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Prepared for the Mason-Griffith Founders Chapter of Trout Unlimited
in cooperation with Lovells Township, Michigan

Evaluation of Legacy and Emerging Organic Chemicals using Passive Sampling Devices on the North Branch Au Sable River near Lovells, Michigan, June 2018

Scientific Investigations Report 2020–5002

U.S. Department of the Interior
U.S. Geological Survey

Cover. The polar organic chemical integrative sampler (POCIS) and semipermeable membrane device (SPMD), and replicate, deployed at the North Branch Au Sable River at The Ford Road near Lovells, Michigan (04135765).

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DAVID BERNHARDT, Secretary

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Contents

Figures

Tables

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
acre	0.004047	square kilometer (km^2)
	Volume	
ounce, fluid (fl. oz)	0.02957	liter (L)
pint (pt)	0.4732	liter (L)
quart (qt)	0.9464	liter (L)
gallon (gal)	3.785	liter (L)
cubic inch (in^3)	0.01639	liter (L)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
picogram (pg)	1.0e-6	microgram (mg)
microgram (mg)	1.0e-6	gram (g)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as

$$°F = (1.8 \times °C) + 32.$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as

$$°C = (°F - 32) / 1.8.$$

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either micrograms per liter (µg/L) or picograms per liter (pg/L).

Abbreviations

CERC	Columbia Environmental Research Center
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
EGLE	Michigan Department of Environment, Great Lakes, and Energy
EPA	U.S. Environmental Protection Agency
EROD	ethoxyresorufin *O*-deethylase
GLRI CEC	Great Lakes Restoration Initiative Contaminants of Emerging Concern
K_{ow}	water partition coefficient
LRL	laboratory reporting level
MDL	method detection limit
MDNR	Michigan Department of Natural Resources
MQL	method quantitation limit
NWQL	National Water Quality Laboratory
PAH	polycyclic aromatic hydrocarbon
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
POCIS	polar organic chemical integrative sampler
SPMD	semipermeable membrane device
TWA	time-weighted average
USGS	U.S. Geological Survey

Acknowledgments

Special thanks to Lovells Township, Michigan, for their support of this research on the North Branch Au Sable River and serving as the cooperator for this project. Without the commitment of the Mason-Griffith Founders Chapter of Trout Unlimited, this study would not have been possible. Thank you Mason-Griffith Founders Chapter of Trout Unlimited for your desire to obtain current data on the presence of organic chemicals in the North Branch Au Sable River and for your ongoing efforts to preserve and protect the Au Sable River.

Evaluation of Legacy and Emerging Organic Chemicals using Passive Sampling Devices on the North Branch Au Sable River near Lovells, Michigan, June 2018

By Angela K. Brennan and David A. Alvarez

Abstract

The North Branch Au Sable River, located in the northern lower peninsula of Michigan near Lovells, Michigan, has historically been known for its brook trout (*Salvelinus fontinalis*) and its status as a blue ribbon trout stream; however, within the past few decades, there has been a decline in fish population. The objectives of this study were to assess if concentrations of organic chemicals were present in quantities in the North Branch Au Sable River that may potentially harm aquatic species and to establish current baseline concentrations of organic chemicals against which future data can be compared. Passive sampling technology was used to collect information on the concentration, occurrence, transport, and fate of organic chemicals; these samplers absorb dissolved organic chemicals in the river over several weeks, as the timing and intensity of pesticide applications and the frequency of storm events and irrigation can cause fluctuations in organic chemical loading to surface waters. The chemical classes investigated as part of this study included pesticides (both legacy [organochlorine] and current use), polychlorinated biphenyls, polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs).

Passive samplers, including semipermeable membrane devices and polar organic chemical integrative samplers, were deployed at four locations along the North Branch Au Sable River, near Lovells, Mich., in June 2018 for a total of 28 days. Several organic chemicals were detected in the North Branch Au Sable River at low concentrations. Organic chemicals were detected at every sampling location on the North Branch Au Sable River; however, not all chemicals were detected at every location. The highest number of organic chemicals were detected at the most downstream sampling site (North Branch Au Sable River at Kellogg's Bridge), and the lowest number of organic chemicals were detected at the next site upstream (North Branch Au Sable River at Twin Bridge Road). The organic contaminants most frequently detected at all sampling locations include the legacy pesticides pentachloroanisole, *trans*-chlordane, p,p'-dichlorodiphenyldichloroethylene, and p,p'-dichlorodiphenyltrichloroethane; the PBDE PBDE-28; and the PAHs 2-methylphenanthrene and perylene.

Organic chemical concentrations detected on the North Branch Au Sable River were below almost all water-quality benchmarks included in this report. However, low concentrations of organic chemicals may still pose a risk to aquatic organisms and throughout the trophic hierarchy because of low-dose additive and synergistic mixture effects, transgenerational effects, and a lack of established water-quality benchmarks for many organic chemicals. This report provides data on the current (2018) state of the North Branch Au Sable River and provided a baseline of organic contaminant data against which future data on the North Branch Au Sable River can be evaluated.

Introduction

The Au Sable River, located in the northern lower peninsula of Michigan, has historically been known for its brook trout (*Salvelinus fontinalis*) and its status as a blue ribbon trout stream (Michigan Department of Natural Resources [MDNR], Fisheries Division, 1987). Within the past few decades the MDNR, local anglers, and environmental groups have noted a decline in fish populations on the North Branch Au Sable River near Lovells, Michigan (fig. 1) (MDNR, 2018). More recently, there has been increased interest in determining whether this observed fish decline may be related to legacy or emerging organic chemicals entering the river from sources within the watershed. Potential chemical sources may include, but are not limited to, golf courses, private residences, gas and oil production wells, atmospheric contribution, and a nearby Department of Defense facility. The timing and intensity of pesticide applications and the frequency of storm events and irrigation can cause fluctuations in organic chemical loading to surface waters. In addition to agricultural use of pesticides, organic chemicals also come from herbicides, insecticides, coal tar and asphalt, manufacturing, fire retardants, combustion, fragrances, flavors, and more (Baldwin and others, 2013).

There are currently no known water-quality datasets describing legacy and emerging organic chemicals in the North Branch Au Sable River. In June 2018, the MDNR and the Michigan Department of Environment, Great Lakes, and Energy (EGLE) led an investigation concurrent with a

