A field analysis of lampricide photodegradation in Great Lakes tributaries

Megan B. McConville,[1] Natan M. Cohen,[2] Shawn M. Nowicki,[3] Stephen R. Lantz,[3]

Jase L. Hixson,[4] Adam S. Ward,[4] and Christina K. Remucal[1,2]*

[1]Environmental Chemistry and Technology Program

University of Wisconsin – Madison

Madison, Wisconsin

[2]Department of Civil and Environmental Engineering

University of Wisconsin – Madison

Madison, Wisconsin

[3]Sea Lamprey Control Program

U.S. Fish & Wildlife Service

Marquette, MI

[4]School of Environmental Affairs

Indiana University

Bloomington, Indiana

Contents (30 pages): Figures: S1-S12, Tables: S1-S10

* Corresponding author address: 660 N. Park St., Madison, WI 53705;
e-mail: remucal@wisc.edu; telephone: (608) 262-1820; fax: (608) 262-0454.

Table of Contents

Section S1. Materials.

Acetonitrile (HPLC grade), methanol (HPLC grade), and formic acid (ACS, 88%) were purchased from Fisher Chemical. 3-Trifluoromethyl-4-nitrophenol (TFM, 99%) and *para*-nitroanisole (PNA, ≥99%) were purchased from Acros Organics. 2',5-Dichloro-4'-nitrosalicylanilide (niclosamide; NIC, ≥98%), 2-chloro-4-nitroaniline (2Cl4NA, 99%), 2-chloro-4-nitrophenol (2Cl4NP, 97%), 4-nitrocatechol (4NCat, 97%), 1,2,4-benzenetriol (4-hydroxycatechol; 4OHCat, 99%), 5-chlorosalicylic acid (5ClSA, 98%), 2-5-dihydroxybenzoic acid (gentisic acid; GA, ≥98%), maleic acid (MA; ≥99%), trifluoroacetic acid (TFA; 99%), benzoic acid (BA; ≥99.0%), 4-hydroxybenzoic acid (4OHBA; 99%), salicylanilide (SAL; 98%), oxyclozanide (OXY; 99.6%), and sodium phosphate dibasic (ACS, ≥99%) were purchased from Sigma Aldrich Co., LLC. Pyridine (≥99%) was purchased from Alfa Aesar. Sodium borate (ultrapure grade) and boric acid (ACS) were purchased from Amresco. Isopropyl alcohol (IPA; HPLC grade, 99.9%) and sodium bromide (NaBr; 99+%) was purchased from Fisher Scientific. The field formulations of TFM include a concentrated liquid (35% active ingredient; AI) and a slow-release chemical bar (23% AI), which were provided by the US Geological Survey Upper Midwest Environmental Sciences Center. All other chemicals were analytical grade from common commercial sources. All chemicals were used as received.

Section S2. Watershed and Stream Characterization.

The general characteristics of the three tributaries assessed in this study are provided in **Table S1**. This data was compiled from the 2015 and 2016 Sea Lamprey Control Annual Reports to the Great Lakes Fishery Commission,[1,2] the Great Lakes Hydrography Dataset,[3] the 2011 National Land Cover Database,[4] and the Great Lakes Aquatic Habitat Framework.[5]

Carpenter Creek, a first order stream, travels through a predominantly forested area before reaching Lake Superior in Grand Marais, MI. The length of chemical treatment spanned 0.8 km and began upstream of a natural three meter high waterfall which prevents sea lamprey migration. Sullivan Creek, a second order stream, is located in Pictured Rocks National Lakeshore. The length of TFM treatment was 1.9 km. The application site is upstream of known sea lamprey inhabited reaches. A thick tree canopy covers both Carpenter and Sullivan Creeks along the treated portion of each stream. Only TFM was applied to Carpenter Creek and Sullivan Creek. The Manistique River is a fifth order tributary and is one of the largest river systems in the upper peninsula of Michigan. The Manistique River watershed drains approximately 3,800 km^2 of land dominated by wetlands and forests. Due to the size of the tributary, canopy cover plays a smaller role in shading the Manistique River from sunlight. The U.S. Fish and Wildlife Service (USFWS) treated approximately 550 km of the Manistique River and its tributaries with a combination of TFM and niclosamide.

Table S1. Tributary length, order, elevation, depth, watershed size and watershed land use of the three field sites.

Parameter		**Carpenter Creek**	**Sullivan Creek**	**Manistique River**	**Reference(s)**
Treated stream length	(km)	0.8	1.9	547	1,2
Total stream length	(km)	NA	3.4	1,356	3,5
Stream order	(-)	1	2	5	3,5
Watershed size	(km^2)	4.1	25.8	3,810	3,5
Measured depth	(m)	0.04-0.15	0.11-0.18	>2	measured in the field
Elevation upstream	(m)	192	219	184	3,5
Elevation downstream	(m)	184	184	177	3,5
Watershed land use	(%)	NA	NA	urban 3.1%, forested 39.1%, agricultural 1.0%, wetland 48.6%	4

Section S3. Record of Climatological Observations.

Climatological data collected by the National Oceanic and Atmospheric Administration (NOAA) is summarized in the tables below. This data includes temperature and precipitation data recorded along the Munising Lakeshore in Munising, MI (Station ID: GHCND:USW00054813; **Table S2**)[6,7] and at the Manistique Wastewater Treatment Plant (WWTP) in Manistique, MI (Station ID: GHCND:USC00205073; **Table S3**).[6,7] Munising is west of Sullivan and Carpenter Creeks; its record demonstrates the significant precipitation that fell June 28 – June 30, 2015 in the region. Due to the size of the Manistique River, climate data from Manistique alone may not fully describe the weather pattern over the full river. Data from Manistique, MI is included here for a general sense of precipitation and temperature data over the lampricide application in September 2016.

Table S2. Precipitation and temperature data collected at the Munising Lakeshore in Munising, MI between June 27, 2015 and July 4, 2015.

Date	Elevation (m)	Latitude	Longitude	Time	Precip. (cm)	Maximum Temp.* (°C)	Minimum Temp.* (°C)
20150627	187	46.417	-86.65	Unk.	0.00	20.5	8.3
20150628					2.31	27.2	13.3
20150629					0.89	27.8	13.3
20150630					1.12	16.7	7.8
20150701					0.00	13.3	7.2
20150702					0.00	22.8	6.7
20150703					0.05	24.4	12.8
20150704					0.00	16.7	11.7

*Temperature maximum and minimum were based on the previous 24 hours; Unk. = unknown

Table S3. Precipitation and temperature data collected at the Manistique WWTP in Manistique, MI between September 22, 2016 and September 29, 2016.

Date	Elevation (m)	Latitude	Longitude	Time	Precip. (cm)	Max. Temp.* (°C)	Min. Temp.* (°C)	Observed Temp. (°C)
20160922	183	45.9512	-86.2513	8:00	0.15	22.2	13.9	14.4
20160923					0.08	20.6	11.7	11.7
20160924					0.00	17.8	8.9	16.1
20160925					0.00	17.8	8.9	16.1
20160926					3.07	18.9	13.9	13.9
20160927					0.05	15.6	11.1	11.7
20160928					0.81	12.8	9.4	10.6
20160929					0.00	18.3	9.4	11.1

*Temperature maximum and minimum were based on the previous 24 hours.

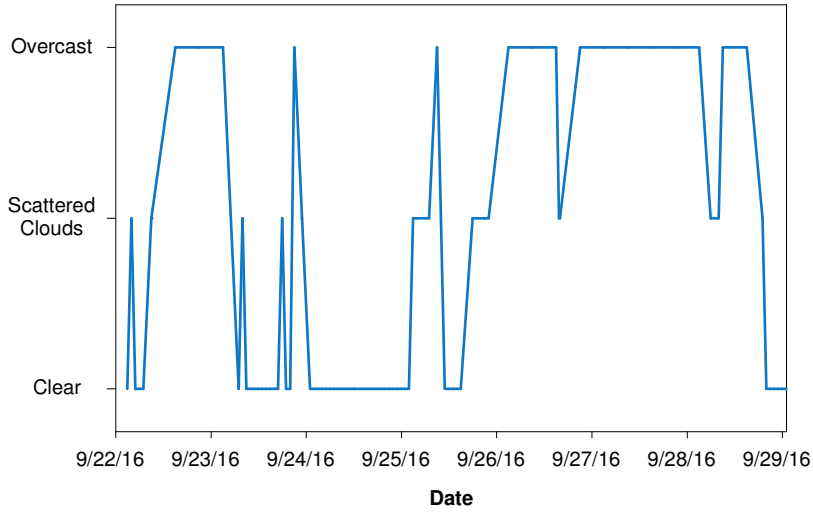

Figure S1. Sky cover observations recorded at Sault Ste. Marie station (latitude: 46.47l; longitude: -84.350) during the lampricide application to the Manistique River. Data collected as part of the National Climatic Data Center Archive.[8]

Section S4. Sample Frequency.

