Integrative Monitoring of Neonicotinoid Insecticides in Baseflow-Dominated Streams on the Wisconsin Central Sand Plain

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PROJECT SUMMARY

Title: Integrative monitoring of neonicotinoid insecticides in baseflow-dominated streams on the Wisconsin Central Sand Plain

Project ID: DATCP2020-1

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Period of contract: July 1, 2019 – June 30, 2021

Background/need: Neonicotinoid insecticides are used widely across the Wisconsin Central Sand Plain (WCSP) to control various pests that inflict damage to crops such as potatoes, corn and soybeans. They are often used as seed coatings, but also sprayed upon foliage, or applied as granules in furrows. Neonicotinoids are systemic insecticides that are considered very water soluble and mobile in groundwater. Coarse sandy soils on the WCSP, a shallow water table, and irrigation increase the propensity for leaching of water-soluble pesticides and nutrients from soil to groundwater. The WCSP has many natural streams that are often connected by drainage ditches to lower the water table for agricultural purposes. These streams and ditches are primarily fed by groundwater discharge and supply a cold-water habitat for aquatic life. The US Environmental Protection Agency (EPA) has adopted acute and chronic aquatic life benchmarks (ALB) for neonicotinoids to aquatic invertebrates, plants, and fish. Of the neonicotinoids targeted, imidacloprid has the most stringent EPA ALB for invertebrates. Acute exposure criteria for aquatic invertebrates often relate to a 48-hour exposure period while chronic assessment criteria are often set at 7-40 days, depending upon species. As a result, traditional grab sampling may not provide an accurate representation of water quality over an extended period which is necessary to address chronic criteria. An evaluation of a passive sampling device to assess chronic toxicity criteria is included in this study.

Objectives:
Phase One of this study was conducted in 2019 - to assess the presence and concentrations of five neonicotinoid pesticides in twenty streams and ditches in the WCSP using both grab sampling and polar organic compound integrative samplers (POCIS). The results were compared with land use in the watersheds.

Phase Two of this study began in late spring of 2020 in one watershed to evaluate seasonal changes in surface water quality for a period of 12 months. POCIS were deployed at ten sites in the Tenmile Creek - South Branch watershed for 30-day periods. Hyporheic water was collected four times, at three locations using mini-piezometers at depths ranging from 30-60 cm across the width of the stream.

Methods: Study sites were selected to survey a wide range of land use activities, position in the watershed, and both on the east and west side of the surface water divide on the WCSP. Surface water grab samples were collected in one-liter amber glass and stored in a refrigerator at 4^{o}C

until the time of analysis. Samples were extracted using solid phase extraction techniques and analyzed by liquid chromatography/mass spectrometry. Similarly, POCIS were disassembled, and the sorption media removed, extracted, and analyzed by LC/MS.

Conclusions from Phase One: Imidacloprid and clothianidin were commonly detected and concentrations often exceeded the US EPA chronic aquatic life benchmarks for invertebrates. Thiamethoxam was frequently detected but usually at concentrations below the chronic aquatic life benchmark. Dinotefuran was infrequently detected and at concentrations near detection limits. Acetamiprid was not detected. Neonicotinoid concentrations in surface water were generally higher in streams and ditches west of the surface/groundwater divide. These areas west of the divide are dominated by irrigated agriculture with ditches connecting natural surface water drainages. Samples collected west of the divide were from both natural streams and ditches. Samples collected east of the divide were all from natural streams.

Surface water grab samples were collected at the time of deployment of POCIS and again upon retrieval approximately 30 days later. Comparisons were made between POCIS-derived TWA concentrations of the three commonly detected neonicotinoid insecticides and surface water grab samples at 20 locations. The average grab sample concentrations (n=2) varied linearly with the POCIS-derived concentration (n=1). Linear regressions between POCIS and grab samples had an r^2 of: imidacloprid = 0.93, clothianidin = 0.96, and thiamethoxam = 0.95.

Neonicotinoid concentrations increased concomitant with agricultural land cover in the groundwater contributing areas for the stream locations. Because neonicotinoids have only been used for the last 25 years, a linear regression model for neonicotinoid concentrations was developed using only the agricultural land cover in the groundwater contributing areas within 10- and 20-year travel time of the stream. The regression model was able to explain about 60% of the variation in neonicotinoid concentrations. That model was used to project future neonicotinoid concentrations by accounting for the percentage of agricultural land in the groundwater contributing area that would be delivering neonicotinoids to the stream. That model suggests that concentrations may double or triple at some of the stream locations over the next 40 years.

Conclusions from Phase Two: During the 12 months of continual monitoring, TWA neonicotinoid insecticide concentrations were relatively stable for clothianidin, imidacloprid and thiamethoxam in surface water of the South Branch of Tenmile Creek. The standard deviation of 12 monthly measurements at 10 sites ranged from less than 1.0 to 21 ng/L. Hyporheic water collected from the streambed had neonicotinoid insecticide concentrations that varied widely consistent with neonicotinoids being present in only a fraction of the total groundwater flowpaths because of travel time and land cover variations.

The agreement between POCIS time-weighted concentrations and grab samples indicate that both provide reliable ways to measure neonicotinoid concentrations in these baseflow-dominated streams. The sensitivity of analytical methods is sufficient to evaluate concentrations of the most abundant neonicotinoids with grab sampling. While POCIS provide a temporally weighted concentration that can incorporate variations during the deployment period, for baseflow dominated streams such as those in the WCSP, those variations are likely small and conventional grab sampling at low flow conditions provides an assessment of the typical concentrations that are likely to be encountered by aquatic biota.

Key words: neonicotinoids, Wisconsin Central Sand Plain, surface water, passive sampling

Funding: Wisconsin Department of Agriculture, Trade and Consumer Protection

Final Report: A final report containing more detailed information on this project is available at the Wisconsin Department of Agriculture, Trade and Consumer Protection. For more information, phone 608/224-4503, or email stan.senger@wisconsin.gov

INTRODUCTION

The Wisconsin Central Sand Plain (WCSP) is an economically important agricultural area that has a history of groundwater impairment. A variety of produce is grown in the WCSP with corn, soybeans and potatoes being the most common. Coarse sandy soils, a shallow water table (< 6 m), and intense agricultural activity combine to degrade water quality and quantity of the WCSP aquifer. Approximately 24% of private wells in the WCSP have nitrate nitrogen concentrations that exceed the 10 mg/L drinking water standard (Masarik et al., 2018). Since aldicarb was first detected in the late 1970s, numerous other pesticides and pesticide metabolites have been detected in private and municipal wells (Wisconsin Department of Agriculture, Trade and Consumer Protection, 2008 and 2017) in the WCSP.

Neonicotinoid insecticides (NNIs) have been used in the United States since imidacloprid was first introduced in 1991. Their use has steadily increased to where, as a group, NNIs constitute 25% of the global insecticide market (Bass et al., 2015). NNIs (Figure 1) are compounds that are structurally similar to nicotine. They are water soluble, resistant to degradation and relatively non-toxic to mammals. NNIs provide an effective mode of action to control insect populations by binding to the post-synaptic nicotinic acetylcholine receptors (nAChR) in the invertebrate central nervous system which leads to nervous system activation (Morrissey et al., 2015). They are systemic insecticides translocated through the plant as it grows. Approximately 80% of all NNIs are used as seed coatings with a smaller amount applied to foliage or as granules in furrows (Bass et al., 2015). Their toxicity to insects has led the US Environmental Protection Agency (EPA) to establish aquatic life benchmarks (ALBs) (US EPA, 2019) for aquatic invertebrates that are shown in Table 1. These ALBs were challenged by Tennekes (2010, 2011) and Morrissey (2015) as too high. They suggest that because NNIs irreversibly bind to the nAChR, the ALBs should be based on the sum of all NNIs. Morrissey used the combined effects of all NNIs which bind to this receptor on 48 species of invertebrates to suggest a total NNI acute benchmark of 200 ng/L and a chronic benchmark of 35 ng/L.

Table 1. US EPA (2019) Aquatic Life Benchmarks – invertebrates.

Neonicotinoid insecticide	Acute[a] 48- or 96-hour EC_{50}	Chronic[b] – NOAEC
Imidacloprid	385 ng/L	10 ng/L
Clothianidin	11,000	50
Thiamethoxam	17,500	740

[a]Acute invertebrate toxicity value is usually the lowest 48- or 96-hour EC_{50} or LC_{50} in a standardized test.
[b] Chronic invertebrate toxicity value is usually the lowest no observable adverse effect concentration (NOAEC) from life-cycle tests with invertebrates.

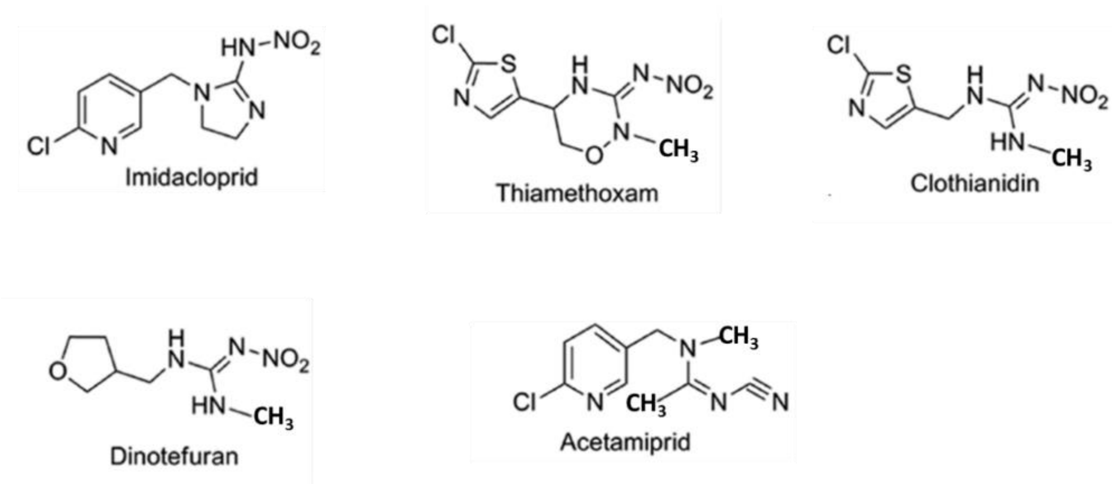

Figure 1. Targeted neonicotinoid insecticides for these studies. Clothianidin is both a primary active ingredient in Poncho 600 (Bayer Corp.) and a degradate from thiamethoxam.

The WCSP is drained by a network of streams and ditches that are fed by groundwater and provide cold water habitat for aquatic life. The extensive use and potential mobility of NNI in the WCSP suggest that these streams may be vulnerable to NNI contamination. It is important to understand current concentrations of NNIs in these streams and be able to predict future concentrations if we are to understand the potential impacts of NNIs to aquatic life.

The objectives of this study are to:

- determine the presence and concentrations of five NNIs (acetamiprid, clothianidin, dinotefuran, imidacloprid, thiamethoxam) in 20 baseflow-dominated streams and ditches on the WCSP;
- evaluate the utility of polar organic compound integrative samplers (POCIS) to estimate a time-weighted average (TWA) water concentration of the NNIs;
- determine mass loading of NNIs from streamflow measurements and NNI concentrations in surface water;
- evaluate land use in 20 watersheds to correlate with NNI concentrations in surface water;
- determine seasonality of NNI concentrations in a single drainage over a 12-month period;
- determine variability of groundwater discharge into a drainage through the use of mini-piezometers to collect hyporheic water samples;
- and, predict how NNI concentrations may change over time.

Acknowledgements

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PROCEDURES AND METHODS

Phase One

The first phase of this study included selection of 20 sites across the WCSP (Figure 2 and Appendix B). Sites were determined with intent to sample watersheds with varying land use, choose sites both on the east and west side of the watershed divide, and sites that varied in position in the watershed. Accessibility was also a consideration. Eight sites were selected on the east side of the groundwater divide and 12 sites on the west side.

NNI concentrations were measured at the 20 sites in late August to late September 2019 in surface water samples using polar organic compound integrative samplers (POCIS) and conventional grab samples. POCIS are passive devices that accumulate polar organic compounds on a media that is in contact with the stream water (Alvarez, 2010). POCIS used in this project were produced by Environmental Sampling Technologies, St. Joseph, MO, USA (Patent #6,478,961 B2). POCIS were deployed at the same time a surface water grab sample was collected. Grab samples were collected in one-liter amber borosilicate bottles. POCIS were retrieved from the stream after a 30-day deployment period and a second grab sample was collected at that time. Aqueous samples and POCIS were stored on ice and transferred to the Water and Environmental Analysis Laboratory (WEAL) at the University of Wisconsin – Stevens Point where they were refrigerated at 4^{o} C. The aqueous samples were processed using solid phase extraction techniques and extracts analyzed via high performance liquid chromatography and tandem mass spectrometry (Agilent 6430 LC/MS). POCIS were disassembled at the WEAL, the sorption media removed, contaminants were extracted using methanol (Alvarez, 2010) and analyzed by LC/MS.

POCIS accumulate NNIs at a rate that is proportional to their concentration in the stream. The quantity of NNIs accumulated is used to calculate a time-weighted average (TWA) concentration. This concentration can then be compared to chronic EPA ALBs. POCIS consist of two porous polyethersulfone membranes (47 mm) that encase a hydrophobic/lipophilic balanced (HLB) polymer. Membranes and polymeric media are held together with large stainless-steel rings and bolted together (Figure 3). The entire device is deployed inside a PVC cage to protect the membrane from puncture from floating debris. The device is suspended in the stream with braided steel cable.