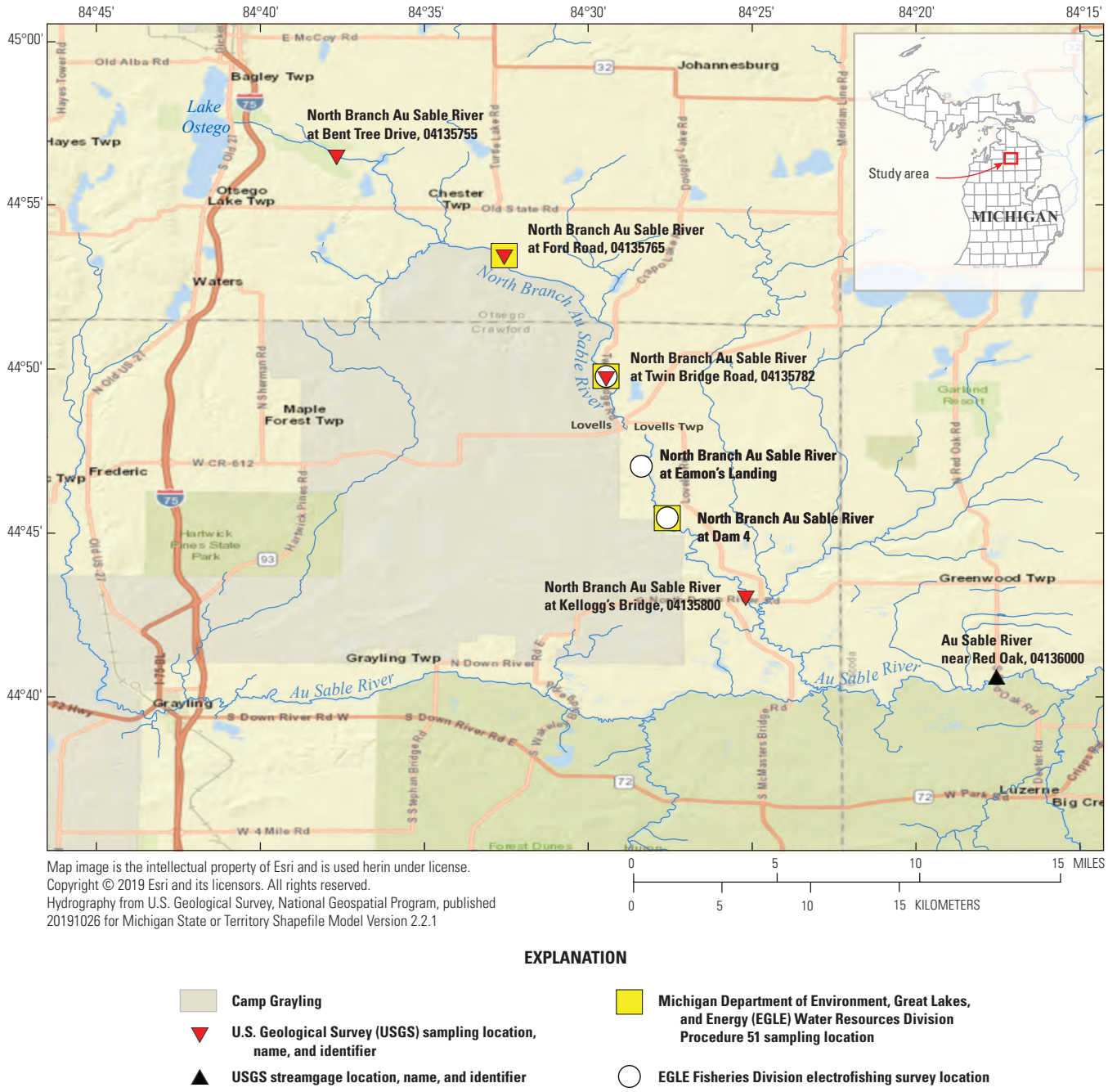

Figure 1. North Branch Au Sable River passive sampler monitoring and streamgage locations near Lovells, Michigan, 2018.

U.S. Geological Survey (USGS) passive sampling study to investigate the trout population in the North Branch Au Sable River. The MDNR/EGLE investigation was prompted owing to anglers' reports of poor fishing and a measured decline in the number of fish surveyed by the MDNR. The EGLE's Water Resources Division led three Procedure 51 habitat and macroinvertebrate surveys (Michigan Department of Environmental Quality, 2008) in mid-June and determined that all three sites surveyed (Twin Bridge Road, The Ford Road, and Dam 4) had excellent macroinvertebrate diversity, indicating excellent water quality (MDNR, 2018). In addition, the EGLE Fisheries Division led electrofishing surveys at three locations on the North Branch Au Sable River (Twin Bridge Road, Eamon's Landing, and Dam 4), revealing a low density and low biomass of brook trout. Brook trout density and biomass at Twin Bridge Road and Dam 4 were at the lowest recorded levels in the past 30 years (MDNR, 2018).

The 2018 USGS study was completed in cooperation with Lovells Township, Michigan and prepared for the Mason-Griffith Founders Chapter of Trout Unlimited, to evaluate the potential presence and concentration of organic chemicals in the North Branch Au Sable River using passive sampling technology,

specifically semipermeable membrane devices (SPMDs) and polar organic chemical integrative samplers (POCISs). The first objective of this study was to assess if concentrations of organic chemicals were present in quantities that may potentially harm sensitive aquatic species in the North Branch Au Sable River. The second objective was to establish the current conditions of organic chemicals for the North Branch Au Sable River against which future data can be compared.

Passive samplers can provide information on the concentration, occurrence, transport, and fate of organic chemicals by absorbing dissolved organic chemicals in the river over the course of their deployment, which typically lasts several weeks. The benefits of using SPMDs and POCISs compared to collecting discrete water samples include the following: (1) passive samplers provide a way to monitor episodic events, such as surface runoff, spills, and other point and nonpoint source contamination, as well as other isolated or short-lived pulses of chemicals in the water; (2) passive samplers are relatively less expensive than trying to collect enough discrete samples to account for episodic events; and (3) passive samplers also offer the ability to simulate a time-period exposure similar to what aquatic species might endure (Alvarez, 2010). Passive, integrative samplers provide a means of measuring time-weighted average (TWA) concentrations of dissolved organic chemicals while meeting many of the detection limit requirements of common instrumental techniques by sampling large volumes of water over prolonged exposure periods (Huckins and others, 2006; Alvarez and others, 2007).

Purpose and Scope

The purpose of this report is to describe the evaluation of legacy and emerging organic chemicals using passive sampling devices that were deployed at four locations along the North Branch Au Sable River, near Lovells, Mich., in June 2018 for a total of 28 days. The chemical classes investigated as part of this study included pesticides (both legacy [organochlorine] and current use), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs).

Background

The Au Sable River watershed is in the northern region of Michigan's lower peninsula (fig. 1) and is known to have some of the best trout fishing in the United States (MDNR, Fisheries Division, 1987). The North Branch Au Sable River is approximately 36 miles long; its headwaters begin in Otsego Lake and the river flows generally southeastward to the north Crawford county line then south at the town of Lovells where it enters the main branch of the Au Sable River about a mile downstream from McMasters Bridge (MDNR, Fisheries Division, 1987) (fig. 1, McMaster Bridge not shown in fig. 1). The width of the North Branch Au Sable River varies from about 40 feet to more than 150 feet nearer the mouth. The National Guard Joint Maneuvering facility (Camp Grayling) artillery range borders the upper North Branch Au Sable River on the south in Otsego County and on the west in Crawford County (MDNR, Fisheries Division, 1987) (fig. 1). The main stem of the Au Sable River is approximately 139 miles long; it runs through the cities of Grayling (fig. 1) and Mio and eventually empties into Lake Huron in Oscoda Township (not shown in fig. 1).

Methods

Passive samplers were deployed at four USGS sampling locations (table 1, fig. 1) on the North Branch Au Sable River, near Lovells, Mich., on June 1, 2018, and retrieved on June 29, 2018, for a total deployment of 28 days. At each location, two SPMDs and one POCIS were installed.

The SPMDs are typically used for sampling neutral organic chemicals (such as PAHs, PCBs, chlorinated pesticides, PBDEs, dioxins, furans, and hydrophobic chemicals) with a log octanol-water partition coefficient (K_{ow}) greater than 3 (Alvarez, 2010). POCISs are designed to sample the more water-soluble organic chemicals (including most pharmaceuticals, illicit drugs, polar pesticides, phosphate flame retardants, surfactants, metabolites, and degradation products) with a log K_{ow} less than 3; however, chemicals with a log K_{ow} between 4 and 5 are frequently reported (Alvarez, 2010).

