \right) \left( \frac{\bar{V}_1 + \bar{V}_0}{2} \right) + (b_2 - b_1) \left( \frac{d_2 + d_1}{2} \right) \left( \frac{\bar{V}_2 + \bar{V}_1}{2} \right) \\
+ (b_{n+1} - b_n) \left( \frac{d_{n+1} + d_n}{2} \right) \left( \frac{\bar{V}_{n+1} + \bar{V}_n}{2} \right)
\end{aligned}
\tag{2}$$

Where,

$\bar{V}$  = the mean water velocity at the station over 20 seconds,

$d$  = the water depth measured at the station, and

$b$  = the location of the station.

A 6.35-mm square mesh screen was placed approximately 0.75 – 2.0 m downstream from the application points to retain any TFM tablets that were dislodged and carried downstream. Estimates of TFM tablet dislodgement and impingement were completed hourly for the first 12 hours after application and then again 24 hours after application.

### *Water sample collection and TFM concentration verification*

Water samples were collected every 30 minutes for 24 hours after application using two automated water samplers (model #3700, Teledyne-Isco, Inc, Lincoln, Nebraska). The samplers were placed approximately 30 to 65 m downstream from application points at locations deemed suitable by SLCP personnel who considered access, hydrodynamics, and prior experience. Water samples were removed from the samplers 12 hours after application and again 24 hours after application and stored frozen (- 20°C) until analyzed for TFM concentration by HPLC (USGS 2019). Sample responses were compared to a linear regression created from analytical standards analyzed on an Agilent model 1260 HPLC (Agilent Technologies Inc., Santa Clara, California) equipped with a diode array detector. Analytical standards were prepared by diluting a known weight of reagent grade TFM with methanol in a volumetric flask. Further dilutions were made using 18 MΩ-cm water to create a series of five standards that bracketed the experimental sample concentrations. A minimum of six replicates of each analytical standard were injected

with the experimental samples (25- $\mu$ L aliquots) with an autosampler and separated using a Kinetex XB-C18 column (3  $\times$  50 mm, 2.6  $\mu$ m particle size) maintained at 50°C. Replicates of the analytical standards used to create the standard curves were injected after each 10 experimental samples to account for potential baseline drift.

Fortified creek water samples were used to assess for potential sample degradation. The fortified samples were prepared immediately following tablet application by diluting a verified SLCP TFM field standard with unfiltered and untreated creek water. The fortified samples were stored frozen (-20°C) with the experimental samples until analyzed for TFM concentration by HPLC.

Samples were analyzed using gradient HPLC elution that used two 10-mM ammonium acetate mobile phase constituents ([A, in a 3:1 mixture of water and methanol] and [B, in methanol]) that were buffered with 3 mL of acetic acid per liter. A combined flow rate of 1.25 mL per minute was maintained over the 1.5-minute elution time with the A:B ratio maintained at 60:40 from 0.0 to 0.5 minute and then adjusted to 75:25 for the remainder of the 1.5-minute run. Sample absorbance was measured at 295.0 nm using a 10.0-nm bandwidth, and the normal influences of gradient analysis were accounted for using a reference absorbance at 350.0 nm with a bandwidth of 80.0 nm.

### *TFM Recovery*

Calculation of the amount of TFM eluted from the tablets required estimating the volume of water discharged at the time of sample collection. In all trials discharge decreased over time; therefore, to increase accuracy and to predict sample time specific water discharge ( $d_i$ ), a linear regression of creek discharge was fit to the discharge calculated prior to, 12 hours after, and 24 hours after application for each trial. Linear regressions were highly correlated ( $r^2 = 0.90955\text{--}0.99176$ ) and all predicted values were within 3.5% of actual recorded values. The percentage of TFM placed in the stream during each trial that could be accounted for (i.e. recovered) was calculated using equation 3.

$$\text{Percent Recovery} = \sum_{i=0}^{24} \left[ \frac{c_i \times d_i \times t_i}{k} \right] \times 100$$

(3)

where

$i$  = the time of sample (hours),

$c_i$  = the concentration of TFM in the sample (mg/L),

$d_i$  = the predicted stream discharge (L/hour),

$t_i$  = the time between samples (hours), and

$k$  = the known amount of TFM applied (mg).

For each sample time, the percentage of TFM remaining was calculated by subtracting the cumulative amount of TFM eluted from the known amount of TFM in the tablets that were applied to the creek. Samples from the trial that exceeded 100% total TFM recovery (Chuckies Creek, 103.6%) were corrected by dividing the predicted values by the total recovery. TFM tablet performance among trials was compared using the percentage of TFM remaining.