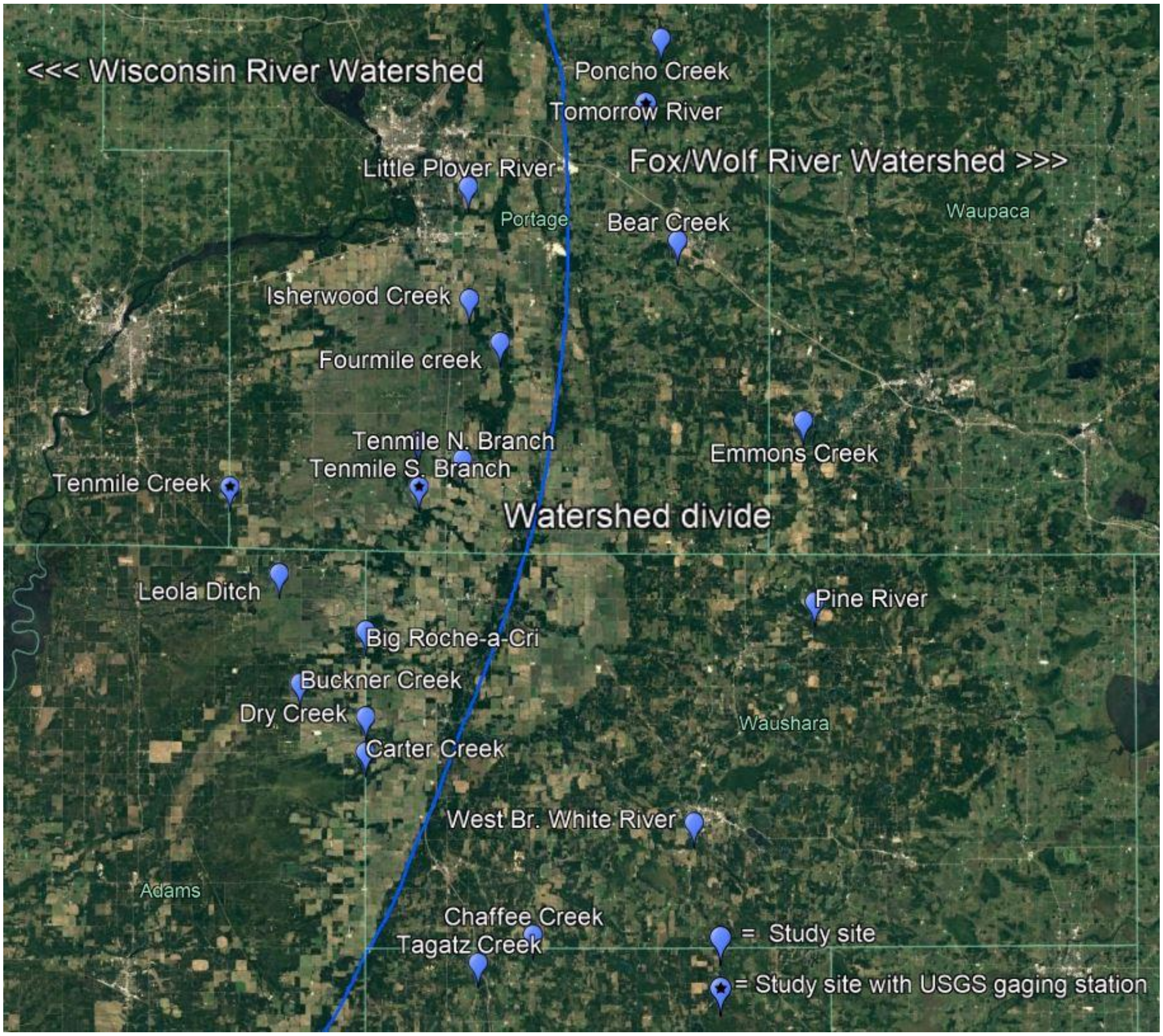


Figure 2. Sample collection sites for neonicotinoid insecticide determinations.

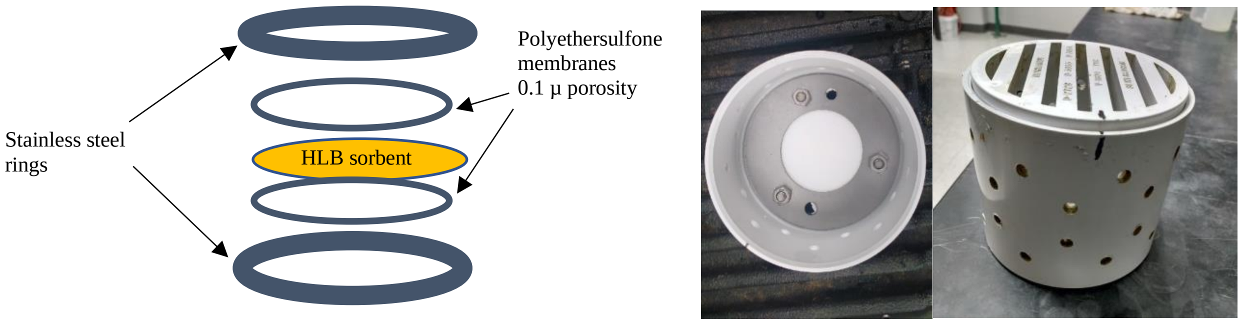


Figure 3. POCIS diagram (left). Inserted into protective PVC cage (center and right image).

Five NNIs were evaluated in both water samples and POCIS extracts. Table 2 lists the compound and limit of detection (LOD) for each along with the empirically determined effective POCIS sampling rates (R_s) for each compound. Sampling rates are used to convert the quantity of accumulated NNI to a time-weighted stream concentration. LODs for POCIS were estimated based upon exposure period and the R_s. The R_s had previously been determined empirically by Ahrens et al. (2015) and Taylor et al. (2020) as the amount of a chemical that can be extracted over a period of time. It is expressed as the volume of water extracted for a compound in liters/day.

Table 2. Target analyte list with limits of detection and frequency of detection.

Compound	Aqueous LOD ng/L	POCIS LOD ng/L[a]	Effective sampling rate (R_s) in L/day
Acetamiprid	1.7	0.06	0.38[b]
Clothianidin	1.5	0.05	0.22[b]
Dinotefuran	0.7	0.02	not available
Imidacloprid	2.3	0.08	0.24[b]
Thiamethoxam	1.5	0.05	0.12[c]

[a] POCIS LODs are theoretically estimated and based upon a 30-day exposure period.
[b] Ahrens et al. (10)
[c] Taylor et al. (11)

Streamflow was also measured at most monitoring locations. Streamflow was measured at 14 stream sites using the velocity-area method and a Flow Tracker 2 and at the other four of the sites with a nearby USGS gaging station. Flow was not recorded on two stream sites. Streamflow measurements were made 20 to 30 days after the POCIS were retrieved when streams were at base flow conditions.

The streamflow was used to calculate the mass loading of the NNIs using the concentration determined from conventional grab samples and the measured flow at each site. Nitrate-nitrogen was analyzed in hyporheic water using an ion specific electrode or an automated flow-injection cadmium reduction process.

The contributing land area for each stream site was determined using a groundwater flow model and end point tracking analysis. Background details of the Central Wisconsin Sand Plain model are presented in Kraft and Mechenich (2010). MODPATH endpoint analysis was used to identify groundwater contributing areas for each sampling location (Mike Parsons, Wisconsin Geologic and Natural History Survey, personal communication). Each contributing area was divided into travel time zones represented by the longest travel time in that zone. For this study, we identified 10-, 20-, 40-, and 60-year groundwater travel times and the complete groundwater contributing area. Land cover in each travel time zone was based on Wiscland 2.0 (WDNR, 2016). Wiscland 2.0 was developed using satellite imagery collected between 2010 and 2014. Agricultural land cover in the Wiscland database is divided into agricultural rotations as most land in the watershed rotates through a combination of crops. The Wiscland agricultural land categories were based on five years (2008-2012) of the United States Department of Agriculture (USDA) National Agricultural Statistics Service Cropland Data Layers (WDNR, 2016). The endpoint areas for each travel time zones were intersected with the Wiscland 2.0 to estimate land cover in each travel time zone.

Phase Two

Phase Two of this study investigated seasonality of NNI concentrations through repeated sampling of surface water in one of the watersheds over a 12-month period. POCIS were used to monitor NNI concentrations at 10 sites in the South Branch of Tenmile Creek Watershed. Approximately 25 kilometers (km) of stream were monitored from its headwaters to within 5 km of its discharge to the Wisconsin River. Inputs from other northern tributaries were monitored at one location downstream of their confluences, yet upstream of the confluence with the south branch (see Figure 4, northern tributary confluence site). Sites along the path of the south branch were selected at road crossings to allow access during winter months with spacing of 1.3 to 6.7 km between sites. A single POCIS was deployed for 28 to 32 days at each of these sites with one field replicate for each month of deployment. Upon retrieval, POCIS were removed from their PVC cages, placed in separate air-tight mylar zipper lock bags and then into clean steel paint cans which were placed on ice. They were returned to the WEAL, stored at -20^{o} C until extraction and analysis as described in Phase One.

Hyporheic (interstitial) water below the streambed was sampled in groundwater discharge areas of Tenmile Creek. Mini-piezometers constructed from polypropylene tubing with 9.5 cm screen length were used to both identify groundwater discharge zones and to collect hyporheic water at 30-60 cm below the saturated streambed. This was performed to identify zones of contaminant input and assess hazards to aquatic invertebrates occupying the streambed habitat. Four hyporheic water samples were collected across the width of the stream channel along with a surface water grab sample to confirm that surface water was not being pulled into the mini-piezometer. Sampling occurred four times over a 12-month period and in three locations along the stream channel. Hyporheic water samples were collected at Cty Hwys D, UU and F (Figures 4 and 16) and analyzed for NNIs and nitrate-nitrogen.

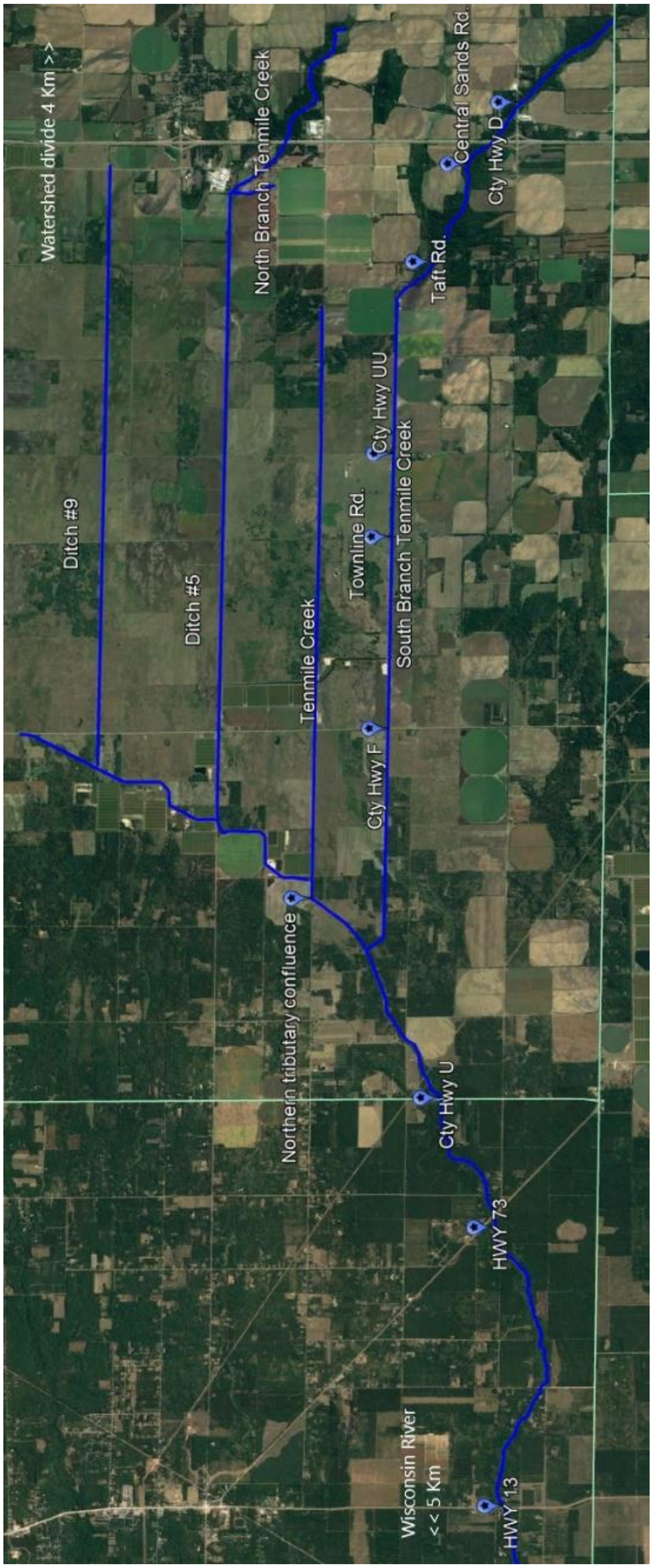


Figure 4. Phase Two study sites on the South Branch of Tenmile Creek.

RESULTS AND DISCUSSION

Phase One

Evaluation of passive sampling devices

Results from the POCIS deployed at 20 locations in the WCSP between August and September 2019 are summarized in Table 3 by a concentration range and frequency of detection. Four of the five NNI were detected but acetamiprid was never detected, and dinotefuran was detected infrequently and at low concentrations. The remainder of this paper will focus on imidacloprid, clothianidin and thiamethoxam as they were most frequently detected and are NNIs that have established toxicity values.

Table 3. Frequency and range of concentration of neonicotinoid insecticides in 20 streams and ditches on the WCSP.

Compound	Aqueous frequency of detection (n=20)	POCIS frequency of detection (n=20)	Concentration range (ng/L)
Acetamiprid	0	0	not applicable
Clothianidin*	16	18	0.52-147
Dinotefuran	2	1	1.1-4.0
Imidacloprid*	11	17	0.08-48.5
Thiamethoxam	14	16	0.15-411

** At least one sample above EPA ALB.*

Table 3 shows that POCIS sampling increased the frequency of detection for three of the NNIs. This most likely resulted because the estimated detection limit with a POCIS is 30 times lower than with a conventional aqueous sample. In both POCIS and grab samples, NNI concentrations often exceed chronic EPA ALBs set for imidacloprid and clothianidin. The greater frequency of detection and concentration range was found in streams on the west side of the watershed divide. Table 4 summarizes data obtained from two grab samples and POCIS derived concentrations of NNIs.

Table 4. Summary of NNI concentrations in WCSP streams and ditches - 2019.