Field Methods

Samplers were deployed and the results were analyzed based on published techniques and methods for use of SPMDs and POCISs in environmental monitoring studies (Alvarez, 2010). General stream water chemistry data (temperature, specific conductance, dissolved oxygen, and pH) were measured during deployment and retrieval using a calibrated YSI 6920 multiparameter water-quality sonde using methods described by U.S. Geological Survey (variously dated). Also measured was the depth of the passive sampler canisters in relation to the water surface, water conditions (clear, murky), flow conditions (characterized using the nearest USGS streamgage, Au Sable River near Red Oak, Mich., 04136000; U.S. Geological Survey, 2018) (fig. 1), and stream substrate type (table 1).

Sampling devices were deployed in approximately 2 to 3 feet of water, ensuring that the devices remain submerged under water for the entirety of the 28 days, as exposure to the atmosphere could potentially contaminate the passive sampling devices owing to the presence of airborne chemicals. Each sampling device was attached to a cinder block using stainless steel clamps and the cinder blocks were placed in a location in the river where there was constant flow; areas of highest flow were avoided to reduce potential damage from debris and boat traffic. The cinder blocks were secured to a fixed point on the streambank so that the samples would be retrievable if there were high flow velocities.

Table 1. Passive sampler deployment and retrieval site conditions, North Branch Au Sable River, 2018.

[Mich., Michigan; M, month; D, day; YYYY, year; EST, eastern standard time; °C, degree Celsius; µS/cm, microsiemen per centimeter; mg/L, milligram per liter; ft, foot]

Site conditions	North Branch Au Sable River at Bent Tree Drive near Gaylord, Mich. (04135755)	North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765)	Replicate - North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765)	North Branch Au Sable River at Twin Bridge Road near Lovells, Mich. (04135782)	North Branch Au Sable River at Kellogg's Bridge near Lovells, Mich. (04135800)
			Deployment		
Deployment date (M/D/YYYY)	6/1/2018	6/1/2018	6/1/2018	6/1/2018	6/1/2018
Deployment time (EST)	8:30 a.m.	10:00 a.m.	10:07 a.m.	11:00 a.m.	12:00 p.m.
Water temperature (°C)	14.4	18.9	18.9	17.5	17.4
Specific conductance (µS/cm)	425	299	299	299	301
Dissolved oxygen (mg/L)	6.9	7	7	8.4	9.6
pH	8.7	8.9	8.9	8.8	8.9
Depth of canister (ft)	1	1.5	1.5	1.5	2.5
Water conditions	Clear	Clear	Clear	Clear	Murky, appears turbid
Substrate conditions	Gravel, sand, muck	Gravel, sand, muck	Gravel, sand, muck	Gravel, sand	Gravel, sand
Flow conditions	Slow	Moderate	Moderate	Moderate	Moderate
Field blank collected	Yes	No	No	No	No
			Retrieval		
Retrieval date (M/D/YYYY)	6/29/2018	6/29/2018	6/29/2018	6/29/2018	6/29/2018
Retrieval time (EST, a.m.)	8:30 a.m.	9:30 a.m.	9:37 a.m.	10:30 a.m.	11:30 a.m.
Water temperature (°C)	14.4	18.9	18.9	16.8	17.4
Specific conductance (µS/cm)	447	325	325	321	319
Dissolved oxygen (mg/L)	7.9	7.8	7.8	8.8	9.9
pH	7.9	7.7	7.7	7.8	8.3
Depth of canister (ft)	0.8	1	1	0.7	1.5
Water conditions	Clear	Clear	Clear	Clear	Clear
Substrate conditions	Sand, muck, silt	Cobble, gravel, sand	Cobble, gravel, sand	Gravel, sand	Gravel, sand
Flow conditions	Slow	Moderate	Moderate	Moderate	Moderate/slow
Field blank collected	Yes	No	No	No	No

A

B

A, Internal view of polar organic chemical integrative sampler (POCIS) and *B*, semipermeable membrane device (SPMD) deployment canister.

Upon retrieval, the SPMD and POCISs were sealed in clean, airtight metal cans and shipped chilled with freezer packs overnight to the USGS Columbia Environmental Research Center (CERC). SPMD and POCIS field blanks were exposed to the air during sampler deployment on June 1, 2018, then resealed in clean, airtight metal cans and placed in the freezer at less than 0 degrees Celsius until sample retrieval on June 29, 2018, when the metal cans were re-opened, exposed to the air during retrieval, and then re-sealed for a final time.

Laboratory Methods

Chemicals were recovered from the SPMDs using a hexane dialysis followed by fractionation using size-exclusion chromatography to isolate chemicals of interest from potential interferences. Fractions designated for PAH analyses were passed through columns of acidic, neutral, and basic silica gel as a final cleanup step. These samples were then analyzed using gas chromatography/mass spectrometry. Fractions designated for legacy pesticides, total PCBs, and PBDEs underwent additional cleanup and fractionation using sequential columns of Florisil® and deactivated silica gel. Analyses for these chemicals were performed using gas chromatography with electron capture detections. Details of the process and analysis methods have been previously described (Alvarez and others, 2008).

Current-use pesticides were extracted from the POCIS using a solvent mixture of 80:20 volume per volume dichloromethane:methyl-*tert*-butyl ether, which was then solvent exchanged into ethyl acetate prior to ampoulation. The sealed ampoules containing the POCIS extracts were then sent to the USGS National Water Quality Laboratory (NWQL) for analysis for current-use pesticides and herbicides (NWQL lab code 8156) using methods described by Zaugg and others (2007).

An approach for providing a TWA assessment is critical for an improved understanding of the consequences of prolonged exposure to environmental chemical mixtures. The TWA assessment provides an average concentration over time; therefore, there is no way to distinguish whether the chemical concentration occurred during one episodic event or many episodic events, or whether there was a continuous input of chemicals to the river. Passive, integrative samplers provide a means of measuring the TWA concentrations of dissolved organic chemicals while meeting many of the detection limit requirements of common instrumental techniques by sampling large volumes of water over prolonged exposure periods (Huckins and others, 2006; Alvarez and others, 2007). TWA water concentrations of targeted chemicals were determined from measured amounts in the SPMDs and POCIS using first-order models for chemical uptake as described in Alvarez (2010).

Quality Control and Quality Assurance

Replicate SPMD and POCIS devices were deployed at the North Branch Au Sable River at The Ford Road near Lovells, Michigan (04135765) (fig. 1). Field replicate data are reported as relative percent difference and calculated for constituents with values above the method detection limit (MDL) and laboratory reporting level (LRL) by using equation 1.

$$RPDaverage = [|sample\ 1 - sample\ 2| / Average] * 100, \quad (1)$$

where

RPDaverage is the average relative percent difference;
sample 1 is the concentration in sequential replicate 1, in picograms or micrograms per liter;
sample 2 is the concentration in sequential replicate 2, in picograms or micrograms per liter; and
Average is the average of concentration in the two concurrent replicates, in picograms or micrograms per liter.

Additionally, SPMD and POCIS field blanks were collected at the North Branch Au Sable River at Bent Tree Drive near Gaylord, Michigan. The field blank was used to determine the MDL and method quantitation limit (MQL), where the MDL is the mean of the blank measurements for a single chemical plus three times the standard deviation (Alvarez, 2010).

Polar organic chemical integrative sampler (POCIS) and semipermeable membrane device (SPMD) deployment canister were attached to a concrete cinder block with stainless steel clamps.

The polar organic chemical integrative sampler (POCIS) and semipermeable membrane device (SPMD), and replicate, deployed at the U.S. Geological Survey streamgage North Branch Au Sable River at The Ford Road near Lovells, Michigan (04135765).

Results and Evaluation of Legacy and Emerging Organic Chemicals

This section of the report presents the concentration results of legacy and emerging organic chemicals in samples collected in June 2018 at four site along the North Branch Au Sable River. An evaluation of the organic chemicals and quality-assurance results also are included in this section.