Carpenter and Sullivan Creek TFM Application. Sample collection was coordinated with USFWS during the TFM application to Carpenter Creek on June 30, 2015. As soon as TFM application was initiated by USFWS personnel (8:30), samples were collected every 2 minutes for the first 10 minutes and every 4 minutes for the next 16 minutes at CC1 (See **Figure 1** for sampling

locations). Samples were then collected every half hour to hour during the 11-hour application until the treatment completed. Prior to terminating the application, sample intervals were again increased to every 2 minutes for 14 minutes. Application was terminated at 19:30. A final sample was collected 2 hours after application termination to ensure baseline stream conditions had been achieved. At the most downstream sampling location (CC2), samples were collected every 5 minutes from 9:30-11:30, then extended to every 10 – 30 minutes, and finally each hour until 0:30 the next day. Two 40 mL aliquots of river water were collected at each sampling time and filtered through 0.45 µm nylon in-line filters. The filtered samples were stored in clean, baked 40 mL amber vials with Teflon seals. Samples were kept in ice filled coolers prior to transport to the laboratory, where they were stored in the dark at 4 °C prior to sample analysis.

TFM application to Sullivan Creek began at 7:30 and ended at 18:40 on July 1, 2015. As soon as TFM application was initiated, samples were collected every 2 minutes for the first 20 minutes, every 5 minutes for the next 20 minutes, and then every 15 minutes for a half hour before sample frequency was reduced to hourly measurements. Prior to terminating the application, sample intervals were again increased to every 2 minutes for 30 minutes, followed by decreased sampling frequency. A final sample was collected 2 hours after application termination to ensure baseline stream conditions had been achieved. At the downstream location, samples were collected every 10 minutes from 9:30-11:50, then extended to each hour until 8:00 the next day.

At periodic intervals, the USFWS monitored in-stream TFM concentrations by UV-visible absorbance spectroscopy at the two sampling sites in both Carpenter and Sullivan Creeks to maintain a near constant concentration.[9] Discharge was measured at each site by the USFWS on the day prior to the TFM application using a combination of stage-discharge relationships in conjunction with physically measuring discharge using a velocity meter.[9]

Carpenter and Sullivan Creeks NaBr Applications. Ten kg of NaBr was added to Carpenter Creek on July 2, 2015. The NaBr was mixed in a separate vessel with Carpenter Creek water before being added as a pulse addition at 14:40. Duplicate samples were collected at the most upstream sampling location (CC1) every 20 seconds for the first five minutes, followed by decreased sampling frequency. Rapid sample frequency terminated at 15:12, however a final sample was collected from CC1 at 17:31 to ensure baseline conditions. Duplicate samples collected with an ISCO sampler from site CC2 were collected every five minutes beginning at 15:40. Sample frequency was extended to hourly at 17:40 and hourly samples were collected until 8:40 am the next morning.

Fifteen kg of NaBr was added to Sullivan Creek on July 3, 2015 at 10:27 am. Two initial samples were collected at one minute intervals and then sample frequency increased to every 20 seconds until 10:37. Sample frequency subsequently decreased and three final samples were collected at approximately 11:20, 12:30 and 13:40. Sampling at the furthest downstream location (SC2) began at 12:30, two hours after sample injection. An ISCO automatic sampler was programmed to collect samples every 10 minutes for 24 samples (16:20). Sample frequency was then increased to hourly and terminated at 8:30 on July 4, 2015.

Section S5. Bulk Water Quality Parameters and Discharge Data.

Table S4. Bulk water quality parameters for the three field sites.

Water Quality Parameter		Units	Carpenter Creek	Sullivan Creek	Manistique River*
Alkalinity		mg $CaCO_3$/L	92.35 ± 4.51	76.00 ± 6.34	145.8 ± 7.8
pH		--	7.83 ± 0.04	7.52 ± 0.21	7.49 ± 0.07
TOC		mg C/L	13.54 ± 2.34	19.74 ± 4.94	17.33 ± 0.72
IC			NA	NA	17.20 ± 1.10
TC			NA	NA	34.53 ± 1.23
anions	F^-	ppm	ND	ND	0.08 ± 0.002
	Cl^-		19.74 ± 4.94	0.39 ± 0.00	2.91 ± 0.02
	NO_2^-		1.98 ± 0.12	1.89 ± 0.16	ND
	NO_3^-		0.08 ± 0.11	ND	0.06 ± 0.00
	SO_4^{2-}		3.24 ± 0.85	3.87 ± 0.33	19.26 ± 0.06
cations	Ca	ppm	25.12 ± 2.64	23.84 ± 1.93	34.24 ± 0.95
	Fe		NA	NA	1.16 ± 0.17
	K		0.94 ± 0.19	0.34 ± 0.06	1.09 ± 0.14
	Mg		ND	ND	7.52 ± 0.40
	Na		7.83 ± 1.19	0.48 ± 0.08	3.04 ± 0.19

*Collected from M3 prior to lampricide block. NA indicates that the data is not available. ND indicates that the concentration was below the instrumental detection limit.

Table S5. Discharge data for Carpenter and Sullivan Creeks.

Tributary	Location	Date	Stream Width (m)	Total Discharge (m^3 s^{-1})	Total Area (m^2)	Mean Depth (m)
Carpenter Creek	CC1	7/2/2015	2.8	0.022	0.116	0.041
	CC2	7/2/2015	2.7	0.032	0.402	0.149
Sullivan Creek	CC1	7/3/2016	3.0	0.097	0.55	0.183
	CC2	7/3/2016	2.0	0.095	0.228	0.114

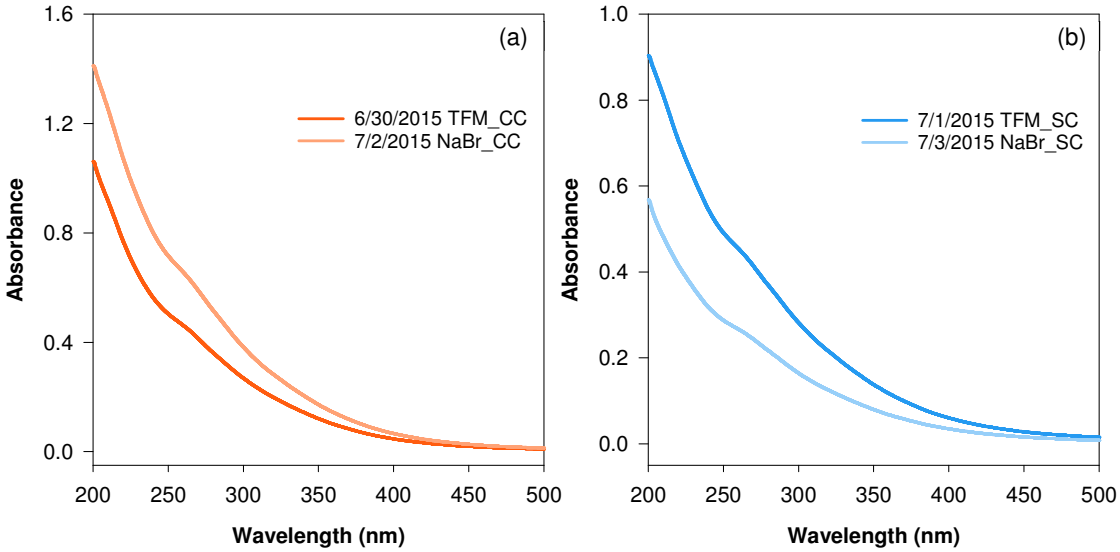

Figure S2. UV-visible absorption spectra of bulk samples collected in (a) Carpenter Creek and (b) Sullivan Creek.