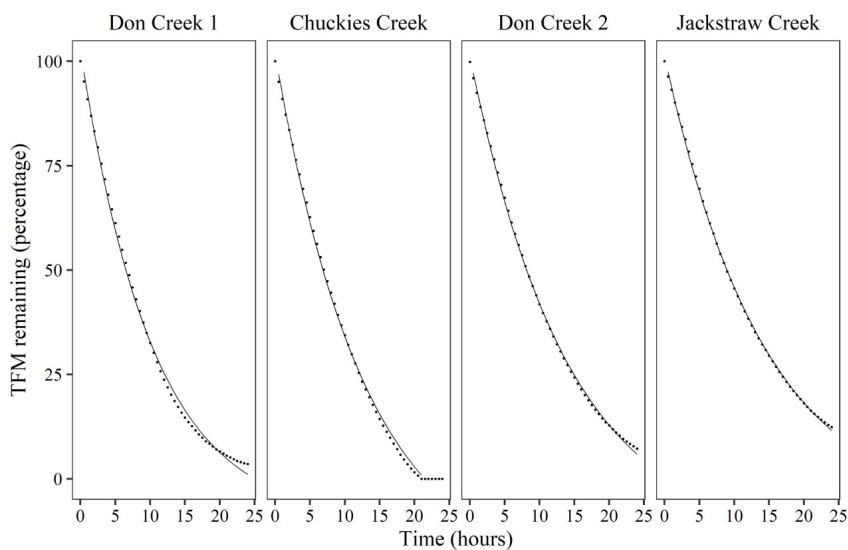
### *Data analysis*

Data were summarized, modeled, and analyzed using R (version 4.0.3, R Core Team 2020) and RStudio software (version 1.4.1103; RStudio Team 2020). Water-quality properties and discharge were summarized with simple descriptive statistics. Differences in water-quality properties were detected using one-way analysis of variance tests (Montgomery 2017), and post-hoc Tukey Honest Significant Difference tests (Montgomery 2017) were used to determine which water-quality properties differed among the trials. Exponential decay curves were fit to the TFM release data for each trial and modeled according to OECD (2014) using the DRC package (Ritz et al. 2015). Model fitness was assessed using the median absolute deviation (MAD) for each creek. The MAD was computed as the median of the absolute value of the distance between the calculated and the predicted percentages of TFM remaining in the tablets. The predicted times required for the tablets to release 25, 50, 75 and 90% of the TFM were determined from

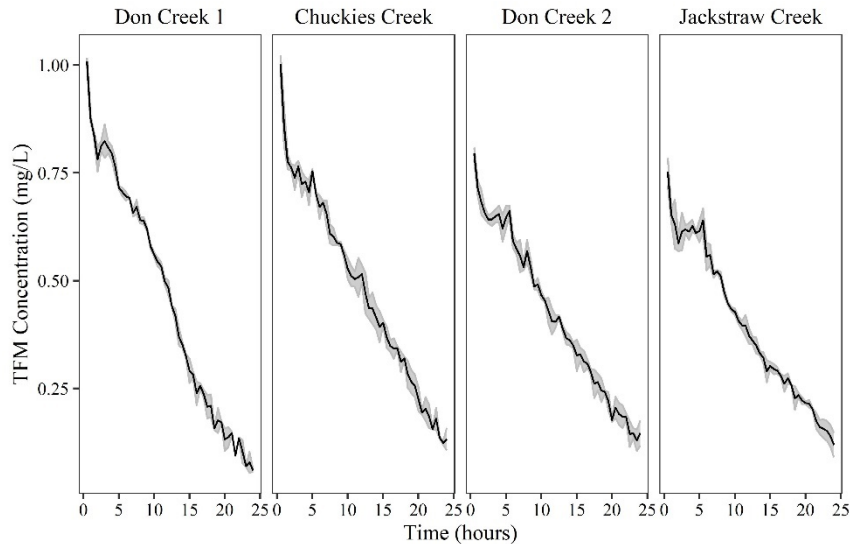
each model. The small number of replicates prevented the inclusion of substrate and water-quality properties as factors in the models.