All organic chemical data detected at concentrations above the MQL (CERC lab results) and above the LRL (NWQL lab results) were compared to eight benchmark water-quality standards, where such standards have been set (table 2). To calculate the estimated water concentration of a chemical, an experimentally derived sampling rate for that chemical must be known; therefore, only those data with a published sampling rate available were included in this analysis (Alvarez, 2010).

Several organic chemicals were detected at concentrations above the MQL (tables 3 and 4) and above the LRL (table 5) and are described in further detail in the following sections. The use of the terms MQL, MDL, and LRL are defined by the laboratory performing the analyses, where CERC reports data using MDL and MQL (Alvarez, 2010), and the NWQL reports data using LRL (Oblinger Childress and others, 1999).

Results of organic chemicals that were detected at concentrations above the MDL but less than the MQL are included in tables 3 and 4. These data are indicated in *italics* and have greater uncertainty in the absolute concentration values. Further information on how the MDL and MQL are calculated are presented in Alvarez, 2010. These results are described in further detail in the "Organic Chemical Detections above the Method Detection Limit" section.

Legacy Pesticides, Total Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers

Organochlorine pesticides, or legacy pesticides, include pesticides that have been banned in the United States or are in limited use and are still being detected in surface water, groundwater, sediment, and biota many years later (Nowell and others, 1999). Similar to legacy pesticides, PCBs are no longer commercially produced in the United States but may be present in products and materials produced before the 1979 ban. These products include transformers, capacitors, hydraulic oil and motor oil, cable insulation, adhesives and tapes, and oil-based paint (EPA, 2019a). Since the 1970s, PBDEs have been used as flame retardants in a wide variety of products, including plastics, furniture, upholstery, electrical equipment, electronic devices, textiles, and other household products (EPA, 2017). PBDEs are still being produced and have been used widely in the United States since the 1970s; however, there is growing concern about their persistence in the environment and their tendency to bioaccumulate (EPA, 2017). Concentrations for legacy pesticides, PCB, and PBDE data collected as part of this study are presented in table 3.

Legacy Pesticides

Eight legacy pesticides were detected above the laboratory MQL (table 3) at low concentrations with one pesticide exceeding the benchmark standards listed in table 2. At North Branch Au Sable River at Bent Tree Drive near Gaylord, Mich. (04135755), p,p'-dichlorodiphenyldichloroethylene (DDE, a common breakdown product of dichlorodiphenyltrichloroethane [DDT]) was detected at a concentration of 0.000021 micrograms per liter (µg/L) (table 3), which is above the EPA human health criteria for the consumption of water plus organism of 18 picograms per liter (pg/L) or 0.000018 µg/L (EPA, 2015). The EPA human health criteria for the consumption of water plus organism includes the two primary pathways of human exposure to pollutants through direct ingestion of drinking water and consumption of fish or shellfish obtained from the water body (EPA, 2015). Heptachlor epoxide was also detected very near the EPA human health criteria for the consumption of water plus

Table 2. Benchmark water-quality standards for those organic chemicals detected above the method quantitation limit.

[EPA, U.S. Environmental Protection Agency; µg/L, microgram per liter; CMC, criterion maximum concentration; CCC, criterion continuous concentration; +, plus; MCL, Maximum Contaminant Level; DWEL, Drinking Water Equivalent Level; na, no benchmark standards available; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; na, not available; PCA, pentachloroanisole; PBDE, polybrominated diphenyl ether; PHA, polycyclic aromatic hydrocarbon; EGLE, Michigan Department of Environment, Great Lakes, and Energy]

Detected compound	Common sources or uses of contaminant[1,2,3,4]	Michigan aquatic life final chronic value (µg/L)[2]	EPA office of pesticide programs aquatic life benchmarks fish acute (freshwater), (µg/L)[3]	EPA aquatic life criteria acute (freshwater CMC), (µg/L)[5]	EPA aquatic life criteria chronic (freshwater CCC) (µg/L)[5]	EPA human health criteria (human health for the consumption of water + organism) (µg/L)[6]	EPA drinking water MCL (µg/L)[7]	EPA lifetime health advisory (µg/L)[4]	EPA DWEL (µg/L)[4]
Legacy (organochlorine) pesticides									
Trifluralin	Used as an herbicide to control grasses, crops, shrubs, and flowers	na	9.25	na	na	na	na	10	700
PCA	Degradate of pentaclorophenol (PCP). A restricted-use pesticide, no longer available to general public. Most commonly used as a wood preservative	na	28	na	na	na	na	[8]40	[8]200
Oxychlordane	Insecticide commonly used for termite control	na	na	na	na	na	na	na	na
Heptachlor Epoxide	Insecticide used for termite control and insect control on farm crops	0.0700	na	0.52	0.0038	0.000032	0.4	na	0.4
trans-Chlordane	Insecticide commonly used for termite control	0.0290	na	na	na	na	2.0	[9]4	[9]20
cis-Chlordane	Insecticide commonly used for termite control	0.0290	na	na	na	na	2.0	[9]4	[9]20
p,p'-DDE	Breakdown product of DDT, which was used in the past as an insecticide	na	na	na	na	0.000018	na	na	na
p,p'-DDT	Used in the past for the control of malaria, typhus, and other insect-transmitted diseases	0.0032	na	1.10	0.0010	0.000030	na	na	na
PBDE									
2,4,4'-tribromodiphenyl ether (PBDE-28)	Flame retardant	na	na	na	na	na	na	na	na

Table 2. Benchmark water-quality standards for those organic chemicals detected above the method quantitation limit.—Continued

[EPA, U.S. Environmental Protection Agency; µg/L, microgram per liter; CMC, criterion maximum concentration; CCC, criterion continuous concentration; +, plus; MCL, Maximum Contaminant Level; DWEL, Drinking Water Equivalent Level; na, no benchmark standards available; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; na, not available; PCA, pentachloroanisole; PBDE, polybrominated diphenyl ether; PHA, polycyclic aromatic hydrocarbon; EGLE, Michigan Department of Environment, Great Lakes, and Energy]

Detected compound	Common sources or uses of contaminant[1,2,3,4]	Michigan aquatic life final chronic value (µg/L)[2]	EPA office of pesticide programs aquatic life benchmarks fish acute (freshwater), (µg/L)[3]	EPA aquatic life criteria acute (freshwater CMC), (µg/L)[5]	EPA aquatic life criteria chronic (freshwater CCC) (µg/L)[5]	EPA human health criteria (human health for the consumption of water + organism) (µg/L)[6]	EPA drinking water MCL (µg/L)[7]	EPA lifetime health advisory (µg/L)[4]	EPA DWEL (µg/L)[4]
				PAHs					
Fluorene	Used in manufacturing of dyes, plastics, and pesticides	12	na	na	na	50	na	na	1,000
Phenanthrene	Used in manufacturing explosives; component of tar, diesel fuel, or crude oil; combustion product	1.7	na	na	na	na	na	na	na
Fluoranthene	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product	1.6	na	na	na	20	na	na	na
2,3,5-trimethylnaphthalene	Used as an insecticide and pest repellent	na	na	na	na	na	na	[10]100	[10]700
1-methylfluorene	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product	na	na	na	na	na	na	na	na
2-methylphenanthrene	Used in manufacturing explosives; component of tar, diesel fuel, or crude oil; combustion product	na	na	na	na	na	na	na	na
3,6-dimethylphenanthrene	Used in manufacturing explosives; component of tar, diesel fuel, or crude oil; combustion product	na	na	na	na	na	na	na	na
Perylene	Used to make dyes, plastics, pesticides, explosives, and drugs. It has also been used to make bile acids, cholesterol, and steroids	na	na	na	na	na	na	na	na