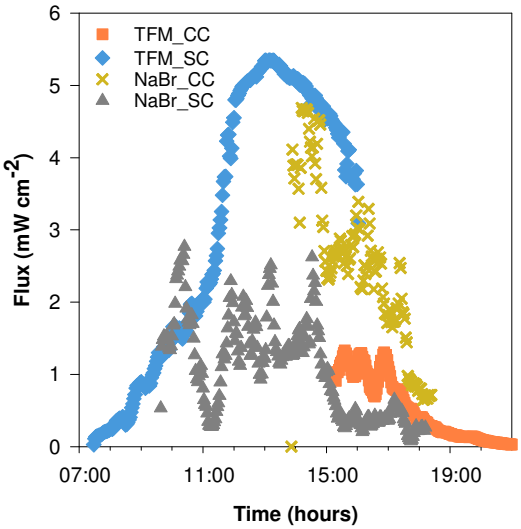

Figure S3. Radiometer profiles during the application of TFM and NaBr to Carpenter and Sullivan Creeks summed over the wavelength range 290 400 nm (UVA and UVB light).

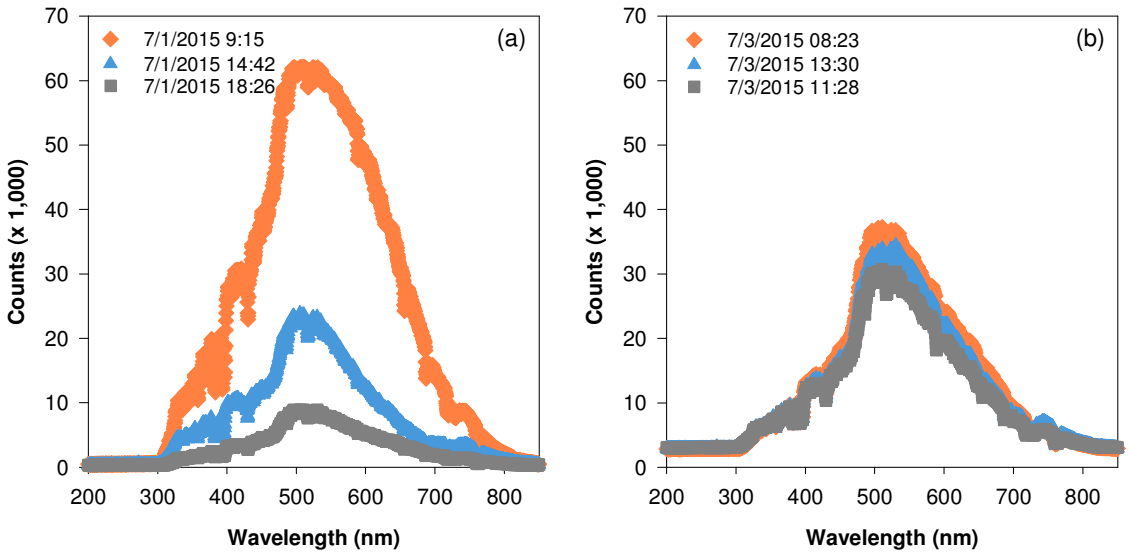

Figure S4. Spectrophotometer data collected during lampricide application to (a) Carpenter Creek and (b) Sullivan Creek.

Table S6. Sonde data collected for Carpenter Creek. Parameters include temperature, conductivity, optical dissolved oxygen, fluorescent dissolved organic matter (FDOM; measured in quinine sulfate units), pH, oxygen reduction potential (ORP), and chlorophyll-a (Chl-a). CC1 = Furthest upstream sampling location for Carpenter Creek, CC2 = Furthest downstream sampling location for Carpenter Creek.

Date	ID	Chemical Added	Temp (°C)	Cond (µS/cm)	ODO (mg/L)	fDOM (QSU)	pH	ORP (mV)	Chl-a (µg/L)
6/30/2015	CC1	TFM	12.01	184.7	10.65	185.3	7.86	129.0	2.32
6/30/2015	CC2	TFM	10.70	178.4	10.82	129.7	7.83	163.2	3.94
7/2/2015	CC1	NaBr	12.15	177.2	10.62	246.4	8.21	130.0	5.52
7/2/2015 - 7/3/2015	CC2	NaBr	12.39	162.2	10.65	270.5	7.79	198.2	3.42

Table S7. Sonde data collected for Sullivan Creek. Parameters include temperature, conductivity, optical dissolved oxygen, fluorescent dissolved organic matter, pH, oxygen reduction potential, and chlorophyll-a. SC1 = Furthest upstream sampling location for Sullivan Creek, SC2 = Furthest downstream sampling location for Sullivan Creek.

Date	ID	Chemical Added	Temp (°C)	Cond (µS/cm)	ODO (mg/L)	fDOM (QSU)	pH	ORP (mV)	Chl-a (µg/L)
7/1/2015	SC1	TFM	13.12	118.7	9.72	72.5	7.29	99.9	2.80
7/1/2015 - 7/2/2015	SC2	TFM	11.61	100.6	11.00	115.5	7.65	176.8	2.16
7/3/2015	SC1	NaBr	15.06	152.6	9.29	91.9	7.40	49.2	0.02
7/3/2015 - 7/4/2015	SC2	NaBr	14.38	124.4	10.21	124.0	7.74	188.3	0.24

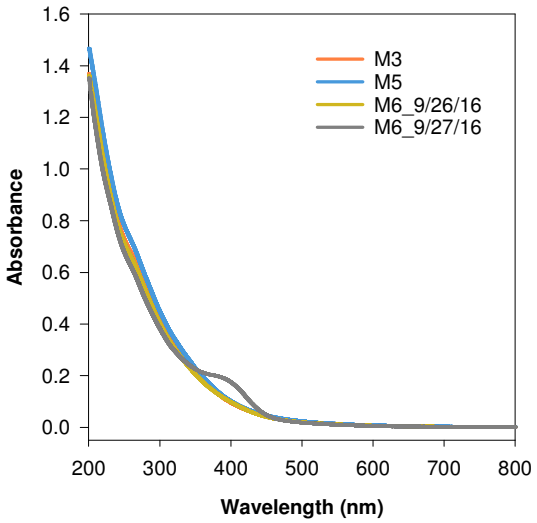

Figure S5. UV-visible absorption spectra of bulk samples collected in the Manistique River from sites M3, M5, and M6. The M6 sample collected on 9/27/16 was collected during the lampricide block, resulting in evidence of TFM absorbance in the spectra.

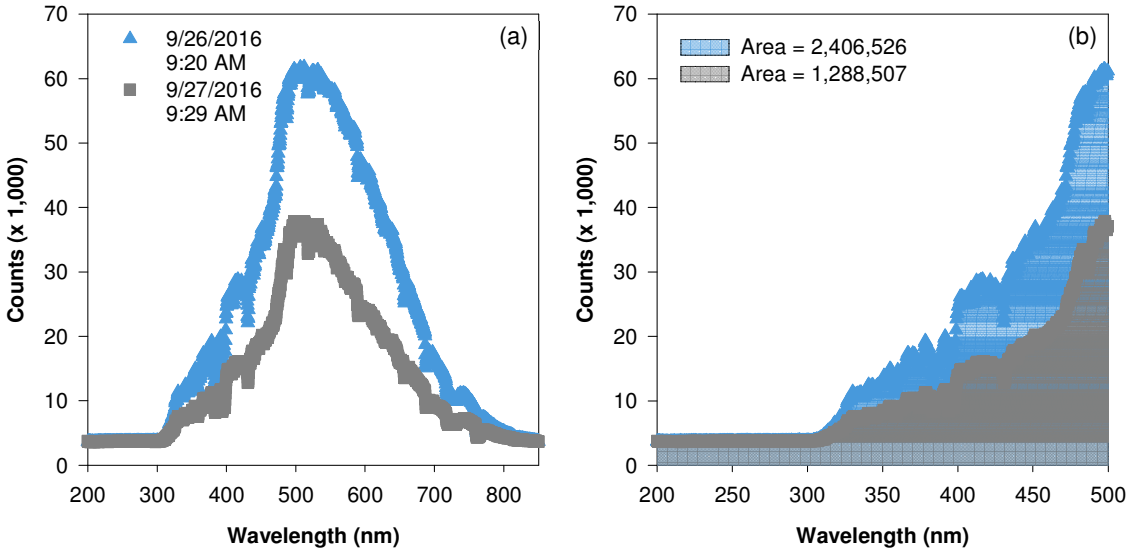

Figure S6. (a) Spectrophotometer data collected during lampricide application to the Manistique River. (b) Integrated spectrophotometer area (from 178 – 450 nm) used to quantitatively compare irradiation spectra. The area is presented in counts x wavelength.