Site	Thiamethoxam ng/L			Clothianidin ng/L			Imidacloprid ng/L		
	Aug. grab	Sept. grab	POCIS R_s= 0.12 L/day	Aug. grab	Sept. grab	POCIS R_s= 0.22 L/day	Aug. grab	Sept. grab	POCIS R_s= 0.24 L/day
East of watershed divide									
Poncho Creek	<1.5	<1.5	ND	<1.5	<1.5	ND	<2.3	<2.3	ND
Tomorrow River	<1.5	<1.5	ND	<1.5	<1.5	ND	<2.3	<2.3	0.13
Chaffee Creek	<1.5	<1.5	0.76	4.0	3.9	2.65	<2.3	<2.3	0.27
Tagatz Creek	<1.5	<1.5	ND	<1.5	<1.5	0.39	<2.3	<2.3	ND
Bear Creek	<1.5	<1.5	ND	<1.5	<1.5	0.52	<2.3	<2.3	ND
Emmons Creek	<1.5	<1.5	0.15	2.3	1.3	0.64	<2.3	<2.3	0.08
Pine River	2.9	2.8	3.36	1.8	1.7	1.55	<2.3	<2.3	0.56
West Branch White River	9.2	3.6	11.0	14.3	5.3	9.21	<2.3	<2.3	1.98
West of watershed divide									
Little Plover River	2.1	2.6	1.33	5.7	5.2	1.87	2.6	1.9	1.75
Isherwood Creek	1.7	3.8	0.53	11.1	11.3	2.03	8.2	7.5	1.37
Fourmile Creek	6.8	7.5	1.96	7.4	4.9	1.55	<2.3	<2.3	0.11
Carter Creek	5.2	8.0	4.3	18.8	16.1	9.88	40.9	31.6	21.4
Dry Creek	197	184	130	74.4	77.7	39.5	21.5	22.5	11.6
Big Roche-a-cri	83.0	115	69.0	61.1	47.8	33.9	33.2	24.0	21.9
Buckner Creek	101	127	116	37.6	34.7	32.0	21.2	22.2	19.8
Leola Ditch	286	234	320	42.8	24.6	12.3	24.7	19.0	6.91
Tenmile Creek	95.3	79.9	63.9	25.8	15.6	14.3	16.8	11.1	9.39
Tenmile Creek S. Branch	74.1	66.2	52.9	59.2	42.9	33.5	30.2	24.8	19.4
Ditch 5 Taft & Mill Rds.	251	212	207	62.5	37.0	37.2	48.5	36.0	29.9
Tenmile Creek N. Branch	411	397	328	147	104	74.3	27.4	23.8	16.4

POCIS-derived TWA concentrations were consistently lower than grab sample concentrations. This could have resulted because there were periods of high flow during the POCIS deployment which could have had led to periods of lower concentrations. Previous work at one of these monitoring locations showed that nitrate-nitrogen concentrations were greater during low flow than high flow and was attributed to nitrate concentrations in groundwater being diluted by less impacted water during the rainfall event (Miller et al., 2017). In the POCIS deployment period, there was approximately 12 cm of rainfall and hydrographs from USGS gaging stations in Figure 5 show higher streamflow response during these periods. The higher flow portion of the hydrograph could have lowered concentrations and led to a lower time-weighted concentration in the POCIS compared to the grab samples collected at or near baseflow conditions.

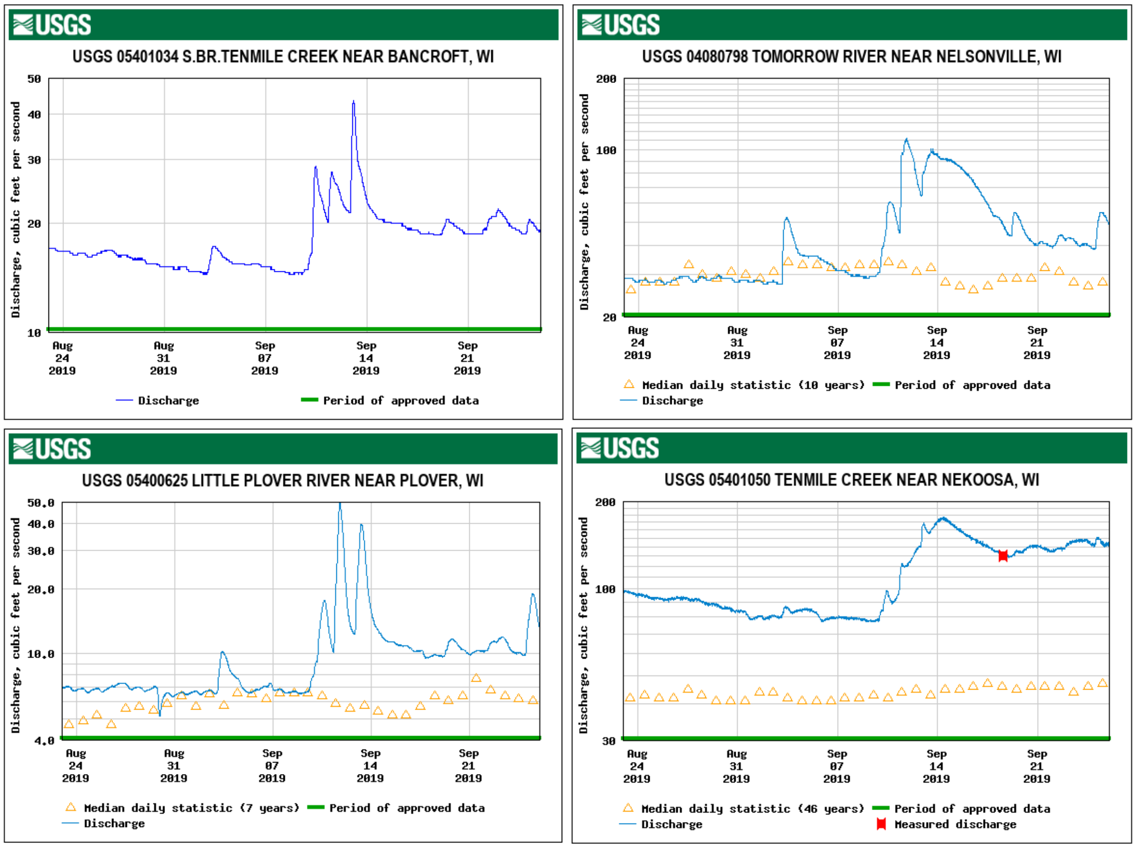


Figure 5. Hydrographs from USGS gaging stations during POCIS deployment period in Phase One of this study (www.usgs.gov).

Relationships between grab samples and POCIS-derived concentrations of NNIs are graphically displayed in Figure 6 with consistent patterns emerging from these bar graphs. Linear regressions comparing the average grab sample concentration (deployment and retrieval sample) with POCIS-derived TWA concentrations are displayed in Figure 7. Linear regressions observed were; imidacloprid =0.93, clothianidin = 0.96 and thiamethoxam = 0.95. The slope of the regression lines show POCIS concentrations were 60 to 90 percent of the grab samples.

EPA ALBs were often exceeded for imidacloprid and clothianidin on the west side of the divide where a greater proportion of land is used for agricultural purposes. Concentrations of thiamethoxam did not exceed the 740 ng/L chronic EPA ALB in any of the study sites.

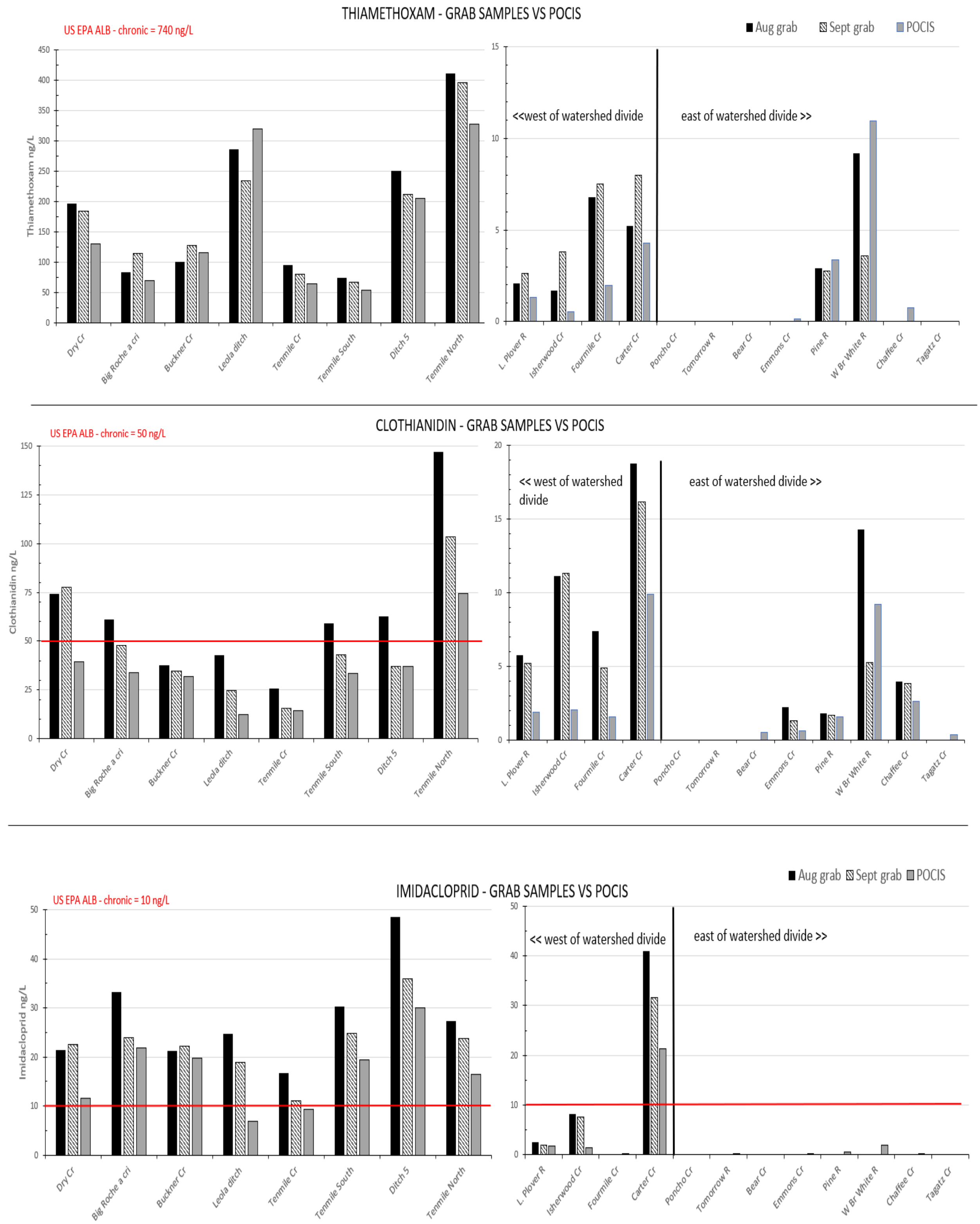


Figure 6. Traditional grab sample analysis and POCIS-derived concentrations of neonicotinoid insecticides.

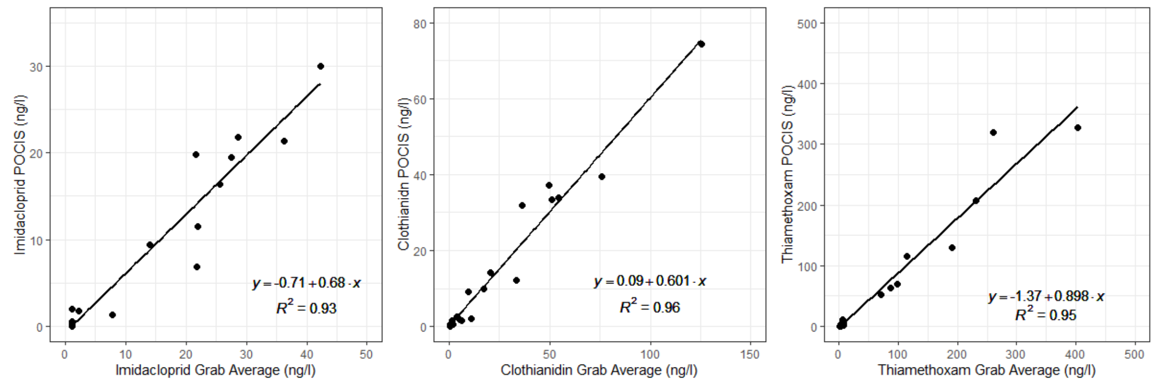


Figure 7. Linear regressions of average grab samples vs POCIS-derived concentrations of neonicotinoid insecticides.

Mass transport of neonicotinoid insecticides

Mass transport of three NNIs were estimated using streamflow discharge data and contaminant analysis for the 30-day period. Surface water grab sample contaminant analyses were used for this determination. Tenmile Creek displays the highest level of NNI transport (Table 5), however there were no flow measurements recorded on the Leola Ditch or Buckner Creek, tributaries to the Fourteenmile and Big Roche a Cri watersheds respectively. Considering the information gained in Phase Two of this study and relatively stable baseflow concentrations of NNIs, a daily mass transport of 17.3 g/day (thiamethoxam on Tenmile Creek @ CTY U) represents approximately 6.3 kg annually.

Table 5. Mass transport of NNIs in streams and ditches on the WCSP.

Study Location on WCSP	Aug-Sept 2019	Mass transport g/day as determined from grab sample water concentration		
	AVG (cfs)	Thiamethoxam	Clothianidin	Imidacloprid
Poncho Cr @ CTY Z	2.1	<LOD	<LOD	<LOD
Tomorrow R @ Clementson Rd	38.3	<LOD	<LOD	<LOD
L. Plover R @ Wetlands lab	9.1	0.05	0.12	0.05
Isherwood Cr @ footbridge	10.4	0.07	0.28	0.20
Fourmile Cr @ CTY JJ &BB	6.7	0.12	0.10	ND
Bear Cr @ CTY Q	20.0	<LOD	<LOD	<LOD
Emmons Cr @ Rural Rd	32.6	<LOD	0.14	<LOD
Pine R @ Apache Rd	63.6	0.44	0.27	<LOD
West Br White R. @ Hwy 22	35.6	0.56	0.85	<LOD
Chaffee Cr @ CTY B	24.5	<LOD	0.24	<LOD
Tagatz Cr @ CTY CH	7.1	<LOD	<LOD	<LOD
Carter Cr @ 1st Ave.	4.2	0.07	0.18	0.38
Dry Cr @ 1st Ave.	5.1	2.38	0.95	0.28
Big Roche a cri @ 1st Ave.	22.9	5.54	3.05	1.60
Buckner Cr @ 4th & Beaver		no flow data		
Leola ditch @ CTY D & 5th		no flow data		
Tenmile Cr @ CTY U	80.7	17.3	4.09	2.75
Tenmile Cr S. Branch @ Taft Rd	18.2	3.12	2.27	1.22
Ditch 5 @ Taft Rd	15.8	8.95	1.92	1.63
Tenmile Cr N. Branch @ Harding	5.5	5.39	1.67	0.34

LOD = Water sample concentration less than limit of detection.

Watershed land use assessment

The size and travel time distribution in the groundwater contributing area of each monitoring location was determined using groundwater flow modeling. Overall, the average flow at the monitoring locations was proportional to the size of the groundwater contributing areas and with an annual water loading of approximately 11 inches/year (0.28 meter/year). This agrees with other research in this area (Kraft et al., 2008; Hart and Schoephoester, 2014). The contributing areas for some of the headwater streams were smaller than their average flow would indicate, suggesting the regional-scale groundwater flow model was less accurate delineating contributing areas for those monitoring locations. Streamflow is a mix of water which has different ages where the age is the time between the precipitation entering the groundwater and that groundwater eventually discharging to the stream. The distribution of water ages depends on the size and shape of the contributing area. The relative size of the travel time zones within each contributing area was used to estimate the age distribution in the streamflow. Figure 8 shows the water age distribution modeled for the monitoring locations. The distribution is different for every location but at many sites, less than half of the streamflow is less than twenty years old.