Table 2. Benchmark water-quality standards for those organic chemicals detected above the method quantitation limit.—Continued

[EPA, U.S. Environmental Protection Agency; µg/L, microgram per liter; CMC, criterion maximum concentration; CCC, criterion continuous concentration; +, plus; MCL, Maximum Contaminant Level; DWEL, Drinking Water Equivalent Level; na, no benchmark standards available; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; na, not available; PCA, pentachloroanisole; PBDE, polybrominated diphenyl ether; PHA, polycyclic aromatic hydrocarbon; EGLE, Michigan Department of Environment, Great Lakes, and Energy]

Detected compound	Common sources or uses of contaminant[1,2,3,4]	Michigan aquatic life final chronic value (µg/L)[2]	EPA office of pesticide programs aquatic life benchmarks fish acute (freshwater), (µg/L)[3]	EPA aquatic life criteria acute (freshwater CMC), (µg/L)[5]	EPA aquatic life criteria chronic (freshwater CCC) (µg/L)[5]	EPA human health criteria (human health for the consumption of water + organism) (µg/L)[6]	EPA drinking water MCL (µg/L)[7]	EPA lifetime health advisory (µg/L)[4]	EPA DWEL (µg/L)[4]
				Current-use pesticides					
Acetochlor	Herbicide used to control weeds and approved for pre-emergent and pre-planting application	na	190	na	na	na	na	na	na
Atrazine	Primarily used in agriculture for weed control on row crops	7.3	2,650	na	na	na	3.0	na	700
Metolachlor	Pre-emergence herbicide used in agriculture for control of broadleaf and annual grassy weeds for several crops, primarily corn and soybeans	15	1,900	na	na	na	na	700	3.5

[1]U.S. Geological Survey Techniques and Methods 5–B4 (Zaugg and others, 2007).

[2]Michigan rule 57 surface water-quality values (EGLE, 2019).

[3]EPA Office of Pesticide Programs, Aquatic Life Benchmarks (EPA, 2019b).

[4]EPA Lifetime Health Advisory and Drinking Water Standards (EPA, 2018).

[5]EPA National Recommended Water Quality Criteria, Aquatic Life Criteria table (EPA, 2019c).

[6]EPA Human Health Criteria Table (EPA, 2015).

[7]EPA National Primary Drinking Water Regulations (EPA, 2019d).

[8]Lifetime Health Advisory and Drinking Water Standards for pentachlorophenol (EPA, 2018).

[9]Lifetime Health Advisory and Drinking Water Standards for chlordane (EPA, 2018).

[10]Lifetime Health Advisory and Drinking Water Standards for naphthalene (EPA, 2018).

Table 3. Legacy (organochlorine) pesticides, total polychlorinated biphenyls (PCBs), and polybrominated diphenyl ether (PBDE) residues sampled by semi-permeable membrane devices (SPMDs) reported as time-weighted average (June 1–29, 2018) water concentrations in units of picograms per liter.

[pg/L, picogram per liter; Mich., Michigan; <, less than; HCB, hexachlorobenzene; PCA, pentachloroanisole; a-BHC, alpha-benzenehexachloride; b-BHC, beta-benzenehexachloride; d-BHC, delta-benzenehexachloride; DDE, dichlorodiphenyldichloroethylene; DDD, dichlorodiphenyldichloroethane; DDT, dichlorodiphenyltrichloroethane; PCB, total polychlorinated biphenyl; PBDE, polybrominated diphenyl ether; EPA, U.S. Environmental Protection Agency; +, plus. Samples analyzed at the U.S. Geological Survey Columbia Environmental Research Center, Columbia, Missouri. Bold values denote reportable values greater than the method quantitation limit. Italic values denote estimated values greater than the method detection limit but less than the method quantitation limit]

Chemical	Method detection limit (pg/L)[1]	Method quantitation limit (pg/L)[1]	North Branch Au Sable River at Bent Tree Drive near Gaylord, Mich. (04135755) (pg/L)[1]	North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765) (pg/L)[1]	Replicate–North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765) (pg/L)[1]	North Branch Au Sable River at Twin Bridge Road near Lovells, Mich. (04135782) (pg/L)[1]	North Branch Au Sable River at Kellogg's Bridge near Lovells, Mich. (04135800) (pg/L)[1]
Legacy (organochlorine) pesticides							
Trifluralin	0.37	1.9	**440**	<0.37	<0.37	<0.37	[2] <0.37
HCB	1.5	7.6	<1.5	<1.5	<1.5	<1.5	<1.5
PCA	1.9	7.4	**18**	**34**	**26**	**12**	**30**
Tefluthrin	3.1	15	<3.1	<3.1	<3.1	<3.1	<3.1
a-BHC	15	45	<15	<15	<15	<15	15
Lindane	7.4	37	<7.4	<7.4	<7.4	<7.4	<7.4
b-BHC	5.4	27	<5.4	<5.4	<5.4	<5.4	<5.4
Heptachlor	1.5	7.6	<1.5	<1.5	<1.5	<1.5	<1.5
d-BHC	3.4	17	<3.4	<3.4	<3.4	<3.4	<3.4
Dacthal	2.8	14	<2.8	<2.8	<2.8	<2.8	<2.8
Chlorpyrifos	20	41	<20	<20	<20	<20	<20
Oxychlordane	1.5	7.4	**9.4**	<1.5	**10**	*5.6*	**9.1**
Heptachlor Epoxide	2.1	11	*3.3*	*6.4*	<2.1	**16**	[3]**31**
***trans*-Chlordane**	1.5	7.4	*4.1*	*3.5*	*3.1*	**7.8**	**16**
trans-Nonachlor	1.9	9.4	*6.7*	<1.9	*2.9*	*4.9*	*4.3*
o,p'-DDE	1.5	7.5	<1.5	<1.5	<1.5	<1.5	<1.5
***cis*-Chlordane**	1.5	7.4	*6.6*	<1.5	*1.7*	*2.1*	**8.9**
Endosulfan	22	110	<22	<22	<22	<22	<22
p,p'-DDE	2.6	8.6	[4]**21**	**9.9**	*8*	*5.5*	**11**
Dieldrin	6.8	14	<6.8	<6.8	<6.8	<6.8	<6.8
o,p'-DDD	1.7	8.4	<1.7	<1.7	<1.7	<1.7	<1.7
Endrin	1.9	9.7	<1.9	<1.9	<1.9	<1.9	<1.9
cis-Nonachlor	1.8	8.8	<1.8	<1.8	<1.8	<1.8	<1.8

Table 3. Legacy (organochlorine) pesticides, total polychlorinated biphenyls (PCBs), and polybrominated diphenyl ether (PBDE) residues sampled by semi-permeable membrane devices (SPMDs) reported as time-weighted average (June 1–29, 2018) water concentrations in units of picograms per liter.—Continued

[pg/L, picogram per liter; Mich., Michigan; <, less than; HCB, hexachlorobenzene; PCA, pentachloroanisole; a-BHC, alpha-benzenehexachloride; b-BHC, beta-benzenehexachloride; d-BHC, delta-benzenehexachloride; DDE, dichlorodiphenyldichloroethylene; DDD, dichlorodiphenyldichloroethane; DDT, dichlorodiphenyltrichloroethane; PCB, total polychlorinated biphenyl; PBDE, polybrominated diphenyl ether; EPA, U.S. Environmental Protection Agency; +, plus. Samples analyzed at the U.S. Geological Survey Columbia Environmental Research Center, Columbia, Missouri. Bold values denote reportable values greater than the method quantitation limit. Italic values denote estimated values greater than the method detection limit but less than the method quantitation limit]