## RESULTS

Calibration curves used to determine the concentration of TFM in samples were linear, the water samples were stable, and analysis methods were robust as indicated by (1) the correlation coefficient (R) values exceeding 0.9999 and (2) the recovery of TFM from field-fortified samples ranging from  $102.02 \pm 2.54$  to  $103.36 \pm 0.93\%$ . The profiles of TFM release from the tablets were similar among trials (Figure 4), and mean TFM concentrations ranged from 0.753 to 1.009 mg/L in water samples collected 0.5 hour after application (Jackstraw Creek and Don Creek trial one, respectively) and 0.060 to 0.199 mg/L in water samples collected 24 hours after application (Don Creek trial one and Jackstraw Creek, respectively; Figure 5).



**Figure 4.** Exponential decay curves (solid lines) and the calculated amount of TFM remaining in the TFM tablets (circles) throughout each trial.



**Figure 5.** Mean (black lines) and standard deviation (gray-shaded areas) TFM concentrations measured in triplicate water samples that were collected every 30 minutes during each trial with an automated water sampler.

Mean water-quality properties during the trials were as follows: temperature 4.7–7.1°C, pH 7.51–8.31, specific conductance 147.0–381.1  $\mu\text{S}/\text{cm}$ , hardness 126.0–258.0 mg/L as  $\text{CaCO}_3$ , and alkalinity 109.0–244.0 mg/L as  $\text{CaCO}_3$  (Table 1). Among creeks, differences were detected in temperature ( $F(3, 52) = 35.36, p < 0.001$ ), pH ( $F(3, 52) = 847.5, p < 0.001$ ), specific conductance ( $F(3, 52) = 24563, p < 0.001$ ), alkalinity ( $F(3, 12) = 6684, p < 0.001$ ), hardness ( $F(3, 12) = 740, p < 0.001$ ), and discharge ( $F(3, 8) = 63.8, p < 0.001$ ). Notable water-quality differences, other than temperature, were among Jackstraw Creek and the others (Table 1).

Mean discharge of the creeks ranged from 0.0163 (Chuckies Creek) to 0.0662  $\text{m}^3/\text{s}$  (Jackstraw Creek) with discharges decreasing over the course of each trial. Discharge decreases ranged from -2.8% to -6.3% between 0 and 12 hours and -7.7% to -14.4% between 0 and 24 hours (Table 2). Substrate was variable among application points with composition as follows: Don Creek trial one – gravel and sand, Chuckies Creek – cobble and rock, Don Creek trial two – detritus and sand, and Jackstraw Creek – detritus/woody debris and sand.

The exponential decay models were appropriate for the TFM release data as demonstrated by MAD values which show that the variations between the calculated and the model predicted amounts of TFM

remaining in the tablets differed by 0.24 to 1.27% for all trials. The calculated and predicted amounts of TFM remaining reveal similar tablet release patterns among the trials; however, slightly slower TFM release was observed in Don Creek trial two and Jackstraw Creek (Figure 4). The predicted time to release 25, 50, 75, and 90% of the TFM from the tablets in the trials ranged from 2.9–3.9, 6.5–9.0, 12.1–16.8, and 16.9–25.1 hours, respectively (Table 2). Divergence of calculated and predicted amounts of TFM remaining are apparent beginning at approximately 85-90% release and only about 88% of the available TFM was released within 24 hours during the Jackstraw Creek trial (Figure 4).

Tablet dislodgment and downstream migration from the application site was only observed during Don Creek trial one and an estimated 50% of the tablets became impinged on the screen located approximately 1-m downstream from the application point. Impinged tablets disintegrated upon removal, precluding enumeration; therefore, calculation of the exact percentage of tablets that were impinged was not possible.

**Table 1.** Application point substrate and mean ( $\pm$  standard deviation) water temperature (n = 14), pH (n = 14), specific conductance (n = 14), alkalinity (n = 4), and hardness (n = 4) [Numbers in columns with different superscripts had detectable differences at  $\alpha < 0.05$ ].