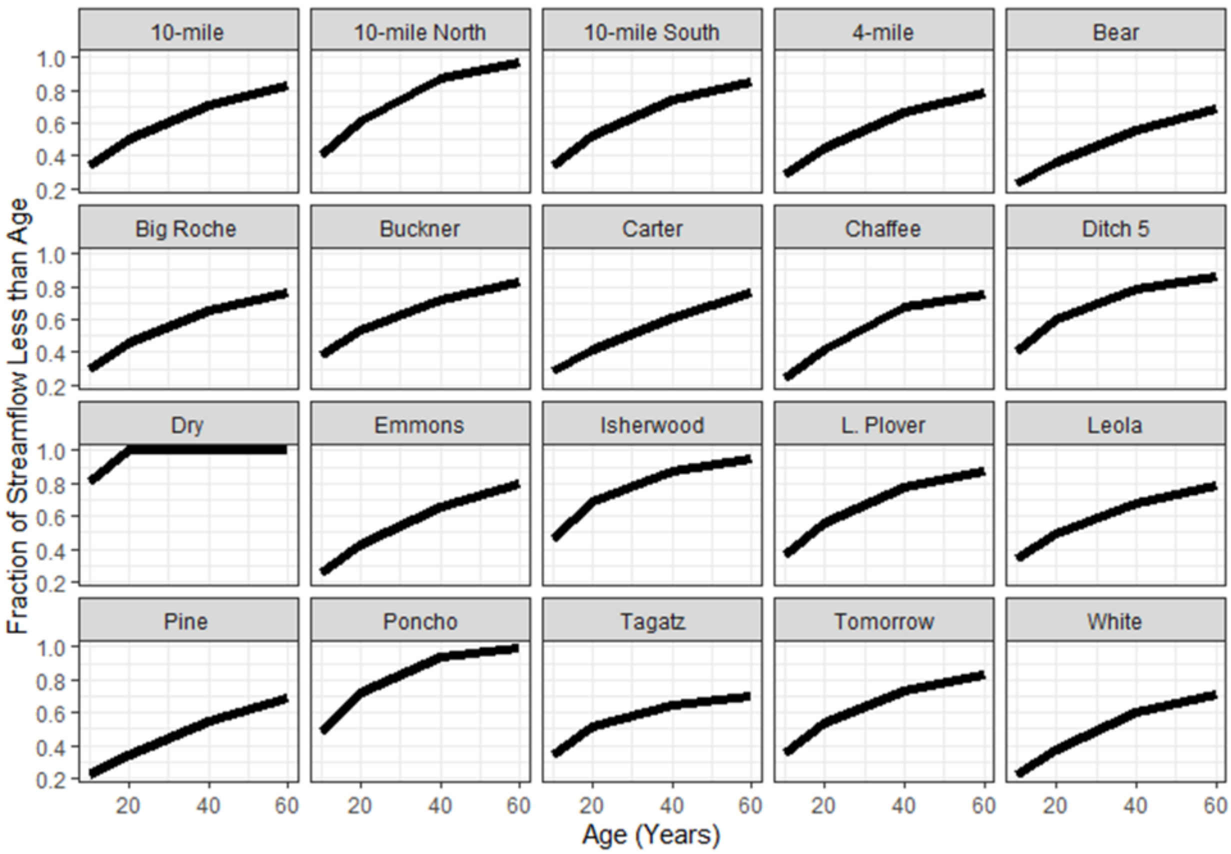


Figure 8. Streamflow age distribution for 20 sites monitored on the WCSP based on groundwater flow modeling.

Land cover within the groundwater contributing areas was primarily agricultural, forested and grassland. Less than 5% of the contributing area for any of the sites was urban. Agricultural land cover ranged from 25% to more than 80% of the groundwater contributing area for the different monitoring locations. The balance of the land cover was forest and grassland with some wetlands. Because neonicotinoids have only been used since the mid-1990s, we would not anticipate they would be entering streams in water from older travel time zones, therefore, we examined the relationships between land cover and neonicotinoid concentrations using the percentage of the entire contributing area that was occupied by land cover within a more recent travel time range. For example, Figure 9 shows how the imidacloprid concentration varies with agricultural and urban land cover that is within a 20-year travel time to the stream when that land is shown as the fraction of the entire groundwater contributing area. Relationships between neonicotinoid concentrations and land cover percentages are shown for urban and all agricultural land cover, all agricultural land cover, and only the potato/vegetable rotation of agricultural land cover. Those figures show that the strongest relationship is between neonicotinoid concentrations and the percentage of land in potato and vegetable rotations. The potato/vegetable rotation is the dominant agricultural land cover category in the study area. Because thiamethoxam and clothianidin usage has been more recent they are plotted in Figures 10 and 11, respectively, as a function of the agricultural land cover 10 years or less travel time from the stream. In all cases, the land cover can explain about one-half of the variation in concentrations. Including urban and all agricultural land cover leads to a more negative intercept in all cases and more variability consistent with a more variable and lower neonicotinoid loss rate for urban and some categories of agricultural land.

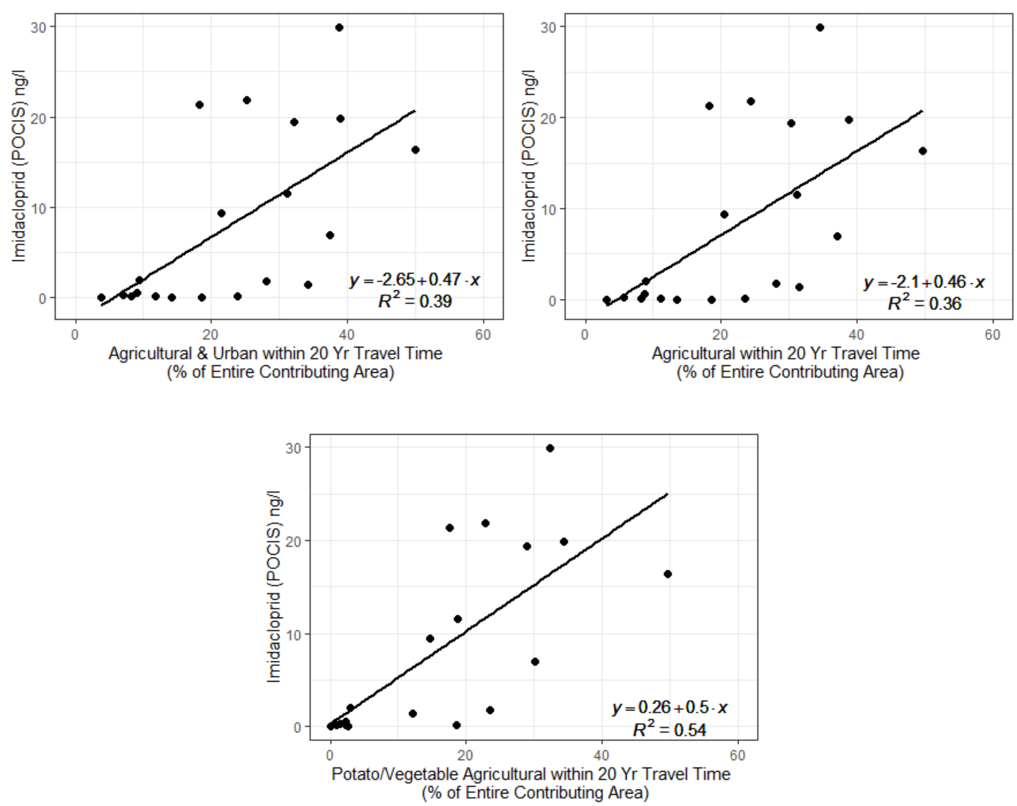


Figure 9. Relationships between imidacloprid concentrations and percentage of the groundwater contributing area from urban and agricultural land cover. The percentage coverage is expressed as the percentage of land within the entire groundwater contributing area that has that land cover with a travel time of less than 20 years to the stream.

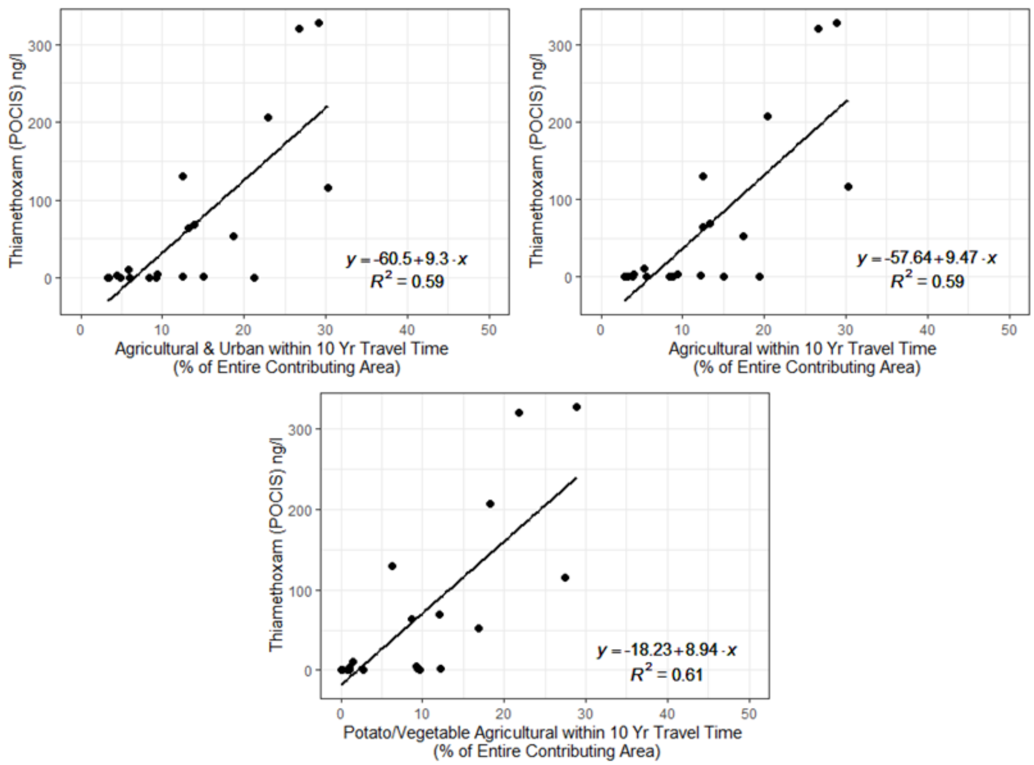


Figure 10. Relationships between thiamethoxam concentrations and percentage of the groundwater contributing area from urban and agricultural land cover. The percentage coverage is expressed as the percentage of land within the entire groundwater contributing area that has that land cover with a travel time of less than 10 years to the stream.

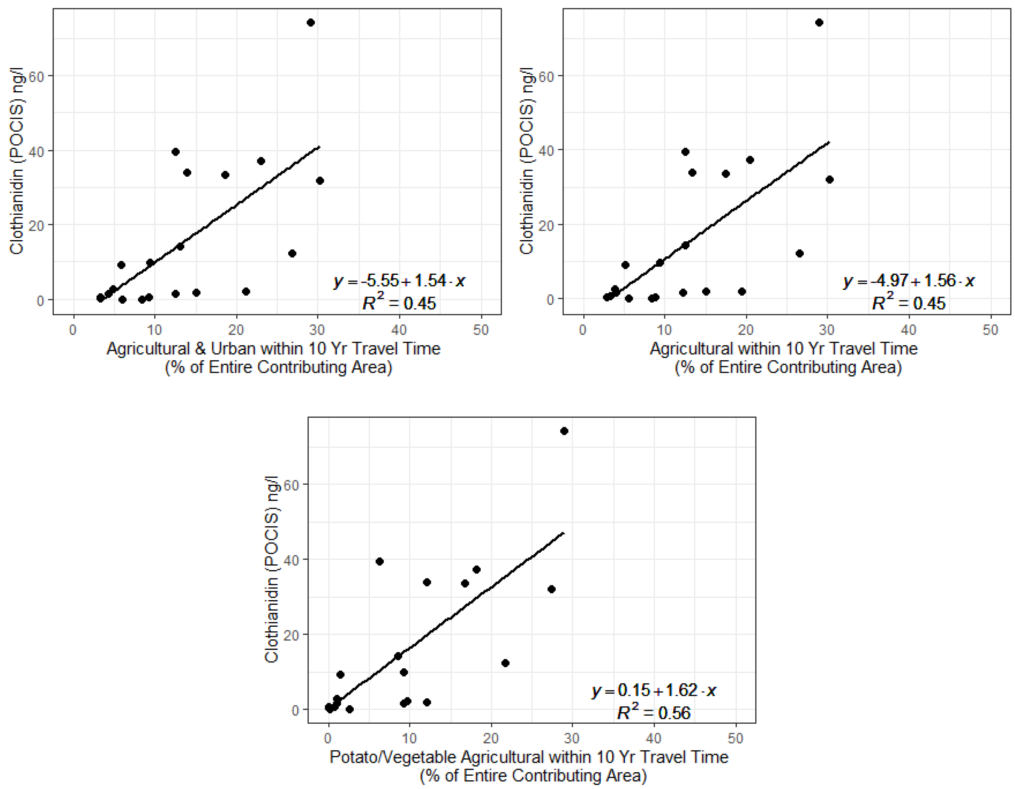


Figure 11. Relationships between clothianidin concentrations and percentage of the groundwater contributing area from urban and agricultural land cover. The percentage coverage is expressed as the percentage of land within the entire groundwater contributing area that has that land cover with a travel time of less than 10 years to the stream.

Environmental Relevance

The significance of the neonicotinoid detections can be evaluated through comparison with benchmark concentrations for aquatic life (ALBs). The EPA ALBs were often exceeded for imidacloprid and clothianidin on the west side of the divide where a greater proportion of land in the groundwater contributing area is used for agricultural purposes. Concentrations of thiamethoxam did not exceed the 740 ng/L chronic EPA ALB in any of the study sites.

It is important to also understand how the neonicotinoid concentrations will change in the future. Although these compounds are being applied to agricultural land throughout the groundwater contributing area, because it may take many decades for water to travel from the field to the stream, it is likely only the water within the 10- or 20-year travel time is currently discharging neonicotinoids to the stream. As a result, we can anticipate the concentration in the stream will continue to increase as a greater percentage of the flow is water that originated on the land after 2001 or 2011 (corresponding to the current 10- and 20-year contributing areas). We projected how those concentrations will change by using the current relationship between stream concentrations and land cover over the remainder of the contributing area based on the water age distribution for each monitoring location. The results, shown in Figure 12, projects imidacloprid concentrations could double over the next 40 years and the thiamethoxam and clothianidin concentrations may eventually be two to three times their current concentrations. These projections assume that there is no additional degradation of the compound during a longer travel time and that land cover and application rates do not change substantially. The projections are likely conservative in some cases as they assume the same loss rate applies to all categories of agricultural land in the groundwater contributing area. Figures 12, 13 and 14 show the projected concentrations of imidacloprid, thiamethoxam and clothianidin at the monitoring locations.