Chemical	Method detection limit (pg/L)[1]	Method quantitation limit (pg/L)[1]	North Branch Au Sable River at Bent Tree Drive near Gaylord, Mich. (04135755) (pg/L)[1]	North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765) (pg/L)[1]	Replicate–North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765) (pg/L)[1]	North Branch Au Sable River at Twin Bridge Road near Lovells, Mich. (04135782) (pg/L)[1]	North Branch Au Sable River at Kellogg's Bridge near Lovells, Mich. (04135800) (pg/L)[1]
Legacy (organochlorine) pesticides—Continued							
o,p'-DDT	1.5	7.5	<1.5	<1.5	<1.5	<1.5	<1.5
p,p'-DDD	5.5	12	<5.5	*6.9*	*5.9*	<5.5	*5.9*
Endosulfan-II	85	250	<85	<85	<85	<85	<85
p,p'-DDT	5.3	7.4	**9.9**	**8.4**	*6.6*	**5.4**	**8.5**
Endosulfan Sulfate	32	160	<32	<32	<32	<32	<32
p,p'-Methoxychlor	20	99	<20	<20	<20	<20	<20
Mirex	2.5	13	<2.5	<2.5	<2.5	<2.5	<2.5
cis-Permethrin	360	980	<360	<360	<360	<360	<360
trans-Permethrin	5.5	27	<5.5	<5.5	<5.5	<5.5	<5.5
PCBs							
Total PCBs	270	1,400	<270	*480*	<270	*300*	*980*

Table 3. Legacy (organochlorine) pesticides, total polychlorinated biphenyls (PCBs), and polybrominated diphenyl ether (PBDE) residues sampled by semi-permeable membrane devices (SPMDs) reported as time-weighted average (June 1–29, 2018) water concentrations in units of picograms per liter.—Continued

[pg/L, picogram per liter; Mich., Michigan; <, less than; HCB, hexachlorobenzene; PCA, pentachloroanisole; a-BHC, alpha-benzenehexachloride; b-BHC, beta-benzenehexachloride; d-BHC, delta-benzenehexachloride; DDE, dichlorodiphenyldichloroethylene; DDD, dichlorodiphenyldichloroethane; DDT, dichlorodiphenyltrichloroethane; PCB, total polychlorinated biphenyl; PBDE, polybrominated diphenyl ether; EPA, U.S. Environmental Protection Agency; +, plus. Samples analyzed at the U.S. Geological Survey Columbia Environmental Research Center, Columbia, Missouri. Bold values denote reportable values greater than the method quantitation limit. Italic values denote estimated values greater than the method detection limit but less than the method quantitation limit]

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PBDEs							
PBDE-28	2.5	7.9	*3.2*	*3.4*	*3.3*	*4.6*	**9.5**
PBDE-47	160	410	<160	<160	<160	<160	<160
PBDE-66	13	36	<13	<13	<13	<13	<13
PBDE-85	58	130	<58	<58	<58	<58	<58
PBDE-99	100	240	<100	<100	<100	<100	<100
PBDE-100	26	67	<26	<26	<26	<26	<26
PBDE-153	130	370	<130	<130	<130	<130	<130
PBDE-154	42	110	<42	<42	<42	<42	<42
PBDE-183	16	81	<16	*19*	*17*	<16	*51*

[1]To convert to micrograms per liter, divide picograms per liter by 1,000,000.

[2]Less than (<) values are concentrations below the method detection limit.

[3]Concentration is near the recommended EPA Human Health Criteria standard, Human Health for the consumption of water + organism (of 32 pg/L).

[4]Concentration exceeds the recommended EPA Human Health Criteria standard, Human Health for the consumption of water + organism (of 18 pg/L).

Table 4. Polycyclic aromatic hydrocarbons (PAHs) sampled by semi-permeable membrane devices (SPMDs) reported as time-weighted average (June 1-29, 2018) water concentrations in units of picograms per liter.

[pg/L, picogram per liter; Mich., Michigan; PAH, polycyclic aromatic hydrocarbon; <, less than. Samples analyzed at the USGS Columbia Environmental Research Center, Columbia, Missouri. Bold values denote reportable values greater than the method quantitation limit. Italic values denote estimated values greater than the method detection limit but less than the method quantitation limit]

Chemical	Method detection limit (pg/L)[1]	Method quantitation limit (pg/L)[1]	North Branch Au Sable River at Bent Tree Drive near Gaylord, Mich. (04135755) (pg/L)[1]	North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765) (pg/L)[1]	Replicate–North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765) (pg/L)[1]	North Branch Au Sable River at Twin Bridge Road near Lovells, Mich. (04135782) (pg/L)[1]	North Branch Au Sable River at Kellogg's Bridge near Lovells, Mich. (04135800) (pg/L)[1]
PAHs							
Naphthalene	13,000	21,000	<13,000	<13,000	<13,000	<13,000	[2]<13,000
Acenaphthylene	150	290	<150	<150	<150	<150	<150
Acenaphthene	240	520	<240	<240	<240	<240	*260*
Fluorene	110	180	<110	<110	<110	<110	**210**
Phenanthrene	95	110	**290**	**250**	**210**	<95	**370**
Anthracene	88	180	<88	<88	<88	<88	<88
Fluoranthene	91	180	**210**	*160*	*120*	<91	**200**
Pyrene	82	160	*150*	*110*	<82	<82	*140*
Benz[a]anthracene	16	80	<16	<16	<16	<16	<16
Chrysene	15	75	*36*	*35*	*24*	<15	*30*
Benzo[b]fluoranthene	15	77	<15	<15	<15	<15	<15
Benzo[k]fluoranthene	18	88	<18	<18	<18	<18	<18
Benzo[a]pyrene	19	94	<19	<19	<19	<19	<19
Indeno[1,2,3-cd]pyrene	23	120	<23	<23	<23	<23	<23
Dibenzo[a,h]anthracene	20	100	<20	<20	<20	<20	<20
Benzo[g,h,I]perylene	25	130	<25	<25	<25	<25	<25
Benzo[b]thiophene	530	2,600	<530	<530	<530	<530	<530
2-Methylnaphthalene	110	270	<110	*120*	*120*	<110	*140*
1-Methylnaphthalene	54	270	*63*	*190*	*190*	<54	*150*
Biphenyl	50	250	<50	<50	<50	<50	<50
1-Ethylnaphthalene	24	120	<24	<24	<24	<24	<24
1,2-Dimethylnaphthalene	28	140	<28	<28	<28	<28	<28

Table 4. Polycyclic aromatic hydrocarbons (PAHs) sampled by semi-permeable membrane devices (SPMDs) reported as time-weighted average (June 1–29, 2018) water concentrations in units of picograms per liter.—Continued

[pg/L, picogram per liter; Mich., Michigan; PAH, polycyclic aromatic hydrocarbon; <, less than. Samples analyzed at the USGS Columbia Environmental Research Center, Columbia, Missouri. Bold values denote reportable values greater than the method quantitation limit. Italic values denote estimated values greater than the method detection limit but less than the method quantitation limit]

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PAHs							
4-Methylbiphenyl	48	130	<48	<48	<48	<48	<48
2,3,5-Trimethylnaphthalene	17	83	*17*	**120**	**95**	<17	*23*
1-Methylfluorene	16	81	<16	**200**	**140**	*50*	**86**
Dibenzothiophene	24	120	*26*	*28*	*24*	<24	*38*
2-Methylphenanthrene	17	83	*45*	**210**	**160**	*44*	*57*
9-methylanthracene	16	78	<16	<16	<16	<16	<16
3,6-Dimethylphenanthrene	15	74	<15	**84**	*56*	<15	<15
2-Methylfluoranthene	15	74	<15	*20*	<15	<15	<15
Benzo[b]naphtho[2,1-d]thiophene	15	75	<15	<15	<15	<15	<15
Benzo[e]pyrene	19	96	<19	<19	<19	<19	<19
Perylene	17	85	**110**	**1,100**	**770**	**220**	**360**

[1]To convert to micrograms per liter, divide picograms per liter by 1,000,000.