Table S8. Representative baseline sonde data collected for the Manistique River. Parameters include temperature, conductivity, optical dissolved oxygen, pH, turbidity (measured in formazin nephelometric units, FNU), chlorophyll-a, and fluorescent dissolved organic matter.

Location	Temp (°C)	Conductivity (µS/cm)	ODO (mg/L)	pH	Turbidity (FNU)	Chl-a (µg/L)	FDOM (QSU)
M3	15.1	164.1	9.18	7.50	6.51	5.00	123.9
M5	15.1	158.9	8.88	7.41	6.98	5.40	132.6
M6	16.0	163.5	8.95	7.55	5.37	5.10	136.8
Average	15.4	162.2	9.00	7.49	6.29	5.17	131.1

Section S6. Analytical Methods.

HPLC and LC-MS/MS Analysis. High performance liquid chromatography (HPLC), liquid chromatography-tandem mass spectrometry (LC-MS/MS), and ion chromatography (IC) were used to analyze the samples collected during this study. HPLC analyses were performed with an Agilent 1260 instrument equipped with a diode array detector (Model 1260 DAD). The concentrations of TFM and *para*-nitroanisole were quantified by HPLC as described previously.[10] LC-MS/MS analyses were performed with an Agilent 1260 HPLC equipped with a 6460 triple

quadrupole mass spectrometer. Niclosamide, 5-chlorosalicylic acid, 2-chloro-4-nitroaniline, 2-chloro-4-nitrophenol, and 4-nitrocatechol were quantified using a previously published method.[10] Benzoic acid (BA), 4-hydroxybenzoic acid (4OHBA), gentisic acid, 4-hydroxycatechol, maleic acid, and trifluoroacetic acid were quantified according to LC-MS/MS method included below.

Quantification of benzoic acid, 4-hydroxybenzoic acid, and TFM organic photoproducts

Column:	Agilent Poroshell 120 Bonus RP (2.1 x 50 mm, 2.7 µm)		
Guard column:	Agilent Poroshell 120 Bonus RP (3.0 x 5 mm, 2.7 µm)		
Injection volume:	20 µL		
Mobile phase:	A: 0.1% Formic Acid, 10% acetonitrile in 18.2 MΩ·cm water		
	B: 100% Acetonitrile		
Flowrate:	0.25 mL/min		
Column temperature:	30 °C		
Gradient:	Time (minutes)	% Solvent A	% Solvent B
	0.00	100	0
	1.00	100	0
	4.00	20	80
	6.00	20	80
	6.10	100	0
Scan time:	1.5-12 minutes (12-minute duration)		
Polarity:	Negative (all except MA) & Positive (MA)		
Dwell time/transition:	70		
Cell accelerator voltage:	4		
Scan type:	MRM		
Source gas temperature:	300 °C		
Gas flow rate:	7 L/min		
Nebulizer pressure:	45 psi		
Sheath gas temperature:	350 °C		
Sheath gas flow rate:	10 L/min		
Cell accelerator voltage:	4		
Ionization mode:	Electrospray ionization		

Target Analyte	Precursor Ion	Product Ion	Fragmentor Voltage	Collision Energy Voltage	Retention Time (min)
4OHCat	125	95.1	130	10	1.79
		51.1	130	20	1.79
4OHBA	137.1	93.1	85	15	3.25
		65.1	85	40	3.25
MA	115	117	46	0	5.58
		99	46	8	5.58
		45.1	46	44	5.58
BA	121.1	121.1	85	0	6.25
		77.1	85	10	6.25

GA	153	108	105	24	6.75
		53.1	105	25	6.75
TFM	206	160	40	12	7.93
		176	40	16	7.93
TFA	113	69.1	50	7	9.12
		45.2	50	7	9.12

Table S9. HPLC and LC-MS/MS detection limits.

Compound	**Instrument**	**Limit of Detection**	
		(µM)	**(nM)**
TFM	HPLC	0.033	33.3
2Cl4NP		0.012	11.8
GA		0.029	29.4
NIC	LC-MS/MS	0.0007	0.7
5ClSA		0.022	22.0
2Cl4NA		0.0018	1.8
4NCat		0.14	140.8
4OHCat		0.12	118.8
GA		0.031	31.4
MA		0.060	59.9
TFA		0.024	23.9
BA		0.22	219.5
4OHBA		0.011	10.6

IC Analysis. Three ion chromatography (IC) methods were used to quantify anions and cations using a Dionex IC system (model ICS-2100). IC Method 1 was used to quantify the bromide concentration during the application of NaBr to Carpenter and Sullivan Creeks. IC Method 2 was used to quantify sodium, ammonium, potassium, magnesium, and calcium. Finally, IC Method 3 was used to quantify fluoride, chloride, nitrite, sulfate, nitrate and phosphate.

IC Method 1: Bromide Analysis.

Column:	Dionex IonPac AS11-HC RFIC™ 4 x 250 mm analytical column
Guard column:	Dionex IonPac AG11 RFIC™ 4 x 50 mm guard column
Gradient:	Isocratic
Flow rate:	0.5 mL/min
Mobile phase composition:	15 mM NaOH, in Milli-Q water
Pressure limits:	200-3000 psi
Sampler delivery speed:	4.0 mL/min
Flush factor:	3
Column temperature:	30 °C
Cell temperature:	30 °C
Suppressor:	ASRS_4mm
Suppressor voltage:	50 mA
Method duration:	30 min

Target Analyte	Retention Time (min)
Bromide	20.4

IC Method 2: Cation Analysis.

Column:	Dionex IonPac CS12A-HC RFIC™ 4 x 250 mm analytical column
Guard column:	Dionex IonPac CS12 RFIC™ 4 x 50 mm guard column
Gradient:	Isocratic
Flow rate:	0.75 mL/min
Mobile phase composition:	20 mM NaOH, in Milli-Q water
Pressure limits:	200-3000 psi
Sampler delivery speed:	4.0 mL/min
Flush factor:	3
Column temperature:	30 °C
Cell temperature:	30 °C
Suppressor:	ASRS_4mm
Suppressor voltage:	50 mA
Method duration:	25 min

Target Analyte	Retention Time (min)
Sodium	6.2
Ammonium	6.9
Potassium	8.2
Magnesium	12.9
Calcium	15.4

IC Method 3: Anion Analysis.

Column:	Dionex IonPac AS11-HC RFIC^{TM} 4 x 250 mm analytical column
Guard column:	Dionex IonPac AG11 RFIC^{TM} 4 x 50 mm guard column
Gradient:	Isocratic
Flow rate:	1.0 mL/min
Mobile phase composition:	30 mM NaOH, in Milli-Q water
Pressure limits:	200-3000 psi
Sampler delivery speed:	4.0 mL/min
Flush factor:	3
Column temperature:	30 °C
Cell temperature:	30 °C
Suppressor:	ASRS_4mm
Suppressor voltage:	65 mA
Method duration:	20 min

Target Analyte	Retention Time (min)
Fluoride	3.1
Chloride	4.2
Nitrite	4.7
Sulfate	5.8
Nitrate	7.1
Phosphate	12.1

TOC Analysis. Total organic carbon (TOC) analysis was performed using a General Electric membrane conductometric Sievers carbon analyzer (Model: M5310C). The total carbon (TC), inorganic carbon (IC), and organic carbon concentrations (TOC) are analyzed according to the following method. Check standards were analyzed in conjunction with the river water samples. Reported check standard concentrations were generally within 2.0% of the known value.

Membrane:	Sievers Selective Membrane
Oxidizer:	15 % ammonium persulfate
Acid:	6 M phosphoric acid solution
Sample flow rate:	0.5 mL/min
Acid & oxidizer flow rates:	Auto reagent method. An initial sample is passed through the unit to set the acid and oxidizer flow rates.
Range acid flow rate:	0.3-2.0 µL/min
Range oxidizer flow rate:	0.0-3.9 µL/min
Samples/analysis:	4 reps, 1 reject
Flush time:	240 seconds
Sample pressure:	100 psig
Method duration:	27 min

Section S7. Solid Phase Extraction.