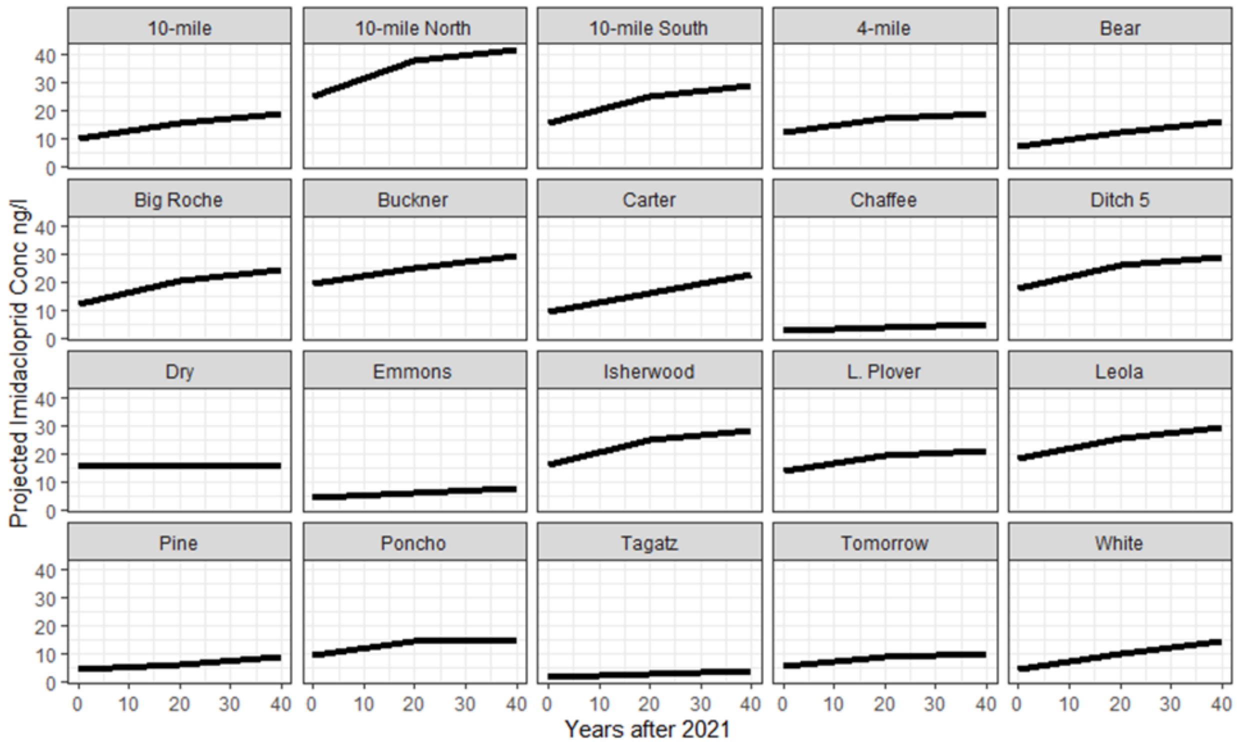


Figure 12. Projected stream concentrations of imidacloprid in years after 2021 assuming the current relationship between concentration and land cover (slope 0.5) and an increasing fraction of the water from post-2001 travel time zones.

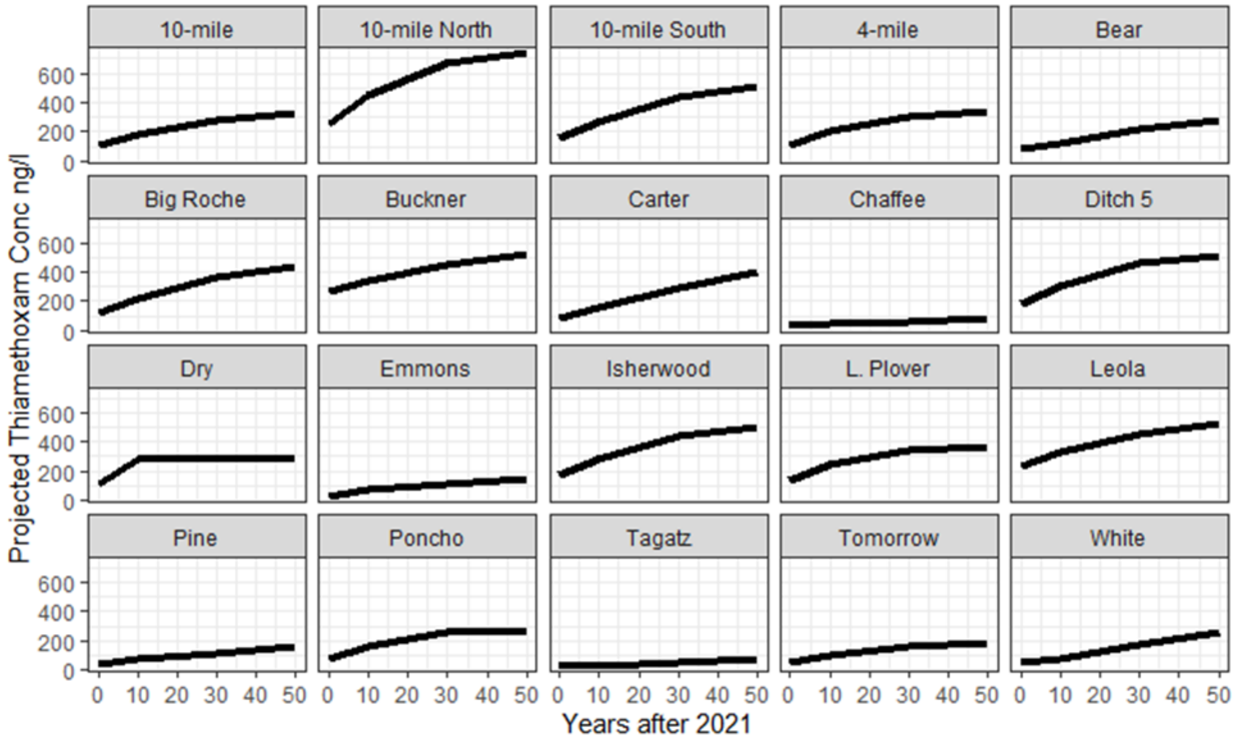


Figure 13. Projected stream concentrations of thiamethoxam in years after 2021 assuming the current relationship between concentration and land cover (slope 4.3) and an increasing fraction of streamflow from post-2011 travel time zones.

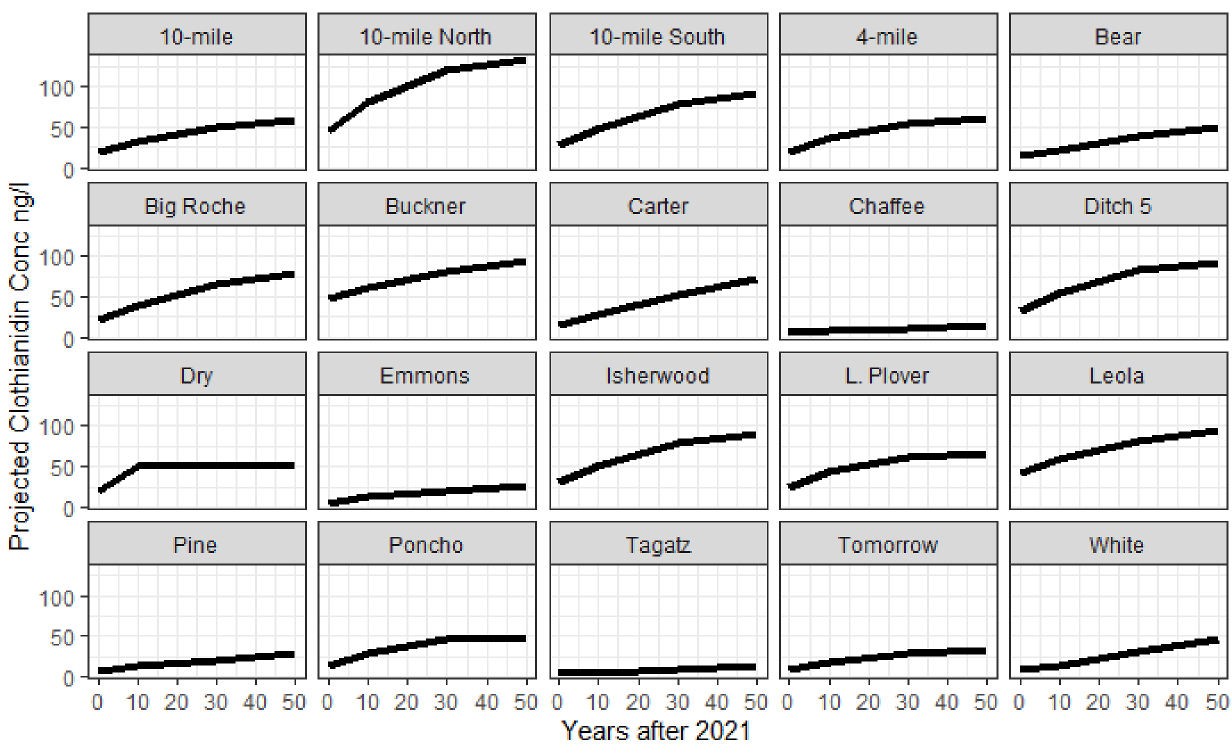


Figure 14. Projected stream concentrations of clothianidin in years after 2021 assuming the current relationship between concentration and land cover (slope 1.6) and an increasing fraction of streamflow from post-2011 travel time zones.

Phase Two

Seasonal variability of neonicotinoid insecticides

Seasonal variability of NNI concentrations in surface water were assessed in Phase Two of this study. The south branch of Tenmile Creek was the selected watershed because its contaminant levels (as determined in Phase One) were high enough to recognize changes, its accessibility throughout the year, and because of limited inputs from other tributaries. Roads throughout the WCSP are often unimproved and not maintained through the winter months and Tenmile South Branch crosses several maintained county roads that allow for accessibility year-round. POCIS were deployed at six locations from the headwaters of Tenmile South Branch near CTY Highway D to its confluence into Tenmile Creek. There were three additional sites on Tenmile Creek downstream to Hwy 13 which is approximately 5 kilometers from its confluence with the Wisconsin River. One additional site was located upstream of the confluence of the Tenmile South Branch and Tenmile Creek to assess contaminant contribution from Tenmile North Branch and other contributing ditches (Figure 4).

Streamflow and concentrations of NNIs varied somewhat throughout the year, however variability differed with compound and site. Changes at each site are displayed in Figures 15 (streamflow) and 16 (concentrations). Note that each point represents one POCIS-derived concentration for each NNI. The standard deviation of the average concentrations of NNIs ranged from 0.8 ng/L imidacloprid to 21.2 ng/L thiamethoxam over the 12-month period.

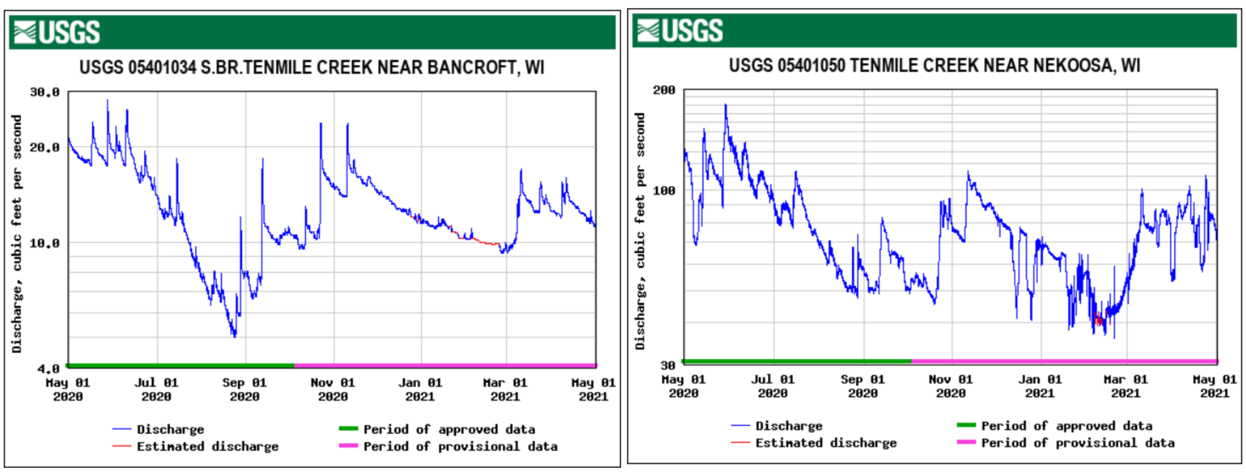
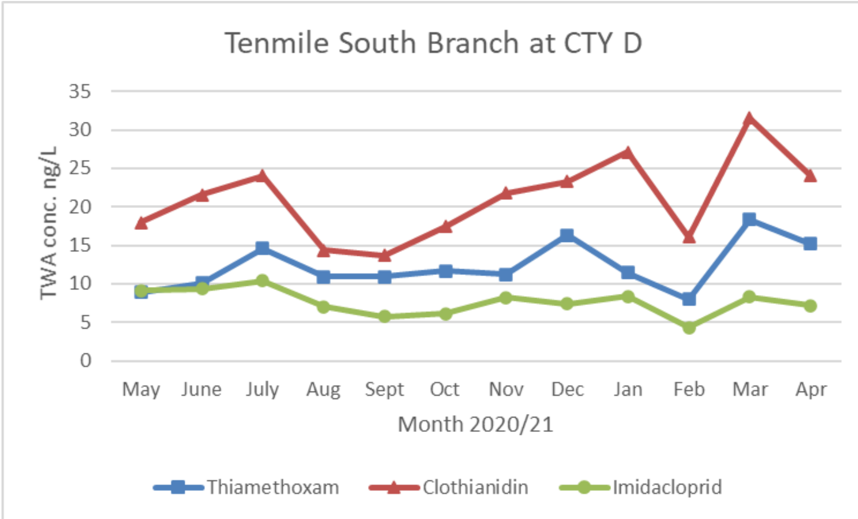
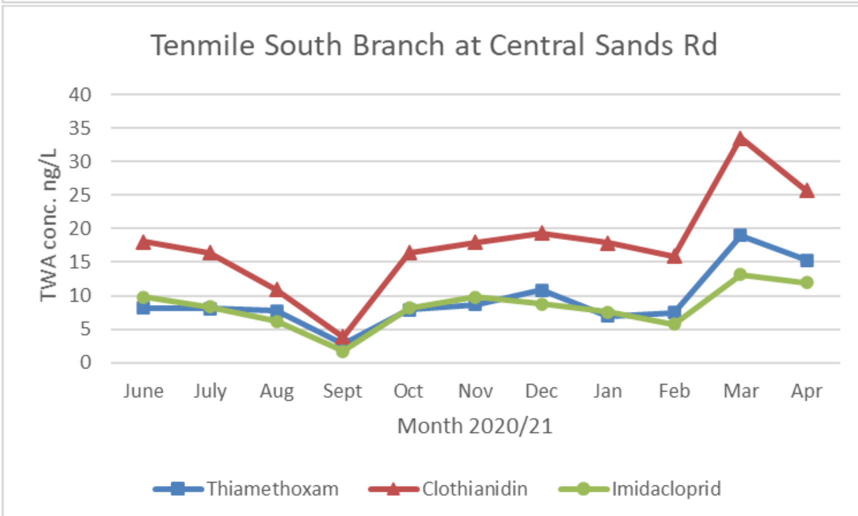
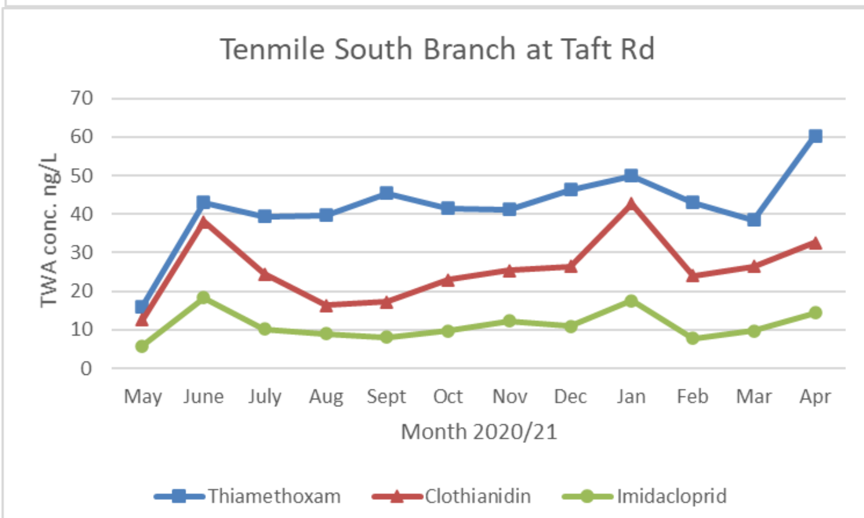
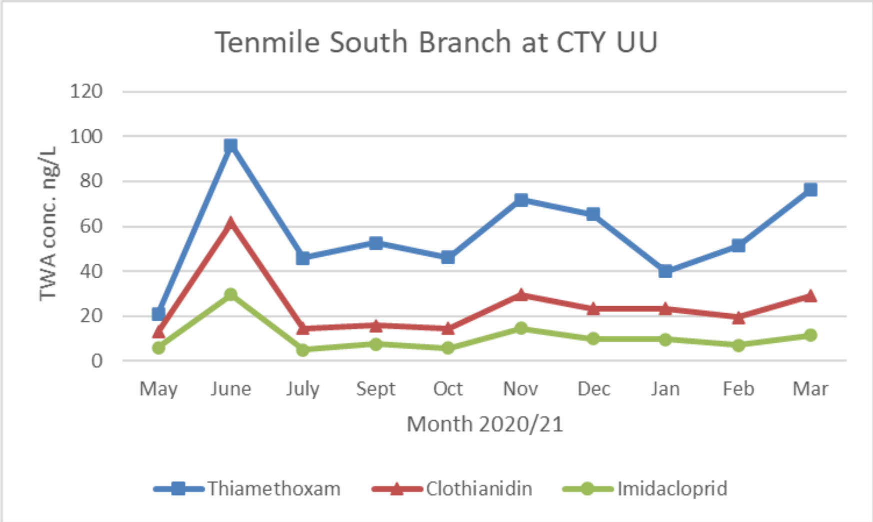