[2]Less than (<) values are concentrations below the method detection limit.

Table 5. Current-use pesticides sampled by polar organic chemical integrative sampler (POCIS) reported as time-weighted average (June 1–29, 2018) water concentrations in units of picograms per liter.

[pg/L, picogram per liter; Mich., Michigan; <, less than; EPTC, s-ethyl dipropylthiocarbamate . Samples analyzed at the U.S. Geological Survey National Water Quality Laboratory, Denver, Colorado. Bold values denote reportable values greater than the laboratory reporting level]

Chemical	Laboratory reporting level (pg/L)[1]	North Branch Au Sable River at Bent Tree Drive near Gaylord, Mich. (04135755) (pg/L)[1]	North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765) (pg/L)[1]	Replicate–North Branch Au Sable River at The Ford Road near Lovells, Mich. (04135765) (pg/L)[1]	North Branch Au Sable River at Twin Bridge Road near Lovells, Mich. (04135782) (pg/L)[1]	North Branch Au able River at Kellogg's Bridge near Lovells, Mich. (04135800) (pg/L)[1]
Current-use pesticides						
Acetochlor	890	[2]<890	**2,000**	**1,800**	**1,200**	**1,100**
Alachlor	850	<850	<850	<850	<850	<850
Alpha-HCH	330	<330	<330	<330	<330	<330
Atrazine	1,200	<1,200	**6,500**	**4,900**	**2,900**	<1,200
Butylate	610	<610	<610	<610	<610	<610
Carbaryl	160,000	<160,000	<160,000	<160,000	<160,000	<160,000
Carbofuran	82,000	<82,000	<82,000	<82,000	<82,000	<82,000
Chlorpyrifos	7,100	<7,100	<7,100	<7,100	<7,100	<7,100
Cyanazine	2,300	<2,300	<2,300	<2,300	<2,300	<2,300
Deethylatrazine	1,900	<1,900	<1,900	<1,900	<1,900	<1,900
Diazinon	670	<670	<670	<670	<670	<670
EPTC	590	<590	<590	<590	<590	<590
Fipronil	1,700	<1,700	<1,700	<1,700	<1,700	<1,700
Linuron	9,100	<9,100	<9,100	<9,100	<9,100	<9,100
Malathion	110,000	<110,000	<110,000	<110,000	<110,000	<110,000
Methyl parathion	2,300	<2,300	<2,300	<2,300	<2,300	<2,300
Metolachlor	970	<970	**2,700**	**2,300**	**1,400**	**1,500**
Metribuzin	2,600	<2,600	<2,600	<2,600	<2,600	<2,600
Pendimethalin	1,600	<1,600	<1,600	<1,600	<1,600	<1,600
Prometon	950	<950	<950	<950	<950	<950
Propachlor	1,200	<1,200	<1,200	<1,200	<1,200	<1,200
Simazine	1,300	<1,300	<1,300	<1,300	<1,300	<1,300

[1]To convert to micrograms per liter, divide picograms per liter by 1,000,000.

[2]Less than (<) values are concentrations below the laboratory reporting level.

organism (table 3), at 0.000031 µg/L but did not exceed the benchmark standard of 0.000032 µg/L (table 2) (EPA, 2015). Those legacy pesticides detected above the MQL include trifluralin (pre-emergence herbicide), pentachloroanisole (pesticide/biocide for wood preservation), oxychlordane (insecticide), heptachlor epoxide (insecticide), *trans*- and *cis*-chlordane (insecticides), DDE, and DDT (pesticide/insecticide) (table 3).

Seven legacy pesticides were detected above the MQL at low concentrations at North Brand Au Sable River at Kellogg's Bridge near Lovells, Mich. (04135800) with fewer quantifiable detections at the remaining three North Branch Au Sable locations (table 3). Pentachloroanisole was the only legacy pesticide detected at all four sampling locations above the MQL (table 3).

Polychlorinated Biphenyls

No PCBs were detected at concentrations above the MQL at any of the four sampling locations on the North Branch Au Sable River (table 3).

Polybrominated Diphenyl Ethers

One PBDE analyte (PBDE-28; used in flame retardants and in a variety of products including building materials, electronics, furnishings, motor vehicles, plastics, polyurethane foams, and textiles) was detected at a concentration above the MQL (table 3). This analyte was detected at North Brand Au Sable River at Kellogg's Bridge near Lovells, Mich. (04135800) where the highest number of legacy pesticides were detected. Presently, there does not appear to be a benchmark water-quality standard for PBDE-28 for which to compare these data.

Polycyclic Aromatic Hydrocarbons

PAHs include chemicals that are released from burning coal, oil, gasoline, wood, and garbage, and PAHs also can occur naturally in coal, crude oil, and gasoline (EPA, 2009). Eight PAH chemicals were detected at concentrations above the MQL and are presented in table 4.

Those PAH chemicals detected at concentrations above the MQL include fluorene; phenanthrene; fluoranthene; 2,3,5-trimethylnaphthalene; 1-methylfluorene; 2-methylphenanthrene; 3,6-dimethylphenanthrene; and perylene. Six PAH chemicals were detected above the MQL in low concentrations at North Branch Au Sable River at The Ford Road (04135765), followed by 5 detections at North Branch Au Sable River at Kellogg's Bridge (04135800) and North Branch Au Sable River at The Ford Road replicate sample. None of the PAH chemicals detected exceeded the benchmark water-quality standards presented in table 2, where available (four of the eight PAHs detected have associated benchmark standards). Of those PAHs detected, perylene was detected above the MQL at each of the four sampling locations, and phenanthrene was detected at all locations except North Branch Au Sable River at Twin Bridge Road (04135782) (table 4).

Current-Use Pesticides

Current-use pesticides include those pesticides, herbicides, and insecticides that are still in use today. Only those current-use pesticides with published sampling rates are presented in table 5. Three current-use pesticides were detected in low concentrations above the LRL and include acetochlor (pre-emergence herbicide), atrazine (widely used herbicide), and metolachlor (widely used herbicide).

North Branch Au Sable River at Bent Tree Drive (04135755), which is the most upstream site sampled, was the only location where current-use pesticides were not detected. Acetochlor and metalachlor were detected at all locations except North Branch Au Sable River at Bent Tree Drive (04135755) (table 5). None of the current-use pesticides detected exceeded the benchmark water-quality standards presented in table 2.

Organic Chemical Detections above the Method Detection Limit

The site with the highest number of organic chemicals detected was North Branch Au Sable River at Kellogg's Bridge (04135800) with 28 organic chemicals detected of the 97 organic chemicals analyzed (approximately 29 percent). North Branch Au Sable River at Kellogg's Bridge (04135800) is the most downstream sampling location and has the largest contributing watershed of all the sites (fig. 1). The North Branch Au Sable River at The Ford Road (04135765), and the replicate at that location, had the second and third highest number of organic chemicals detected (with 25 and 24 organic chemical detections, respectively; and approximately 26 percent and 25 percent, respectively). North Branch Au Sable River at Bent Tree Drive (04135755) had 19 organic chemicals detected (approximately 20 percent), and lastly North Branch Au Sable River at Twin Bridge Road (04135782) with 16 organic chemicals detected (approximately 16 percent) (tables 3–5). No current-use pesticides were detected at North Branch Au Sable River at Bent Tree Drive (04135755) (table 5).