Selected samples collected from the Manistique River were concentrated using solid phase extraction (SPE) to verify that TFM photoproducts were not present at concentrations below the LC-MS/MS detection limit. Benzoic acid and 4-hydroxybenzoic acid were used as internal standards because they are structurally similar to gentisic acid, the major TFM photoproduct. Two side-by-side comparisons were made. First, a control experiment was conducted to test the target compounds and assess internal standard recovery. In the control experiment, a 250 mL sample of water collected at site M3 prior to the chemical block was spiked with TFM, GA, 4OHCat, MA, BA, and 4OHBA (spiked concentration = 0.1 μM of each chemical). Second, 250 mL of the bulk sample collected at M6 during the lampricide block was spiked with only the internal standards (i.e., BA and 4OHBA). This location was chosen as it was most likely to contain the highest concentration of photoproducts.

The spiked samples were extracted and concentrated by SPE following a published method.[11] Briefly, the samples were acidified to pH 2 using 1 M HCl. The SPE cartridges (Agilent Bond Elut-PPL cartridges; 500 mg, 6 mL) were cleaned using 5 mL of methanol. 250 mL of each sample was passed through a prepared column at a flow rate of approximately 4-5 drops per second. A 1 mL solution of 0.01 M HCl was used to wash the column, and the sample was eluted in 5 mL of methanol. Triplicate analysis was performed for TFM, its known organic photoproducts, and the two internal standards by LC-MS/MS.

The concentration of TFM in the methanol eluent of the spike control was 4.83 ± 0.71 μM, corresponding to a concentration factor of 48.3. This demonstrates that TFM was well retained using this method given that the maximum concentration factor is 50 (i.e., 5 mL methanol vs. 250 mL of sample). The recovery of the internal standards was similar in both samples, with

concentration factors of 5.2 – 6.1 for BA and 8.6 – 9.1 for 4OHBA. Similarly, the concentration factors of GA and 4OHCat were 1.8 and 3.0 for the spike control. While the recoveries of the internal standards, GA, and 4OHCat were lower than TFM, the four compounds were retained and concentrated on the SPE cartridges. In contrast, MA was not retained on the SPE cartridge and had a concentration factor of 0.6 in the spike control. None of the photoproducts were detected in the concentrated bulk M6 sample collected during the lampricide block. Given the low LC-MS/MS detection limits (**Table S9**) and the absence of inorganic photoproducts, no additional efforts were made to further optimize the SPE method for improved concentration of the relatively polar TFM photoproducts.

Section S8. Laboratory Photochemical Experiments.

A series of laboratory confirmation experiments were conducted using a Rayonet photoreactor with fixed-wavelength bulbs (365 ± 9 nm) and a 450 W Xe lamp (627NS, Newport Corporation) equipped with an Oriel Company 59450 filter to cut off light below 290 nm. The Rayonet reactor was used to enable comparison with previously published data,[10] while the Xe lamp was used because its spectrum is more similar to sunlight. A chemical actinometer (10 µM *p*-PNA in 1,000 µM pyridine) was used to monitor light intensity.[12,13]

First, the direct photodegradation rates of pure TFM (purchased from Sigma Aldrich) were compared to TFM chemical formulations used by USFWS in the field (**Figure S7**). These experiments were carried out at pH 5, 7, and 9, which bracket the pK_a of TFM (6.38 ± 0.02).[10] Second, water samples collected from the Manistique River were irradiated in the laboratory to assess the susceptibility of TFM to indirect photodegradation. Bulk river water collected at M6 during the lampricide application contained 7.2 µM TFM. The M6 sample and a direct control (7.2 µM TFM in 5 mM borate buffer at pH 7.8) were irradiated using the Xe lamp over 5 hours (**Figure**

S8). Finally, a similar experiment was repeated for niclosamide. River water collected at M6 (0.04 µM niclosamide) and a direct control (1.0 µM niclosamide in 5 mM borate buffer at pH 7.8) were irradiated in the Rayonet photoreactor for 25 hours (**Figure S9**).

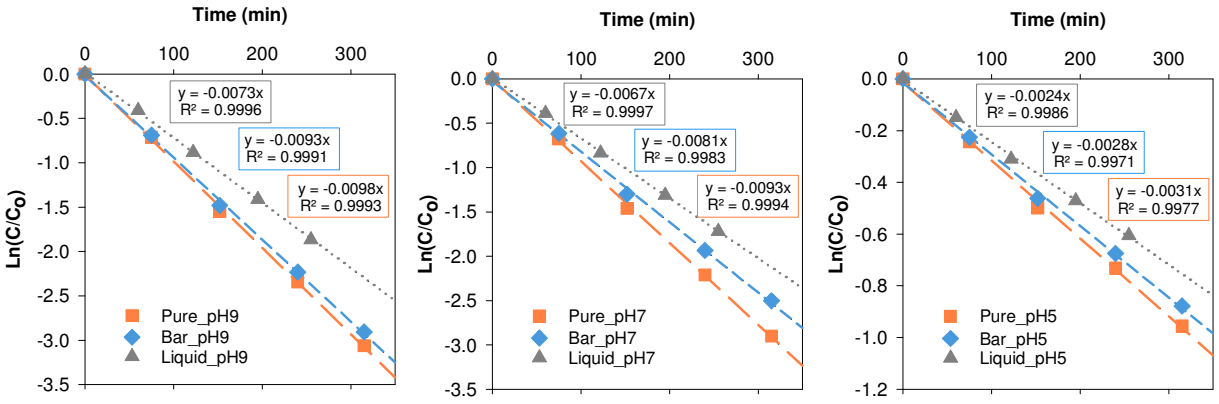

Figure S7. Direct photodegradation of TFM using the pure chemical, the concentrated liquid formulation, and a solid formulation designed for slow release (TFM bar) at (a) pH 9, (b) pH 7, and (c) pH 5. Experiments were conducted using 365 nm bulbs in a Rayonet photoreactor. Dashed lines indicate linear fits to the data assuming first-order kinetics.

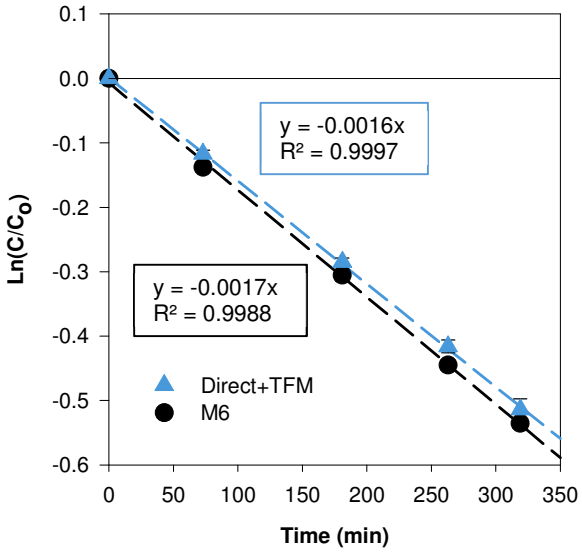

Figure S8. Observed photodegradation of TFM in Manistique River water (M6) and 5 mM borate (Direct + TFM). Both samples contained 7.2 µM TFM and had a pH value of 7.8. Experiments were conducted using the 450 W Xe lamp. Dashed lines indicate linear fits to the data assuming first-order kinetics.

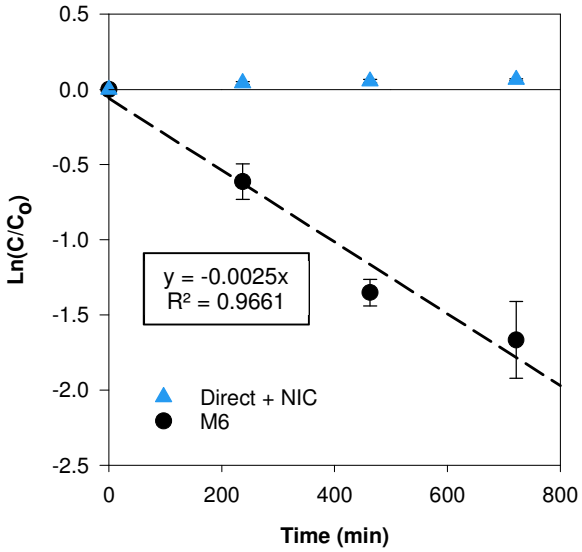

Figure S9. Niclosamide photodegradation profiles of laboratory irradiated samples collected at M6 (0.04 µM niclosamide) and a direct degradation control (1.0 µM added niclosamide) at pH 7.8. Experiments were conducted using 365 nm bulbs in a Rayonet photoreactor. Dashed lines indicate linear fits to the data assuming first-order kinetics.