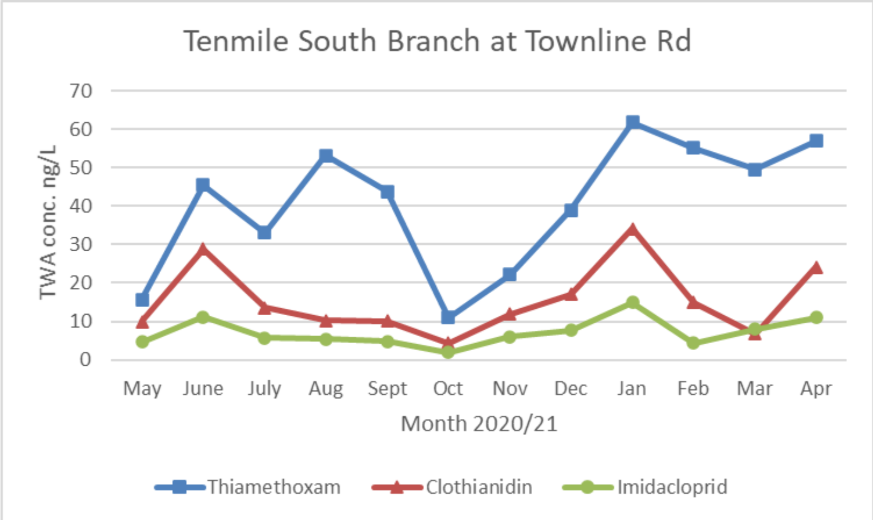
Figure 15. Streamflow on Tenmile Creek during Phase Two of this study. (www.usgs.gov)

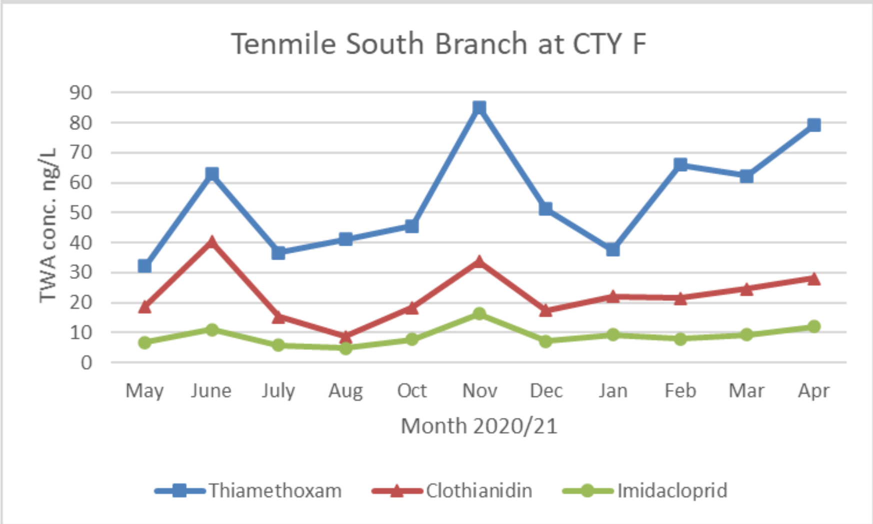

Tenmile South Branch at CTY D
TWA conc. ng/L
35
30
25
20
15
10
5
0
May
June
July
Aug
Sept
Oct
Nov
Dec
Jan
Feb
Mar
Apr
Month 2020/21
Thiamethoxam
Clothianidin
Imidacloprid

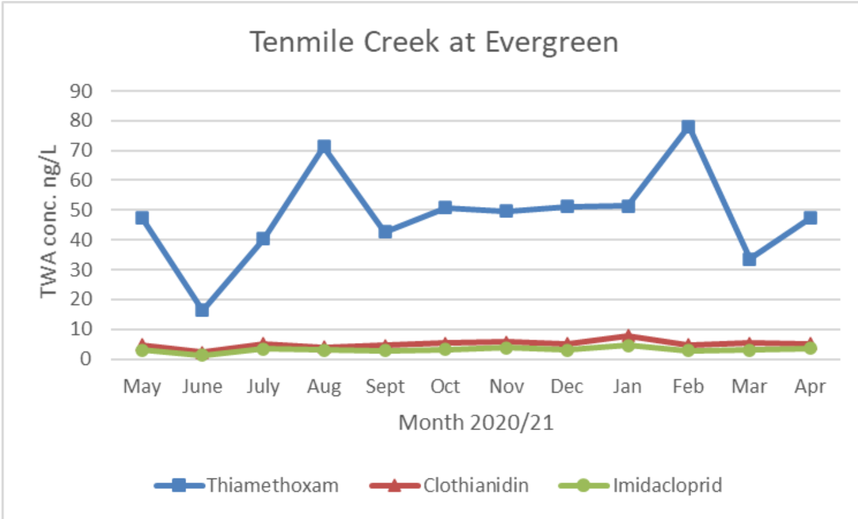

Tenmile South Branch at Central Sands Rd
TWA conc. ng/L
40
35
30
25
20
15
10
5
0
June
July
Aug
Sept
Oct
Nov
Dec
Jan
Feb
Mar
Apr
Month 2020/21
Thiamethoxam
Clothianidin
Imidacloprid

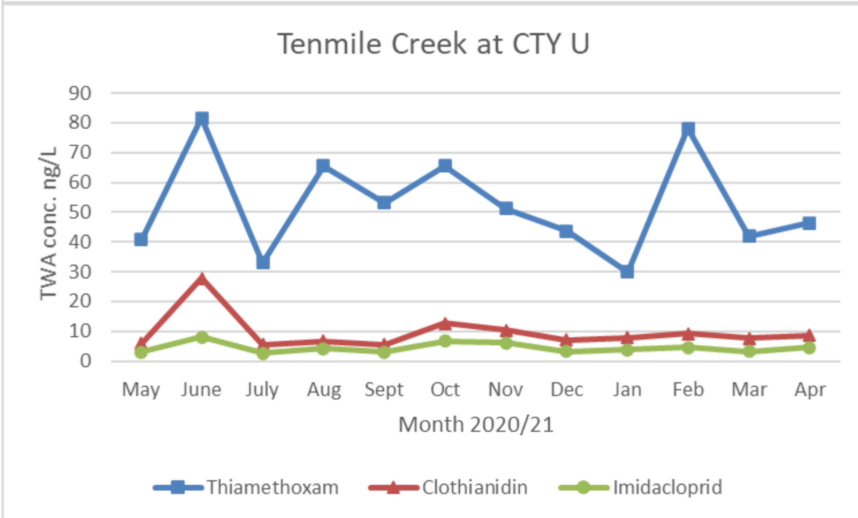

Tenmile South Branch at Taft Rd
TWA conc. ng/L
70
60
50
40
30
20
10
0
May
June
July
Aug
Sept
Oct
Nov
Dec
Jan
Feb
Mar
Apr
Month 2020/21
Thiamethoxam
Clothianidin
Imidacloprid


Tenmile South Branch at CTY UU
TWA conc. ng/L
0
20
40
60
80
100
120
May
June
July
Sept
Oct
Nov
Dec
Jan
Feb
Mar
Month 2020/21
Thiamethoxam
Clothianidin
Imidacloprid


Tenmile South Branch at Townline Rd
TWA conc. ng/L
0
10
20
30
40
50
60
70
May
June
July
Aug
Sept
Oct
Nov
Dec
Jan
Feb
Mar
Apr
Month 2020/21
Thiamethoxam
Clothianidin
Imidacloprid


Tenmile South Branch at CTY F
TWA conc. ng/L
0
10
20
30
40
50
60
70
80
90
May
June
July
Aug
Oct
Nov
Dec
Jan
Feb
Mar
Apr
Month 2020/21
Thiamethoxam
Clothianidin
Imidacloprid


Tenmile Creek at Evergreen
TWA conc. ng/L
90
80
70
60
50
40
30
20
10
0
May June July Aug Sept Oct Nov Dec Jan Feb Mar Apr
Month 2020/21
Thiamethoxam
Clothianidin
Imidacloprid


Tenmile Creek at CTY U
TWA conc. ng/L
90
80
70
60
50
40
30
20
10
0
May June July Aug Sept Oct Nov Dec Jan Feb Mar Apr
Month 2020/21
Thiamethoxam
Clothianidin
Imidacloprid

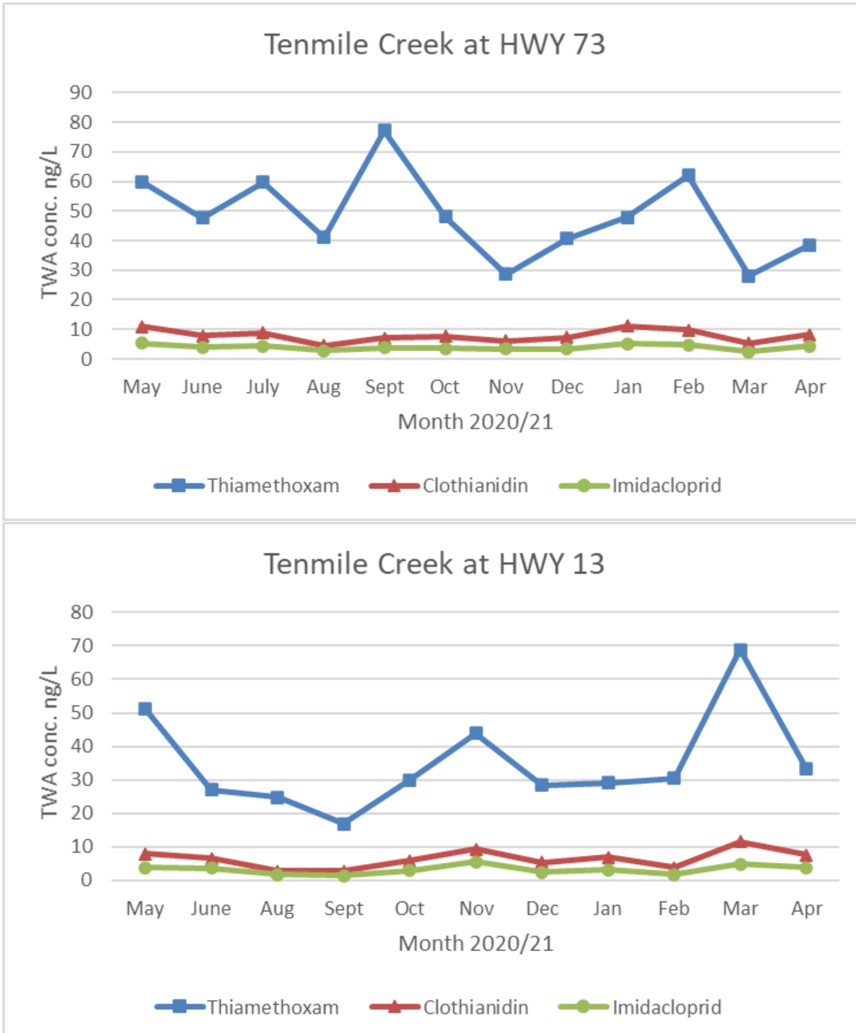


Figure 16. NNI time-weighted average (TWA) monthly surface water concentrations in the Tenmile Creek watershed by site and month.

Interestingly, the two sites in the headwater area (at CTY D and Central Sands Rd.- Figure 16) consistently displayed higher concentrations of clothianidin for the duration of the 12-month period, but further downstream, thiamethoxam became the more abundant NNI. Inputs from the northern tributaries appear to contribute a larger load of thiamethoxam. Figures 17 and 18 show how agriculture land cover within a ten-year travel time decreases from approximately 20% to 10% of the entire groundwater contributing area with distance downstream. Figure 19 shows that the average concentrations decrease downstream consistent with the reduction in agricultural land cover in the ten-year travel time area.