The most frequently detected organic contaminants that were detected at all sampling locations (including replicate sample at North Branch Au Sable River at The Ford Road 04135765) include the legacy pesticides pentachloroanisole, *trans*-chlordane, p,p'-DDE, and p,p'-DDT; the PBDE PBDE-28; and the PAHs 2-methylphenanthrene and perylene (tables 3–5). Legacy pesticides oxychlordane, heptachlor

epoxide, *trans*-nonachlor, *cis*-chlordane were detected at all four sampling locations; however, at North Branch Au Sable River at The Ford Road (04135765) these legacy pesticides were detected in either the replicate or the routine sample but not in both the replicate and routine samples (tables 3–5).

Quality-Control and Quality-Assurance Results

Relative percent differences were calculated at the North Branch Au Sable River at The Ford Road near Lovells, Mich., for replicate organic chemical concentrations when both constituent pairs were greater than the MDL and (or) LRL. Relative percent difference for the paired replicates ranged from 0 to 40 percent difference depending on the constituent, with an average percent difference of 21 percent, and was considered an acceptable indication of variability in the sample-collection method and laboratory methods.

SPMD and POCIS field blanks were used to determine the MDL and MQL and are reported as MDL and MQL in tables 3 and 4 (Alvarez, 2010). The field blank was used to determine the MDL and MQL, where the MDL is the mean of the blank measurements for a single chemical plus three times the standard deviation (Alvarez, 2010).

Evaluation of Organic Chemicals

The North Branch Au Sable River can be considered a forest-dominated watershed with a smaller percentage of wetland, agricultural, livestock, and government-owned land uses (Zorn and Sendek, 2001). Land use may be an important predictor of organic contaminant detection, as streams located in developed urban and (or) agricultural watersheds have been shown to have more frequent detections and higher concentrations of many organic compounds compared to undeveloped watersheds (Baldwin and others, 2016). Seasonality may also affect the presence and detection of organic contaminants in the watershed, as some herbicide concentrations have shown distinct seasonal variation (Baldwin and others, 2016) related to agricultural and recreational applications in the watershed. The amount of precipitation affecting the watershed is another factor that could contribute to contaminant transport to surface waters.

These current findings are not dissimilar from previous studies in the Great Lakes where organic chemicals have been generally detected at concentrations in the nanogram or microgram per liter range and often below water-quality standards (Baldwin and others, 2016). However, low concentrations of organic chemicals may still pose a risk to aquatic organisms, as well as throughout the trophic hierarchy, because of low-dose effects, additive and synergistic mixture effects, transgenerational effects, and a lack of established water-quality benchmarks for many compounds (Baldwin and others, 2016). In Baldwin and others (2016), water samples from 35 percent of sites were composed of 10 or more chemicals. In the North Branch Au Sable study, water samples from all four locations (plus the replicate), or 100 percent of sites, were composed of 16 to 26 organic chemicals. Water-quality benchmarks are often established for singular chemicals and do not account for synergistic effects of these chemicals. In 1993, a Texas A&M study evaluated manufactured gas plant-PAH mixtures that indicated that benzo[a]pyrene and other PAHs (which are known to induce hepatic microsomal ethoxyresorufin *O*-deethylase [EROD] activity in mice) were only present as trace components of this mixture. A comparison of the EROD potencies of benzo[a]pyrene and the PAH mixture showed that the mixture was approximately 706 times more potent than expected based on the benzo[a]pyrene content alone thereby changing the overall carcinogenicity of the mixture (Chaloupka and others, 1993).

Organic contaminants and other contaminants in the North Branch Au Sable River could be evaluated using the R-script ToxEval that was developed by the USGS and includes a set of functions to analyze, visualize, and organize water quality data as it relates to EPA ToxCast data or other water quality criteria (De Cicco and others, 2018). ToxEval is used to develop a better understanding of the potential biological relevance of environmental chemistry data. ToxEval is often used as a screening technique to predict those chemicals that ultimately can be evaluated using aquatic bioassays to help evaluate the cumulative and synergistic mixture of chemicals present in the river (De Cicco and others, 2018).

Summary

Semi-permeable membrane devices and polar organic chemical integrative samplers are useful in their ability to monitor stream water quality during episodic events and during other isolated events where pulses of chemicals can enter the water. Passive samplers simulate a time-period exposure similar to what the aquatic species might endure in the same environment, and the results are calculated using a time-weighted average concentration. The time-weighted average assessment provides an average concentration over time; therefore, there is no way to distinguish whether the chemical concentration occurred during one episodic event or many episodic events, or whether there was a continuous input of chemicals to the river. Semi-permeable membrane devices and polar organic chemical integrative samplers provided an improved understanding of the prolonged exposure and environmental chemical mixtures aquatic organisms were exposed to in the North Branch Au Sable River.

Passive samplers were deployed at four locations along the North Branch Au Sable River, near Lovells, Michigan, in June 2018 for a total of 28 days in a study completed by the U.S. Geological Survey in cooperation with Lovells Township, Michigan, and prepared for the Mason-Griffith Founders Chapter of Trout Unlimited, to evaluate the potential presence and concentration of organic chemicals in the

river. The objectives of this study were to assess if concentrations of organic chemicals were present in quantities in the North Branch Au Sable River that may potentially harm aquatic species and to establish current baseline concentrations of organic chemicals against which future data can be compared. The chemical classes investigated as part of this study included pesticides (both legacy [organochlorine] and current use), polychlorinated biphenyls, polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs).

Several organic chemicals were detected in the North Branch Au Sable River at low concentrations with one detection of p,p'-dichlorodiphenyldichloroethylene (21 picograms per liter) detected at North Branch Au Sable River at Bent Tree Drive exceeding the recommended U.S. Environmental Protection Agency Human Health Criteria standard for the consumption of water plus organism (of 18 picograms per liter). Organic chemicals were detected at every sampling location on the North Branch Au Sable River; however, not all chemicals were detected at every location. The highest number of organic chemicals were detected at the North Branch Au Sable River at Kellogg's Bridge (04135800), and the North Branch Au Sable River at The Ford Road (04135765), and replicate, had the second and third highest number of organic chemicals detected. The most frequently detected organic contaminants detected at all sampling locations include the legacy pesticides pentachloroanisole, *trans*-chlordane, dichlorodiphenyldichloroethylene, and dichlorodiphenyltrichloroethane; PBDEs, including polybrominated diphenyl ether-28; and PAHs, including 2-methylphenanthrene and perylene.

These data establish current conditions of organic chemicals in the North Branch Au Sable River against which future data can be compared. The organic chemical concentrations detected on the North Branch Au Sable River were relatively low and below almost all water-quality benchmarks. Further evaluation would be necessary to determine the effects of seasonality and precipitation on the detection of organic chemicals on the North Branch Au Sable River. Low concentrations of organic chemicals may still pose a risk to aquatic organisms and throughout the trophic food web because of low-dose additive and synergistic mixture effects, transgenerational effects, and a lack of established water-quality benchmarks for many organic chemicals. Some tools that could be used to evaluate these cumulative and synergistic mixture effects of chemicals include R-script ToxEval and aquatic bioassays to provide an ecological endpoint and additional information about the effect of the observed chemicals on the ecological community in the North Branch Au Sable River.

This dataset of organic contaminants in the North Branch Au Sable River provides baseline information on the current (2018) state of the North Branch Au Sable River and against which to evaluate and compare the future health of the North Branch Au Sable River.

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