Section S9. Calculations and Modeling.

Calculation of Bromide and TFM losses and Chemical Water Exchange with Groundwater. Using the measured discharge and in-stream solute tracer concentration time series, we estimated losses of the injected mass and exchange flows between the main channel and transient storage locations.[14] For clarification, in this section the upstream site refers to locations CC1 and SC1 where samples were collected 20-50 m downstream of the chemical application site. Similarly, the use of downstream site refers to sampling locations CC2 and SC2 which are located near the river mouth. First, the solute mass observed at a monitoring location (M) can be calculated as:

$$M = \int_{t=0}^{t=t_{final}} Q(t)C(t)dt \quad (1)$$

where Q is stream discharge, C is solute concentration, and t_{final} is the time the last sample was collected, when in-stream concentration returned to pre-injection levels. For bromide, the injection mass was recorded when the injectate was mixed at the upstream location (MU). The mass

recovered at the downstream end (MD) was calculated using the downstream discharge and concentration time series. Using the upstream and downstream masses (i.e. MU and MD), we calculated mass loss as $M_{loss} = MU - MD$.

Using the observed discharges, we calculated the net gain or loss of stream water as $Q_{net} = QD - QU$. The gross loss of water from the stream (Q_{loss}) can be bounded by the values:

$$Q_{loss,min} = \frac{M_{loss}}{\int_{t=0}^{t=t_{final}} C_U(t)dt} \quad (2)$$

$$Q_{loss,max} = \frac{M_{loss}}{\int_{t=0}^{t=t_{final}} C_D(t)dt} \quad (3)$$

The minimum loss case ($Q_{loss,min}$) represents the condition where all loss would occur before dilution (i.e., assumes all losses occur before all gains and therefore represents the loss of the most concentrated water), while the maximum loss case ($Q_{loss,max}$) reflect all dilution occurs before loss (i.e., all gains occur before all losses and therefore represents the loss of the least concentrated water). Given Q_{net} and Q_{loss}, the gross gains of water can be calculated as $Q_{gain,min} = Q_{net} - Q_{loss,min}$ and $Q_{gain,max} = Q_{net} - Q_{loss,max}$. These calculations acknowledge that the net exchange of water and solute between the stream channel and groundwater system are bi-directional, and that gross fluxes are larger than observed net fluxes which only consider the net gain or loss. One important criteria for these estimates is that bromide moves as an inert tracer in the system and is not expected to degrade biologically or photochemically.

For TFM, the injected mass was calculated using the upstream discharge and concentration time series. The recovered mass was calculated using the downstream discharge and concentration time series. Mass losses for TFM were calculated based on the injected and recovered masses. Water balances were not calculated for TFM because this solute is not expected to be conservative.

Table S10. Calculated TFM and bromide mass losses and channel water-groundwater exchange rates.

Modeling parameters	Carpenter Creek		Sullivan Creek	
	TFM	Bromide	TFM	Bromide
Q_{net} (m^3 s^{-1})	0.0000	0.0100	0.0000	-0.0020
MU (µmol or g)	12.28	10,000	92.17	15,000
MD (µmol or g)	8.14	6,967.2	74.79	10,650.5
M_{loss} (µmol or g)	-8.57E+04	-3.03E+03	-4.22E+03	-4.35E+03
$M_{loss,percent}$	-0.3400	-0.3033	-0.1886	-0.2900
$Q_{loss,min}$ (m^3 s^{-1})	NA†	-0.0266	NA†	-0.0284
$Q_{loss,max}$ (m^3 s^{-1})	NA†	-0.0139	NA†	-0.0388
$Q_{gain,min}$ (m^3 s^{-1})	NA†	0.0366	NA†	0.0264
$Q_{gain,max}$ (m^3 s^{-1})	NA†	0.0239	NA†	0.0368
QU (m^3 s^{-1})	0.0140‡	0.0220	0.1600‡	0.0970
QD (m^3 s^{-1})	0.0140‡	0.0320	0.1600‡	0.0950

†Water balances were not calculated for TFM because it is not expected to be conservative.
‡Discharge rates in Carpenter and Sullivan Creeks were determined from USFWS observations. In Carpenter Creek USFWS reported discharge rates of 0.014 m^3 s^{-1} (0.5 ft^3 s^{-1}) at both sampling locations. In Sullivan Creek USFWS reported discharge rates of 0.16 m^3 s^{-1} (5.5 ft^3 s^{-1}) at both sampling sites.

Legend:
Q_{net} = the net gain or loss of stream water, calculated as $Q_{net} = QD - QU$ (m^3 s^{-1})
MU = mass of TFM (µmol) or Br^-(g) measured at the upstream location (CC1, SC1)
MD = mass of TFM (µmol) or Br^-(g) measured at the downstream location (CC2, SC2)
M_{loss} = mass loss of TFM (µmol) or Br^-(g) between the two sampling locations
$M_{loss,percent}$ = mass loss between the two sampling locations (as fraction of input, e.g., -0.3 is equivalent to a 30% loss)
$Q_{loss,min}$ = minimum gross loss of water from the channel (assumes all losses occur before all gains, meaning loss of the most concentrated water; m^3 s^{-1})
$Q_{loss,max}$ = maximum gross loss of water to the channel (assumes all gains occur before all losses, meaning loss of the least concentrated water; m^3 s^{-1})
$Q_{gain,min}$ = minimum gross gains, calculated from water balance of Q_{net} and $Q_{loss,min}$ (m^3 s^{-1})
$Q_{gain,max}$ = maximum gross gains, calculated from water balance of Q_{net} and $Q_{loss,max}$ (m^3 s^{-1})
QU = discharge at upstream end of study reach (m^3 s^{-1}) (CC1, SC1)
QD = discharge at upstream end of study reach (m^3 s^{-1}) (CC2, SC2)

Incorporating Field Parameters into Rate Predictions for the Manistique River. The Simple Model of the Atmospheric Radiative Transfer of Sunshine (SMARTS; Version 2.9.5) was used to model the spectral properties of natural sunlight in this study.[15] Initial TFM half-life calculations were based on the modeled, cloud free actinic spectrum from August 1, 2015 in Madison, WI, as described previously.[10] This calculation was adapted to more closely match the conditions of the lampricide application by modeling solar intensity for Manistique, MI (45.9578° N, -86.2463° W) for each hour from sunrise to sunset (8 am – 7 pm) on September 26, 2016. The resulting difference in light intensity is presented in **Figure S10**.

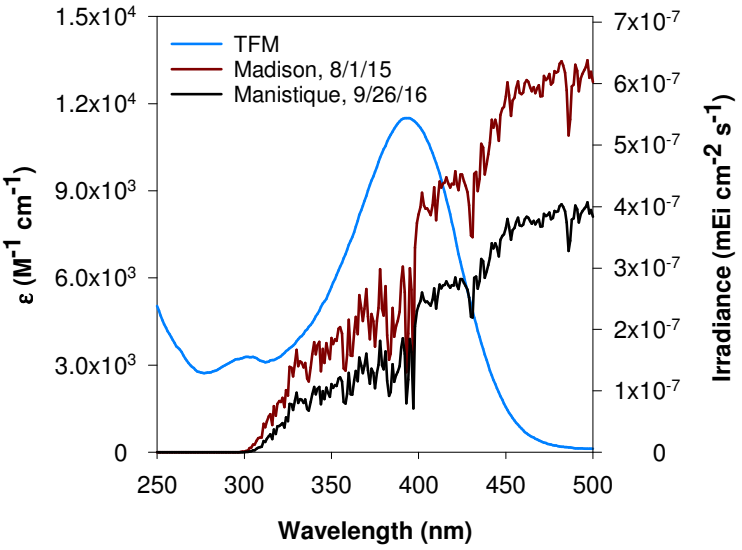

Figure S10. Comparison of the molar extinction coefficient (**ε**) of TFM at pH 8 and the modeled solar irradiance for Madison, WI (August 1, 2015) and Manistique, MI (September 26, 2016) at noon.