While the chronic EPA ALB for clothianidin is far less than thiamethoxam (50 and 740 ng/L respectively), clothianidin concentrations exceeded this benchmark in one POCIS sample while thiamethoxam never exceeded the criteria in any POCIS sample over the two-year study. The single exceedance of the clothianidin criteria occurred at the CTY UU site in June of 2020. That was the only ALB exceedance recorded for this compound.

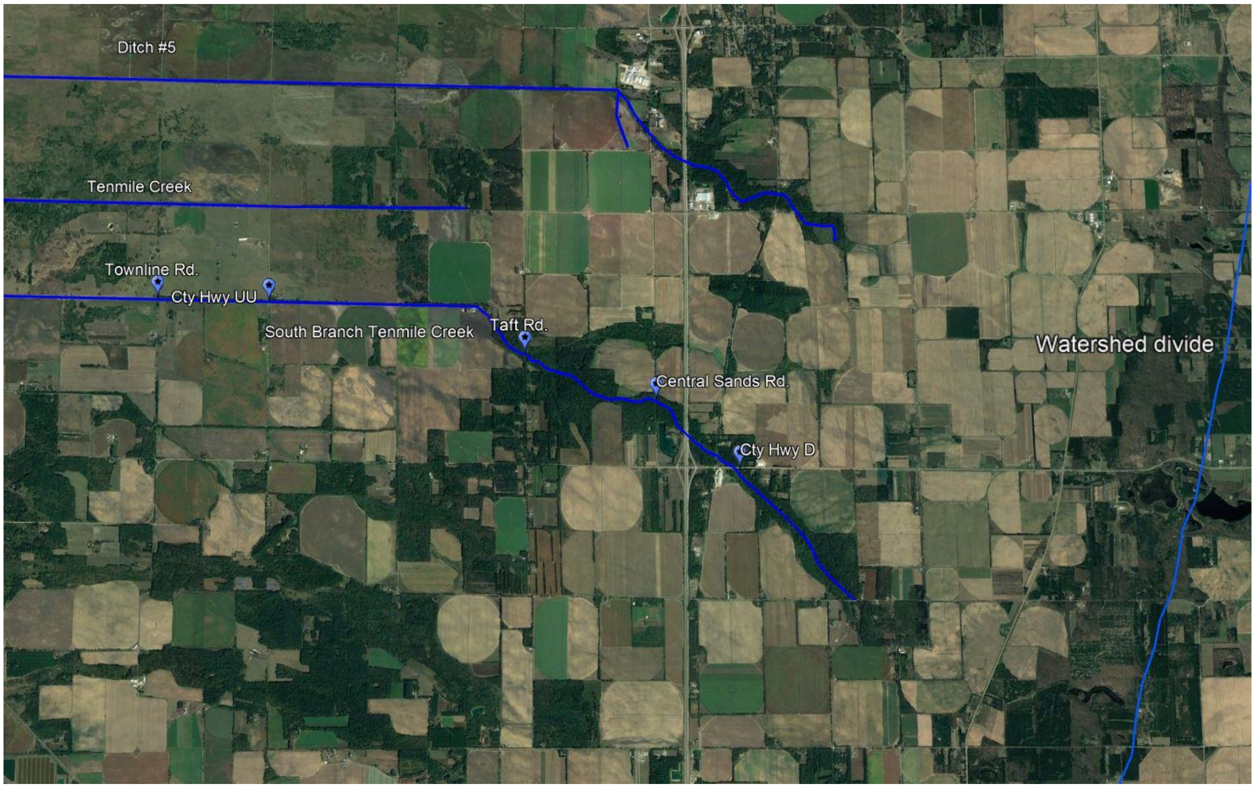


Figure 17. Land use in headwaters region of Tenmile South Branch Creek.

Imidacloprid often exceeded the chronic EPA ALB concentration of 10 ng/L. Imidacloprid was usually found at concentrations near the ALB with variations above and below that could occur due to flow changes influencing the groundwater contribution, or merely minor differences in recovery of compound within the analytical process. With higher chronic EPA ALBs, clothianidin concentrations less frequently exceeded these criteria.

With consideration to total NNI concentrations as suggested by Morrissey (5) and Tennekes (7,8), a benchmark of 35 ng/L total NNI is exceeded in 9 out of 20 sites (45%) monitored during Phase One of this study across the WCSP and 100 out of 114 samples (88%) collected during Phase Two of this study on the Tenmile watershed.

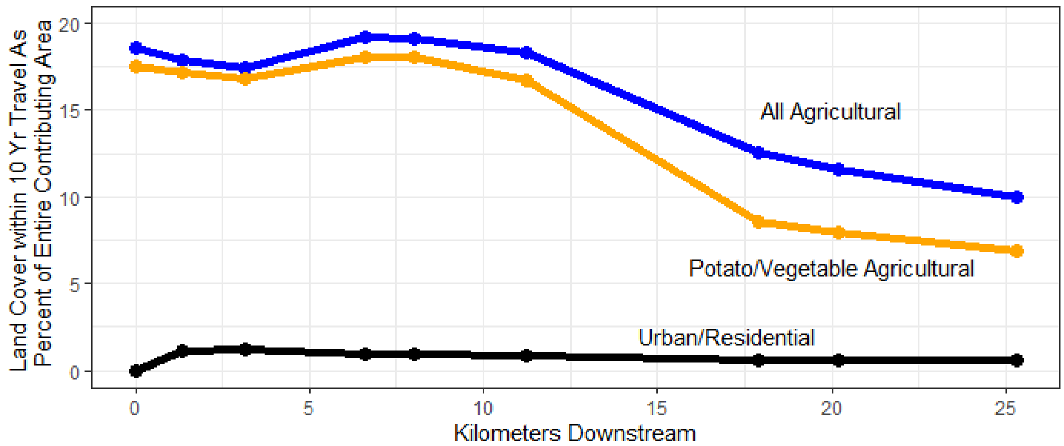


Figure 18. Land cover within a 10-year groundwater travel time of Tenmile Creek shown as a percentage of the total contributing area for each monitoring location.

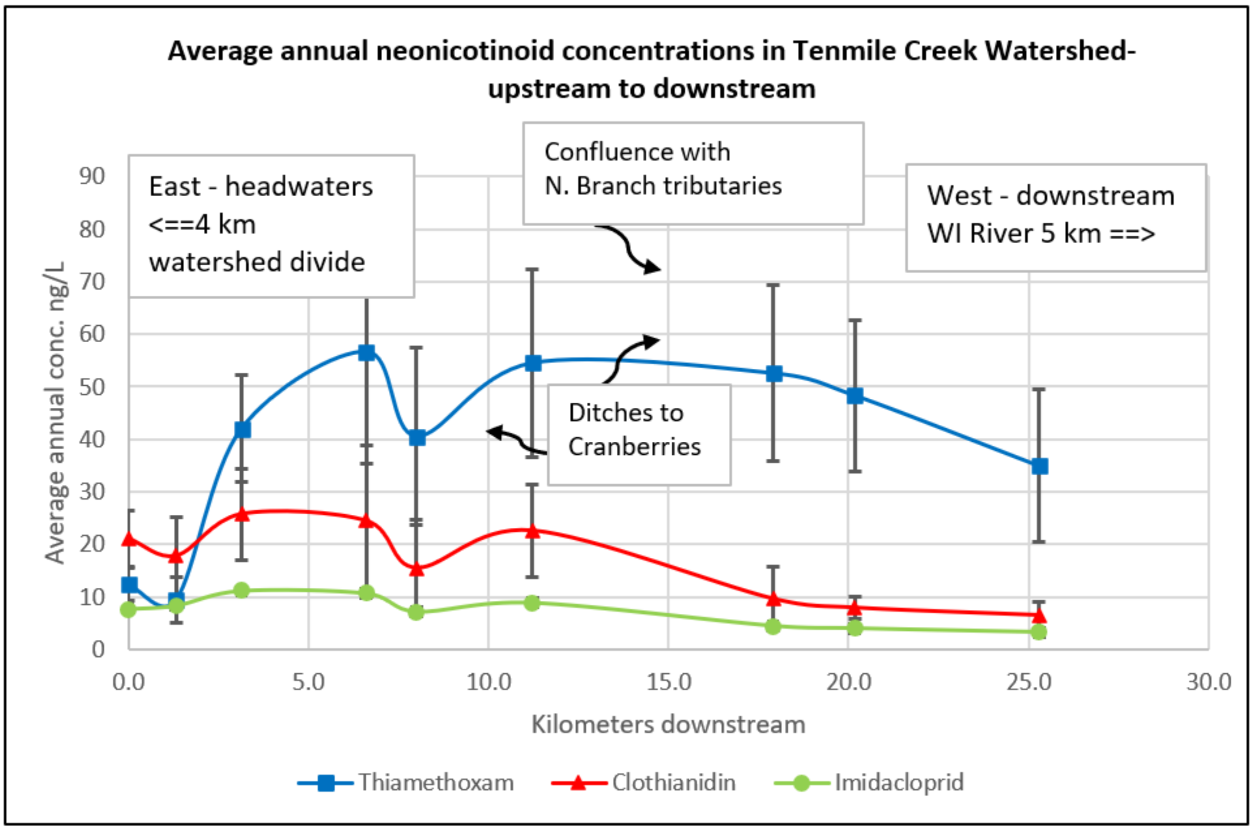


Figure 19. Annual average of monthly POCIS derived NNI concentrations with distance from headwaters.

Hyporheic Water

Hyporheic water was collected using mini-piezometers and analyzed four times in Phase Two of this study during August and November of 2020 and March and May of 2021. Results from four to five samples collected across the streambed at 30-60 cm of depth are displayed in Table 6. The sites are identified with the closest road crossing on Tenmile Creek South Branch, the date of sample collection, discharge on the date of collection, and NNI concentration. Identification of each sample point is distance from the northernmost edge of stream and then distance from that point. For example, "CTY D – 0 m" is the north edge of the stream and "CTY D – 1.1 m" is 1.1 meters from the north stream bank. Hyporheic water samples collected using mini piezometers displayed wide variations across the stream as evident by the CTY UU and CTY F samples.

Most hyporheic water sampled had concentrations lower than the surface water grab sample collected at the same site. Occasionally, a sample was obtained that displayed concentration greater than surface water and above EPA ALBs or those proposed by Morrissey. These data suggest distinct flowpaths exist that deliver a highly varied contaminant load and are consistent with the majority of the groundwater delivered to these streams having an age greater than the ten to twenty years of neonicotinoid application.

CTY D CROSS SECTION				
distance from north bank	8/24/2020	5.1 cfs		
	Thiamethoxam	Clothianidin	Imidacloprid	NO2+NO3
0 m	<1.5	<1.5	<2.3	0.5
1.1 m	<1.5	<1.5	<2.3	0.5
2.3 m	<1.5	<1.5	<2.3	0.5
3.3 m	<1.5	2.0	<2.3	13.5
Surface water	15.4	34.2	11.4	11.1
POCIS TWA	10.9	14.4	7.0	
distance from north bank	11/16/2020	17.2 cfs		
	Thiamethoxam	Clothianidin	Imidacloprid	NO2+NO3
0 m	<1.5	4.5	<2.3	4.2
1.2 m	<1.5	<1.5	<2.3	<0.1
2.4 m	<1.5	<1.5	<2.3	<0.1
3.7 m	<1.5	2.5	<2.3	5.2
Surface water	18.4	40.8	11.9	8.5
POCIS TWA	11.3	21.8	8.2	
distance from north bank	3/9/2021	12.7 cfs		
	Thiamethoxam	Clothianidin	Imidacloprid	NO2+NO3
0 m	5.3	3.8	3.5	6.2
1.1 m	<1.5	<1.5	<2.3	0.2
2.1 m	<1.5	<1.5	<2.3	<0.1
3.3 m	<1.5	<1.5	<2.3	<0.1
Surface water	23.3	54.9	14.9	12.7
POCIS TWA	18.3	31.6	8.3	
distance from north bank	5/11/2021	11.5 cfs		
	Thiamethoxam	Clothianidin	Imidacloprid	NO2+NO3
0 m	<1.5	20.5	<2.3	14.8
1.2 m	<1.5	<1.5	<2.3	0.1
2.4 m	<1.5	<1.5	<2.3	<0.1
3.7 m	<1.5	<1.5	<2.3	<0.1
Surface water	22.9	63.5	14.2	12.8
POCIS TWA	15.2	24.1	7.1	

CTY UU CROSS-SECTION				
distance from north bank	8/24/2020	5.1 cfs		
	Thiamethoxam	Clothianidin	Imidacloprid	NO2+NO3
0 m	<1.5	<1.5	<2.3	0.5
1.1 m	60.7	26.7	9.4	9.7
2.3 m	18.3	7.4	<2.3	13.9
3.3 m	114.9	65.0	<2.3	1.1
Surface water	81.2	37.3	15.0	12.2
POCIS TWA	lost	lost	lost	

distance from north bank	11/16/2020	17.2 cfs		
	Thiamethoxam	Clothianidin	Imidacloprid	NO2+NO3
0 m	<1.5	<1.5	<2.3	<0.1
1.5 m	<1.5	<1.5	<2.3	5.5
3.0 m	179.7	42.9	6.4	8.6
4.6 m	2.7	4.8	<2.3	0.9
Surface water	96.6	58.4	24.7	8.6
POCIS TWA	71.8	29.6	14.6	

distance from north bank	3/9/2021	12.7 cfs		
	Thiamethoxam	Clothianidin	Imidacloprid	NO2+NO3
0 m	<1.5	<1.5	<2.3	1.5
1.3 m	<1.5	<1.5	2.8	9.5
2.6 m	63.3	13.0	8.0	11.6
4.0 m	32.9	44.5	<2.3	<0.1
Surface water	91.8	54.0	22.5	no sample
POCIS TWA	76.2	29.1	11.5	

distance from north bank	5/11/2021	11.5 cfs		
	Thiamethoxam	Clothianidin	Imidacloprid	NO2+NO3
0 m	<1.5	<1.5	2.4	6.2
1.5 m	<1.5	<1.5	<2.3	10.7
3.0 m	71.4	17.4	9.9	15.1
4.6 m	97.8	76.4	<2.3	21.7
Surface water	96.5	62.2	21.2	13.6
POCIS TWA	lost	lost	lost	

CTY F CROSS-SECTION				
distance from north bank	8/24/2020	5.1 cfs		
	Thiamethoxam	**Clothianidin**	**Imidacloprid**	**NO2+NO3**
0 m	<1.5	<1.5	<2.3	0.6
1.2 m	<1.5	<1.5	<2.3	0.5
2.4 m	40.0	5.7	<2.3	0.5
3.7 m	1.6	<1.5	<2.3	0.5
4.9 m	<1.5	<1.5	<2.3	0.5
Surface water	70.0	27.4	11.7	10.1
POCIS TWA	41.1	8.8	4.7	
distance from north bank	11/16/2020	17.2 cfs		
	Thiamethoxam	**Clothianidin**	**Imidacloprid**	**NO2+NO3**
0 m	<1.5	<1.5	<2.3	<0.1
1.5 m	<1.5	<1.5	<2.3	<0.1
3.0 m	4.8	<1.5	<2.3	<0.1
4.6 m	<1.5	<1.5	<2.3	<0.1
6.1 m	<1.5	<1.5	<2.3	no sample
Surface water	89.8	43.9	19.0	
POCIS TWA	85.2	33.7	16.3	
distance from north bank	3/9/2021	12.7 cfs		
	Thiamethoxam	**Clothianidin**	**Imidacloprid**	**NO2+NO3**
0 m	4.9	<1.5	<2.3	<0.1
1.8 m	46.1	21.0	6.6	<0.1
3.7 m	6.1	<1.5	<2.3	<0.1
5.5 m	41.0	10.1	<2.3	10.2
Surface water	68.1	37.2	19.3	10.0
POCIS TWA	62.2	24.5	9.3	
distance from north bank	5/11/2021	11.5 cfs		
	Thiamethoxam	**Clothianidin**	**Imidacloprid**	**NO2+NO3**
0 m	<1.5	<1.5	<2.3	<0.1
1.4 m	<1.5	<1.5	<2.3	<0.1
2.7 m	<1.5	<1.5	<2.3	<0.1
4.1 m	<1.5	<1.5	<2.3	<0.1
5.5 m	<1.5	<1.5	<2.3	<0.1
Surface water	80.1	50.6	16.7	11.9
POCIS TWA	79.2	28.2	11.9	

Table 6. Hyporheic water from Tenmile Creek South Branch. Four sampling events all samples collected between 30-60 cm below streambed. NNI concentrations in ng/L, NO_2 + NO_3 in mg/L.