Ford River Tributary	Application Point Substrate	Water Temp. (°C)	pH (standard units)	Specific Conductance ( $\mu$ S/cm)	Hardness (mg/L as CaCO <sub>3</sub> )	Alkalinity (mg/L as CaCO <sub>3</sub> )
Don Creek (trial one)	Gravel/sand	7.1 <sup>a</sup> (0.8)	8.31 <sup>a</sup> (0.07)	327.4 <sup>a</sup> (1.8)	223.0 <sup>a</sup> (6.2)	213.8 <sup>a</sup> (1.9)
Chuckies Creek	Cobble/rock	4.9 <sup>b</sup> (0.7)	8.15 <sup>b</sup> (0.04)	381.1 <sup>b</sup> (3.4)	258.0 <sup>b</sup> (2.8)	244.0 <sup>b</sup> (0.8)
Don Creek (trial two)	Detritus/sand	5.2 <sup>b</sup> (0.6)	8.15 <sup>b</sup> (0.03)	323.3 <sup>c</sup> (2.0)	219.5 <sup>c</sup> (1.9)	209.3 <sup>c</sup> (1.4)
Jackstraw Creek	Detritus/woody debris/sand	4.7 <sup>b</sup> (0.7)	7.51 <sup>c</sup> (0.03)	147.0 <sup>d</sup> (2.3)	126.0 <sup>d</sup> (4.3)	109.0 <sup>d</sup> (1.4)

**Table 2.** Model-predicted release times of the TFM tablets, mean creek discharge, and the drop in creek discharge observed during the trials from 0 to 12 hours and 0 to 24 hours [Numbers in columns with different superscripts had detectable differences at  $\alpha < 0.05$ ].

Tributary	25% Release (hours)	50% Release (hours)	75% Release (hours)	90% Release (hours)	Mean Discharge (m <sup>3</sup> /s)	Discharge Change 0–12 hours (%)	Discharge Change 0–24 hours (%)
Don Creek (trial one)	2.9	6.5	12.1	17.9	0.0437 <sup>a</sup> (0.0067)	-6.0	-8.3
Chuckies Creek	3.1	6.9	12.2	16.9	0.0163 <sup>b</sup> (0.0019)	-6.3	-10.3
Don Creek (trial two)	3.6	8.1	14.9	21.5	0.0347 <sup>a</sup> (0.0035)	-5.6	-14.4
Jackstraw Creek	3.9	9.0	16.8	25.1	0.0662 <sup>c</sup> (0.0045)	-2.8	-7.7

## DISCUSSION

The profile of TFM release from the tablets was similar among trials and the order to achieve 75% TFM release (fastest to slowest) from the tablets was: Don Creek trial one, Chuckies Creek, Don Creek trial two, and Jackstraw Creek. Divergence of the calculated and predicted amounts of TFM remaining and the incomplete release in the Jackstraw Creek trial indicate that comparisons are more appropriate at the 50 or 75% TFM release level than at the 90% release level.

A replicated laboratory study by Luoma et al. (2020) demonstrated that water temperature influences the release rates of the TFM tablets; however, the laboratory study was completed in waters ranging from 12–20°C and water temperatures during the field applications were considerably colder (4.7–7.1°C). If water temperature was the only factor controlling TFM release, the expected fastest to slowest release order would have been Don Creek trial one, Don Creek trial two, Chuckies Creek, and then Jackstraw Creek. The time to achieve 75% release was 22% longer in Don Creek trial two compared to Chuckies Creek, whereas the temperature was 0.3°C warmer in Don Creek trial two. This provides evidence that water temperature cannot be the only factor that influenced release of TFM from the tablets during the field trials.



While water quality has a well-known influence on TFM toxicity (Hlina et al. 2017, Bills et al. 2003), there is no known relationship among water-quality properties and TFM solubility, which has been reported to be 5,000 mg/L at 25°C (Thingvold and Lee 1981). Although differences were detected for all water-quality properties evaluated, the effect of those differences are likely negligible and there does not appear to be a correlation with the observed release of TFM from the tablets.

Water velocity, which is a factor used to calculate discharge, has been demonstrated to influence the release of TFM from the tablets (Luoma et al. 2020). Therefore, variations in discharge after application could influence TFM release, with decreases in discharge resulting in longer release times. Precipitation prior to our trials resulted in increased discharges which then subsequently decreased during the trials. Discharge decrease ranged from -2.8 to -6.3% during the first 12 hours and -7.7 to -14.4% over the entire 24-hour trial (Table 2). Jackstraw Creek retained the most stable discharge and presumably TFM would have released the fastest in this creek, not the slowest as it did, if change in discharge was a primary factor.