The global horizontal irradiance generated by SMARTS was combined with UV-vis absorbance data to calculate the rate of light absorbance for both TFM and niclosamide under sunlight irradiation. The rate of light absorbance was combined with the previously published TFM quantum yield (pH 8)[10] to predict the direct photodegradation rate and half-life of TFM exposed to natural sunlight. The observed degradation rate was calculated at each depth by varying path

length from 1 cm to 200 cm. These calculations are described in detail in our previous publication.[10]

We conducted additional calculations to assess the impact of location, pH, TFM concentration, application time, and water depth on TFM photodegradation rates under conditions that could occur within sea lamprey-infested tributaries of the Great Lakes. To emphasize the range of predicted TFM half-lives two extreme latitudes were chosen: Burns Ditch (located at the southern tip of Lake Michigan) and Nipigon River (northernmost Lake Superior tributary). The pH (pH 6-9), concentration (5 μM and 30 μM), application time (July 1 vs. Oct 15), and depth (surface, 20 cm, 1 m and 2 m) were varied to demonstrate the range in predicted degradation rates and lifetimes (**Figure S11**).

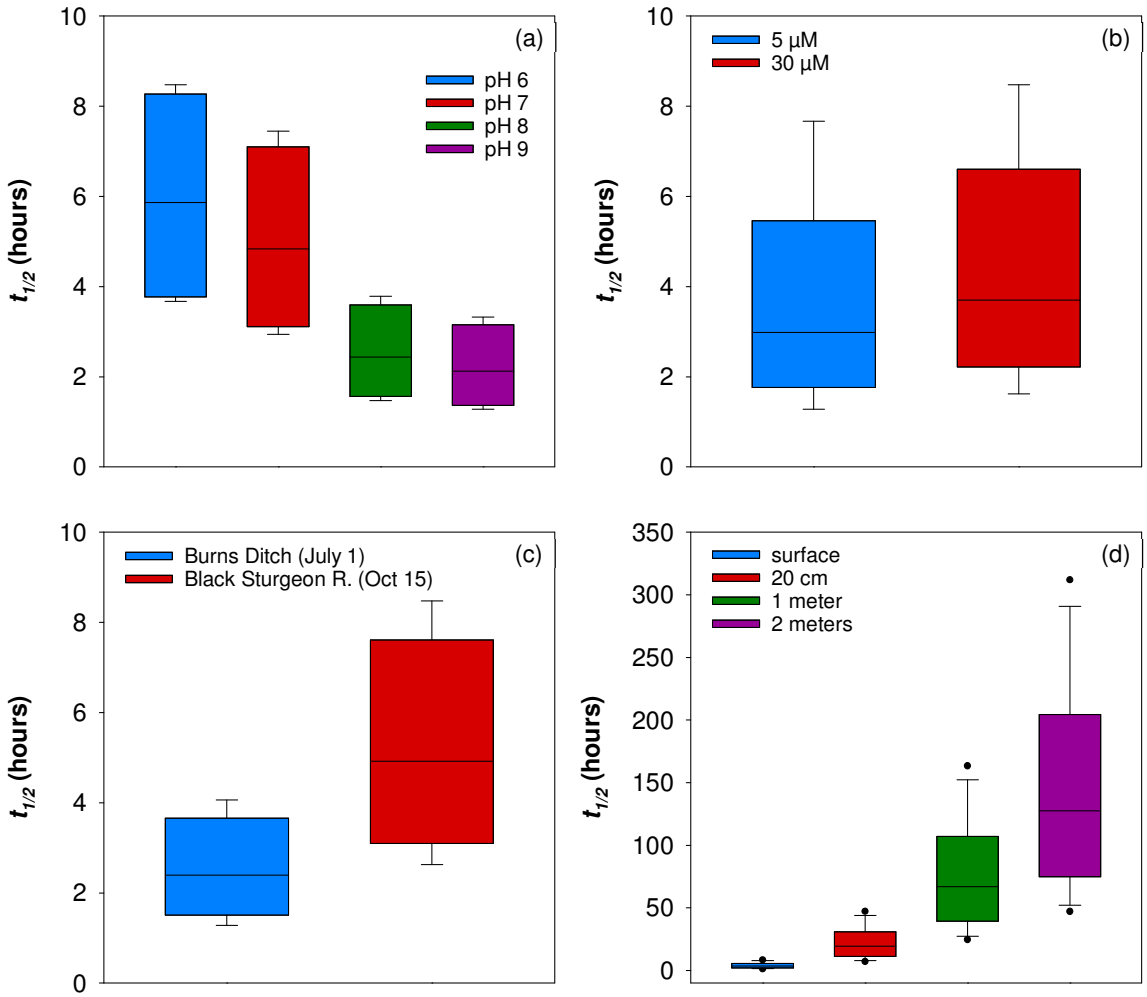

Figure S11. Influence of (a) pH, (b) concentration, (c) location and time of year, and (d) depth on predicted degradation rates and half-lives of TFM across extreme conditions. Box midlines represent the median concentrations, top and bottom edges of the boxes denote the interquartile range, and whiskers denote the 10th and 90th percentiles. All observations <10% or >90% (i.e., outliers) are plotted individually.

Predicted Photodegradation Rate Calculations Across US Tributaries. The maximum photodegradation potential in all US tributaries treated with lampricides in 2015 and 2016 was calculated by combining hydrologic data and modeled solar intensity with the quantum yield and UV-vis absorbance spectra of TFM. Data available from USFWS was used to calculate the estimated depth, width, and chemical residence time in all US tributaries treated in 2015 and

2016.[1,2] USFWS data included tributary name, application date, latitude, longitude, distance of the longest reach (l), and stream discharge (Q). Hydraulic geometries were employed to estimate stream width and depth according to the following two equations:

$$w = aQ^b \quad (4)$$

$$d = cQ^f \quad (5)$$

where width (w) and depth (d) can be described by stream discharge (Q) and several exponents or coefficients (a, b, c, and f) that can be derived from physical characteristics or calculated empirically.[16] Miller *et. al.* applied these fundamental equations to the Mississippi River, identifying values for a, b, c, and f that apply to the Mississippi basin.[17] Because the geography of the Great Lakes region is relatively similar to the Mississippi watershed, the values identified for the Mississippi basin (a = 13.4, b = 0.46, c = 0.18, and f = 0.47) were used to approximate the average width and depth of all US Great Lake tributaries treated in 2015 and 2016 for lampricides. Velocity was calculated by dividing Q by the cross-sectional area (A = w * d). Finally, stream residence time (Θ) was estimated by dividing the river volume (V, where V = l * w * d) by the flow rate, Q (i.e. Θ = V/Q).

The depth-integrated TFM photodegradation rates were then calculated in each tributary using three approaches. First, the maximum possible photodegradation rate was calculated using solar intensity data from the Galien River on June 4, 2016. This river is a tributary of southern Lake Michigan and represents the maximum solar intensity for all systems treated in 2015 and 2016. The photodegradation rate was integrated over the average depth of each tributary to produce the depth-integrated photodegradation rate (k), and the percent of expected loss due to light was calculated according to the following equation assuming first-order kinetics:

$$\%\ \text{loss}_{photodegradation} = (1\text{-}e^{-k\Theta}) \cdot 100 \quad (6)$$

where Θ is the stream residence time calculated using hydraulic geometries. This calculation also assumes that the block of lampricides can be represented by a plug flow reactor, which assumes the lampricides and stream water move uniformly downstream. This photodegradation loss rate represents the maximum theoretical TFM loss possible in each tributary due to sunlight and was used to screen out tributaries with conditions that were not amenable for TFM photolysis.

Second, tributaries that had an expected percent loss greater than 50% using the maximum solar intensity data from the Galien River were further analyzed. 42 of 76 tributaries in 2015 and 31 of 63 tributaries in 2016 met this requirement. The depth-integrated photodegradation rate was modified using modeled hourly solar intensity data for the individual application location and date as described in the manuscript for the Manistique River. The scaled degradation rates over the residence time of the chemical in each tributary were used to calculate an average photodegradation rate. This rate, combined with the residence time, was then used in **equation 6** to determine a tributary-specific estimated percent loss due to photodegradation.