Our Experimental Use Permit waiver limited the number of streams in which we could conduct trials; therefore, we did not have enough replication to statistically compare application point substrate to the release of TFM from the tablets. However, the results demonstrate that substrate was an indicator of TFM release with the most rapid release observed when applications were made on hard substrates. The application points in Chuckies Creek and Don Creek trial one consisted of cobble/rock and gravel/sand, respectively. Chuckies Creek had the second coldest water in which the tablets were applied (4.9°C) and Don Creek trial one had the warmest water in which the tablets were applied (7.1°C) but TFM released considerably faster in both of these trials than in either Don Creek trail two or Jackstraw Creek (i.e. > 1 and 2 hours less time to achieve 50 and 75% release, respectively; Table 2). Detritus containing substrates are often found in lower water velocity depositional areas. Applications in these areas would result in a slower release of TFM from the tablets compared to applications made in higher velocity areas that are typically characterized by harder substrates. Although water velocities were measured to determine stream discharge, they were not measured at each individual application point. Therefore, additional replicated

applications would be needed to confirm that differences in water velocity, as indicated by substrate type, were responsible for observed difference in the release of TFM from the tablets.

This study indicates that TFM tablets appear to have potential for development as a replacement for the TFM bars. Remaining areas of uncertainty include: (1) tablet storage stability, (2) TFM tablet handling durability, and (3) potential challenges associated with mass production (TFM isolation/preparation, high volume coating, coating uniformity, potential changes in TFM release, etc.).

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## **ACKNOWLEDGEMENTS**

Funding for this study was provided by the Great Lakes Fishery Commission. The authors thank peer reviewers for their constructive reviews of earlier versions of this report. A special thanks to the U.S. Fish and Wildlife Staff from the Marquette Biological Station, including Lori Criger, Jesse Haavisto, Sara Ruitter, Justin Oster, Dan Suhonen, and Kevin Hensiak for their invaluable logistical assistance that was essential to the successful completion of these field trials. The authors thank Dr. Jean Adams, Ms. Jillian Hebert and Dr. Richard Erickson for their assistance in analyzing the results from this study. Any use of trade, firm, or product names in this paper is for descriptive purposes only and does not imply endorsement by the U.S. Government.

## **DELIVERABLES**

### *Reports*

Luoma, J.A., Robertson, N. J., Schueller, J.R., Schloesser, N.A., Johnson T.J., Severson T.J., and Meulemans E.K. (2021). Field Evaluation of an Alternate Solid TFM Formulation for Use in Treating Small Tributary Streams. Project completion report submitted to the Great Lakes Fisheries Commission. 20 pp.

### *Presentations*

Luoma (2021). Upper Midwest Environmental Sciences Center Lampricide Formulations Update. Presented at the Lamprey Control Task Force 21-01 virtual meeting. February 09, 2021.

Luoma (2020). Upper Midwest Environmental Sciences Center GLFC Technical Assistance Update. Presented at the Lamprey Control Task Force Standard Operating Procedure virtual meeting. December 08, 2020.

### *Data and Analysis Code*

Schueller, J.R., Schloesser, N.A., and Luoma, J.A., (2021). Data Release: Field Evaluation of an Improved Solid TFM Formulation for Use in Treating Small Tributary Streams. Project completion report

submitted to the Great Lakes Fisheries Commission. U.S. Geological Survey Data Release.  
<https://doi.org/10.5066/P94G3FYW>.

## RESEARCH HIGHLIGHTS

- A tableted TFM formulation containing 66.5% TFM and low regulatory concern inert ingredients was evaluated as a potential replacement for TFM bars using field applications. The release of TFM from the tablets was compared from four independent applications conducted in three small tributaries of the Ford River (Delta County, Michigan). TFM tablets were applied over various substrate types to achieve a target concentration of 1.0 mg/L using the procedures described in the SLCP TOP 015 (Procedures for the Supplemental Application of TFM Bar Formulation), and water samples were collected every 30 minutes for 24 hours and analyzed for TFM content.
- The field study demonstrates that TFM tablets have potential to replace the TFM bars thereby eliminating the discharge of formulated surfactants into the environment and eliminating the need for reformulation due to inert ingredient availability.
- TFM tablets were 50 and 75% depleted in all applications between 6.5–9.0 hours and 12.1–16.8 hours, respectively. TFM concentrations ranged from 0.753 to 1.009 mg/L in water samples collected 0.5 hour after application and 0.060 to 0.199 mg/L in water samples collected 24 hours after application.
- This study demonstrates the potential suitability of the tableted TFM formulation; however, further evaluation may be desired before proceeding with registration and use. Further study objectives could include: (1) determining the storage stability of the tablets, (2) determining the handling durability of the TFM tablets, and (3) critically evaluating any challenges associated with mass production of the TFM tablets (TFM isolation/preparation, high volume coating, coating uniformity, potential changes in TFM release, etc.).