Finally, the TFM photodegradation rates in the remaining 67 tributaries (i.e., those with <50% expected loss using the maximum solar intensity data) was adjusted using SMARTS data for noon on September 26, 2016 in Manistique, MI, rather than June 4, 2016 in the Galien River. The percentage loss due to photodegradation ranged from 1.1 – 30.1% using the Manistique data (mean, 13.6%) and 2.1 – 49.5% using the Galien River data (mean, 24.2%). Therefore, even under ideal, noontime conditions, minimal photolysis of TFM is expected in these 67 tributaries due to their short hydraulic retention times and/or large depths. For further comparison, the percentage loss due to photodegradation calculated using the site-specific solar intensity adjusted for diurnal variability in the 73 tributaries was compared to the percentage loss calculated using continuous noon-time solar intensity from Manistique, MI. In nearly all cases, the percent loss due to

photolysis calculated in the 73 systems using site-specific data was smaller than the percent loss calculated using the Manistique, MI solar intensity data. Therefore, using the percent loss calculated using the Manistique, MI data for the remaining 67 systems is a reasonable conservative assumption.

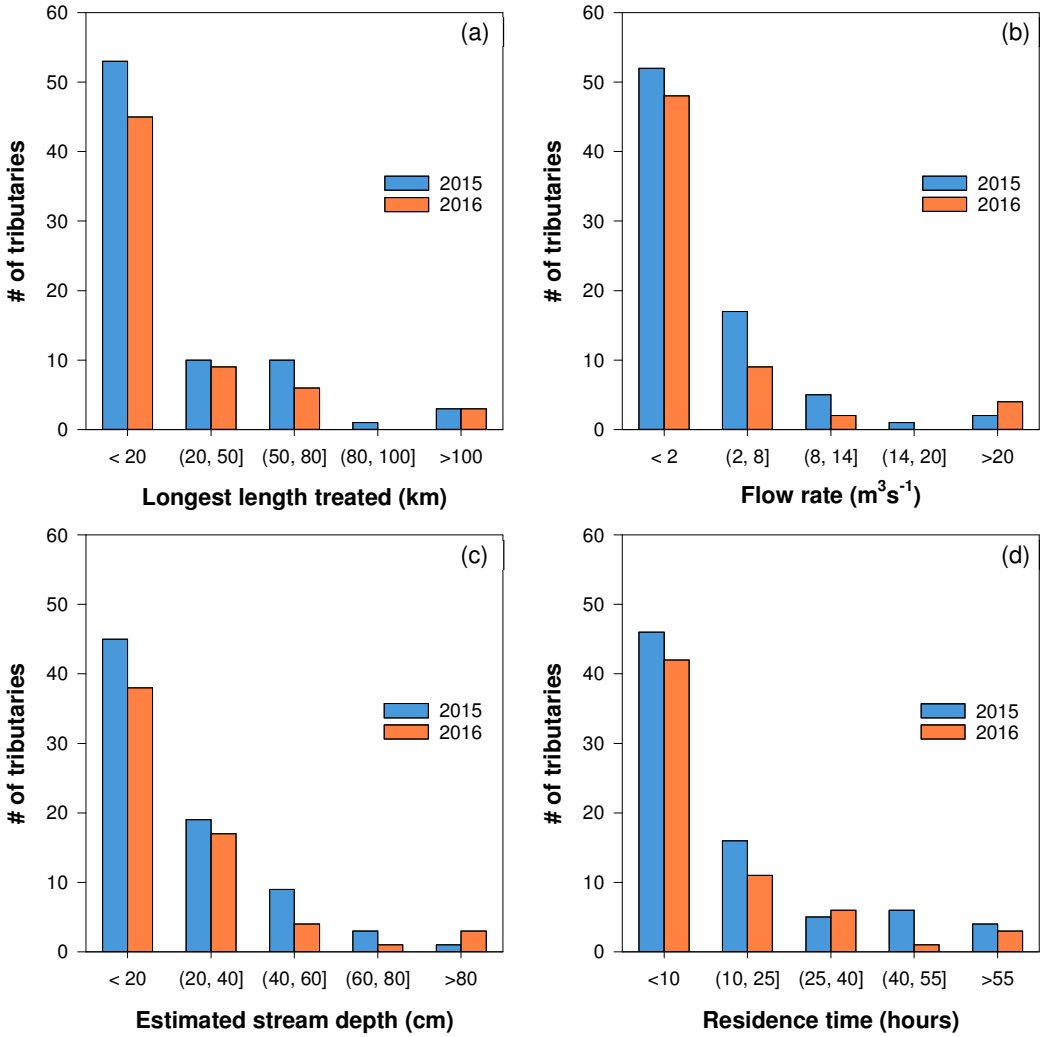

Figure S12. Histograms of the 140 tributaries treated with lampricides in 2015 and 2016 describing (a) treatment length, (b) flow rate, (c) estimated stream depth, and (d) estimated residence time.

References.

1 P. Sullivan, R. Adair and A. Woldt, *Sea Lamprey Control in the Great Lakes 2015; Annual Report to the Great Lakes Fishery Commission.*, 2016.

2 In Preparation, *Sea Lamprey Control in the Great Lakes 2016; Annual Report to the Great Lakes Fishery Commission.*, 2017.

3 D. K. Forsyth, C. M. Riseng, K. E. Wehrly, L. A. Mason, J. Gaiot, T. Hollenhorst, C. M. Johnston, C. Wyrzykowski, G. Annis, C. Castiglione, K. Todd, M. Robertson, D. M. Infante, L. Wang, J. E. McKenna and G. Whelan, *J. Am. Water Resour. Assoc.*, 2016, **52**, 1068–1088.

4 C. G. Homer, J. A. Dewitz, L. Yang, S. Jin, P. Danielson, G. Xian, J. Coulston, N. D. Herold, J. D. Wickham and K. Megown, *Photogramm. Eng. Remote Sens.*, 2015, **81**, 345–354.

5 L. Wang, C. M. Riseng, L. A. Mason, K. E. Wehrly, E. S. Rutherford, J. E. McKenna Jr., C. Castiglione, L. B. Johnson, D. M. Infante, S. Sowa, M. Robertson, J. Schaeffer, M. Khoury, J. Gaiot, T. Hollenhorst, C. Brooks and M. Coscarelli, *J. Gt. Lakes Res.*, 2015, **41**, 584–596.

6 M. J. Menne, I. Durre, R. S. Vose, B. E. Gleason and T. G. Houston, *J. Atmos. Ocean. Tech.*, 2012, **29**, 897–910.

7 M. J. Menne, I. Durre, R. S. Vose, B. E. Gleason and T. G. Houston, *NOAA Natl. Clim. Data Cent.*, 2012.

8 National Climatic Data Center, NESDIS, NOAA, U.S. Department of Commerce, *NOAA Natl. Cent. Environ. Inf.*

9 A. Woldt and W. P. Sullivan, *Standard Operating Procedures for Application of Lampricides in the Great Lakes Fishery Commission Integrated Management of Sea Lamprey (Petromyzon Marinus) Control Program*, U.S. Fish and Wildlife Service, Marquette Biological Station, Marquette, MI, 2016.

10 M. B. McConville, T. D. Hubert and C. K. Remucal, *Environ. Sci. Technol.*, 2016, **50**, 9998–10006.

11 T. Dittmar, B. Koch, N. Hertkorn and G. Kattner, *Limnol. Oceanogr. Methods*, 2008, **6**, 230–235.

12 D. Dulin and T. Mill, *Environ. Sci. Technol.*, 1982, **16**, 815–820.

13 J. R. Laszakovits, S. M. Berg, B. G. Anderson, J. E. O'Brien, K. H. Wammer and C. M. Sharpless, *Environ. Sci. Technol. Lett.*, 2017, **4**, 11-14.

14 R. A. Payn, M. N. Gooseff, B. L. McGlynn, K. E. Bencala and S. M. Wondzell, *Water Resour. Res.*, 2009, **45**, W11427.

15 C. A. Gueymard, *Energy*, 2005, **30**, 1551–1576.

16 L. B. Leopold and T. Maddock Jr., *The hydraulic geometry of stream channels and some physiographic implications*, 1953.

17 Z. F. Miller, T. M. Pavelsky and G. H. Allen, *Hydrol. Earth Syst. Sci.*, 2014, **18**, 4883–4895.