POCIS performance

The POCIS passive sampler performed satisfactorily when considering the many steps in the entire process of deployment, retrieval, removal of the sorbent, extraction, and analysis of the sorbent. Field replicates were conducted at a 10% frequency rate throughout the study. Phase

One consisted of four field duplicates while Phase Two had 10 successful monthly duplicates. Relative percent difference (RPD) of the three detected NNIs averaged from 16-32% (App B). While RPD is an often-used metric for precision, low concentrations will often record greater differences. However, it is noted that even at higher concentrations, RPD varied and there are several factors that might contribute to this. This could be due to an accumulation of fine sediment on the surface of the membrane that might limit water contact with the media, media that escaped the membrane during deployment or analytical process, reduced extraction efficiency, or interferences in the LC/MS process.

Unlike other passive samplers such as SPMDs, the POCIS do not typically rely upon a performance reference compound (PRC) (Alvarez, 2010). The PRC can provide an estimate of loss of an analyte after it has been accumulated by the passive sampler. With media-based passive samplers such as the POCIS, loss of an analyte is governed by the surrounding matrix (water in this case) and its ability to remove the analyte from the media. Typically, water is not a strong enough solvent to remove compounds from the HLB media in a POCIS (Alvarez, 2010). For this reason, PCRs were not used, and matrix spike recoveries were based up adding a NNI mixture to clean, unexposed HLB media, then extracted. Interferences were minimal in these spiked POCIS and therefore recoveries were typically >80%.

Typical POCIS deployment often rely upon multiple units (2-3) within one protective cage. This is often performed to combine POCIS extracts to achieve lower detections limits. It can also prove useful in the event of a puncture or an unexplained loss of media. Considering the cost of a POCIS ($65 each), ambient concentrations of NNIs in exploratory efforts in WCSP streams, and detection limits obtained by LC/MS, it was determined that lower detection limits were not necessary and a single POCIS per site was used. Out of 156 POCIS deployed during the two phases of this project, only three were invalidated due to loss of media (most likely from puncture), one was lost when the braided steel cable eroded, and two were lost to vandalism. This vandalism occurred with a field duplicate in September 2020 (CTY F site) where the devices were removed from the stream and suspended from an adjacent bridge structure. Altogether, 96% of all deployed POCIS were successfully returned for analysis.

CONCLUSIONS AND RECOMMENDATIONS

This study shows that both grab sampling and POCIS can effectively monitor NNIs in surface water or groundwater with detection limits far below regulatory standards or US EPA aquatic life benchmarks. Grab sampling followed by solid phase extraction of water samples combined with advanced instrumentation such as LC/MS can provide detection limits of < 5 ng/L. Time-weighted average (TWA) concentrations of NNIs determined with POCIS can provide detection limits that are < 1 ng/l. Selection of a sampling method should be based on the characteristics of the stream and goals of the study. In the baseflow dominated streams of the WCSP, the TWA concentration from the POCIS were similar to the grab samples. Watersheds with more overland flow from agricultural fields may experience greater changes in surface water concentrations than those seen here on the WCSP. In watersheds with more variable flow, a TWA concentration provided by a POCIS or other similar passive device would be useful to determine chronic exposure levels of NNIs.

NNIs were pervasive in surface water throughout the WCSP where land includes irrigated agriculture, cranberry production, and grasslands. Concentrations were correlated with agricultural land use and by assuming only the more recent groundwater entering the stream is impacted, relationships between land cover and neonicotinoid concentrations were developed.

Concentrations of clothianidin and imidacloprid exceeded the EPA ALB in nine of the 20 sites in the WCSP stream survey conducted in 2019. Thiamethoxam concentrations did not approach the EPA ALB in any of the sites surveyed. However, if the toxicological concerns expressed by Morrissey (2015) and Tennekes (2010) are considered, then ecological damage would be expected to populations of aquatic invertebrates at the concentrations observed. Total NNIs exceeded their benchmark of 35 ng/L level in 45% of the sites monitored during the 20-stream survey across the WCSP and in 88% of all samples collected during the 12-month study on Tenmile Creek watershed. Our projections of future concentrations, assuming that the current relationships between land cover and concentrations can be extrapolated to groundwater that will take longer to arrive at the stream, suggest that many of these concentrations may double or triple. Since there is now an understanding of NNI concentrations in surface water across the WCSP, biological surveys should be conducted across these sites to investigate the connection between NNIs and aquatic invertebrate populations to assess changes with predicted contaminant increases.

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APPENDIX A: Awards, Publications, Reports, Patents, Presentations, Students, Impact

Presentations:
DeVita, W.M. Use of passive sampling devices to monitor neonicotinoid insecticides in surface water on the Central Sand Plain. The Wisconsin Potato and Vegetable Growers Association Annual meeting. February 2020.
DeVita, W.M. Use of Polar Organic Chemical Integrative Samplers (POCIS) to monitor neonicotinoid insecticides in surface water on the Central Wisconsin Sand Plain. Wisconsin Chapter of the American Water Resources Association, annual (virtual) meeting. March 2021.
DeVita, W.M. Use of Polar Organic Chemical Integrative Samplers (POCIS) to monitor neonicotinoid insecticides in surface water on the Central Wisconsin Sand Plain. Groundwater Coordinating Council, May 2021.

Hankard, M., D. Franzke, A Dremel, W. DeVita, P. McGinley. A neonicotinoid concentration and agricultural land use comparison between two headwater streams in Central Sands region of Wisconsin. UW-Stevens Point College of Natural Resources Undergraduate Research Symposium, April 2020.

Students participated in efforts to collect surface water samples, construct POCIS deployment cages, assemble POCIS for deployment, deploy, retrieve, and analyze POCIS devices. Students also engaged in land use assessment in surface watersheds to understand a relationship between crops and neonicotinoids in stream. This required GIS mapping skills and watershed delineation techniques. This assessment was not used in the final report as it was limited to surface watersheds, while this report focuses on ground watersheds. Students who worked directly on this project include Dylan Franzke, Maxwell Hankard, Abby Dremel, Jacob Gerner, Nicholas Wiedemann, Adam Laehn, and Sam Krebsbach.

APPENDIX B:

PHASE 1 STUDY SITE LOCATIONS

SITE No.	Date deployed	Date retrieved	Location Name	Crossing	Side of divide	Latitude	Longitude	Q avg (cfs) baseflow
1	8/20/2019	9/20/2019	Poncho Creek	CTY Z	East	44°34'9.84"N	89°19'28.27"W	1.4
2	8/20/2019	9/20/2019	Tomorrow River	Clementson Rd.	East	44°31'27.75"N	89°20'19.39"W	24.3
3	8/20/2019	9/20/2019	Little Plover River	UWSP/DNR wetlands lab	West	44°28'15.59"N	89°30'13.37"W	3.8
4	8/20/2019	9/20/2019	Isherwood Creek	Isherwood Rd. at footbridge	West	44°23'46.52"N	89°30'09.38"W	6.8
5	8/20/2019	9/20/2019	4-mile creek	CTY JJ and BB	West	44°22'03.77"N	89°28'25.93"W	1.9
6	8/23/2019	9/20/2019	Bear Creek at Q	CTY Q	East	44°26'06.24"N	89°18'33.01"W	14.5
7	8/22/2019	9/20/2019	Emmons Creek	Rural Rd.	East	44°18'55.71"N	89°11'34.04"W	24.0
8	8/22/2019	9/20/2019	Pine River	Apache Rd.	East	44°11'42.83"N	89°10'57.97"W	44.9
9	8/22/2019	9/20/2019	West branch White River	HWY 22	East	44°02'56.82"N	89°17'40.41"W	26.5
10	8/22/2019	9/20/2019	Chaffee Creek	CTY B	East	43°58'29.03"N	89°26'35.23"W	20.4
11	8/22/2019	9/20/2019	Tagatz Creek	CTY CH	East	43°57'21.89"N	89°29'37.08"W	6.2
12	8/22/2019	9/25/2019	Carter Creek	1st Ave.	West	44°05'44.49"N	89°35'52.18"W	2.7
13	8/22/2019	9/25/2019	Dry Creek	1st Ave.	West	44°07'44.99"N	89°35'51.68"W	2.6
14	8/22/2019	9/25/2019	Big Roche-a-cri	1st Ave.	West	44°10'34.17"N	89°35'52.51"W	11.7
15	8/27/2019	9/25/2019	Buckner Creek	4th and Beaver	West	44°08'28.23"N	89°39'31.23"W	5.9
16	8/27/2019	9/25/2019	Leola Ditch	CTY D and 5th	West	44°12'50.08"N	89°40'41.42"W	
17	8/27/2019	9/25/2019	10-mile creek	U/80th St.	West	44°16'17.37"N	89°43'27.72"W	53.0
18	8/27/2019	9/25/2019	10-mile south branch	Taft Rd.	West	44°16'18.33"N	89°32'56.10"W	7.3
19	8/27/2019	9/25/2019	Ditch 5 Taft and Mill Rds.	Taft Rd.	West	44°18'08.28"N	89°32'58.62"W	6.3
20	8/27/2019	9/25/2019	10-mile north branch	Harding Rd.	West	44°17'24.29"N	89°30'31.40"W	1.2

PHASE 2 STUDY SITE LOCATIONS

SITE No.		Location Name	Crossing	Side of divide	Latitude	Longitude
1	monthly sampling	Tenmile South Branch	CTY D	West	44°15'35.60"N	89°30'51.82"W
2	monthly sampling	Tenmile South Branch	Central Sands Rd.	West	44°15'59.11"N	89°31'42.51"W
3	monthly sampling	Tenmile South Branch	Taft Rd.	West	44°16'18.33"N	89°32'56.10"W
4	monthly sampling	Tenmile South Branch	CTY UU	West	44°16'40.26"N	89°35'20.74"W
5	monthly sampling	Tenmile South Branch	Townline Rd.	West	44°16'41.97"N	89°36'23.65"W
6	monthly sampling	Tenmile South Branch	CTY F	West	44°16'43.95"N	89°38'48.51"W
7	monthly sampling	northern trib confluence	Evergreen Rd.	West	44°17'26.47"N	89°40'56.31"W
8	monthly sampling	Tenmile Creek	CTY U/80th	West	44°16'17.37"N	89°43'27.72"W
9	monthly sampling	Tenmile Creek	HWY 73	West	44°15'48.92"N	89°45'06.03"W
10	monthly sampling	Tenmile Creek	HWY 13	West	44°15'43.92"N	89°48'37.14"W

Relative percent differences of replicate field-exposed POCIS.

			Days	Thiamethoxam		Clothianidin		Imidacloprid	
PHASE ONE	Deployed	Retrieved	deployed	Final Conc.	RPD	Final Conc.	RPD	Final Conc.	RPD
Carter Creek	8/22/2019	9/25/2019	34	4.6	16%	9.9	18%	21.4	19%
Carter Creek field duplicate				4.0		8.3		17.7	
Ditch 5	8/27/2019	9/25/2019	29	205.4	2%	37.2	1%	29.9	5%
Ditch 5 field duplicate				208.9		37.7		31.5	
PHASE TWO									
HWY 73	5/2/2020	5/31/2020	29	31.3	63%	6.9	46%	3.5	43%
HWY 73 duplicate				60.0		11.0		5.4	
HWP 13	5/31/2020	7/2/2020	32	26.7	2%	6.8	6%	3.4	5%
HWP 13 field duplicate				27.1		6.4		3.6	
CTY U	7/2/2020	7/31/2020	29	32.6	2%	5.0	18%	2.4	21%
CTY U field duplicate	7/2/2020	7/31/2020	29	33.4		6.0		2.9	
Evergreen	7/31/2020	9/1/2020	32	98.0	74%	4.6	27%	3.3	25%
Evergreen field duplicate				44.8		3.5		2.6	
CTY F	9/1/2020	10/2/2020							
CTY F field duplicate	This field duplicate was vandalized - removed from the stream and hung over the bridge railing.								
Evergreen	10/2/2020	11/2/2020	31	30.1	81%	4.2	40%	2.6	36%
Evergreen fiel duplicate				71.3		6.4		3.7	
Townline	11/2/2020	12/2/2020	30	23.4	10%	12.6	11%	6.3	9%
Townline field duplicate				21.1		11.3		5.7	
CTY UU	12/2/2020	1/2/2021	31	65.2	43%	23.4	40%	9.9	40%
CTY UU field duplicate				41.9		15.5		6.6	
Taft Rd.	1/2/2021	2/2/2021	31	52.2	9%	46.9	20%	19.2	19%
Taft Rd. field duplicate				47.7		38.3		15.9	
Taft Rd.	2/2/2021	3/2/2021	28	36.3	31%	24.2	2%	8.2	10%
Taft Rd. field duplicate	2/2/2021	3/2/2021	28	49.6		23.8		7.4	
Central Sands	3/2/2021	4/2/2021	31	media lost from POCIS					
Central Sands field duplicate				19.0		33.5		13.1	
CTY D	4/2/2021	5/4/2021	32	29.1	55%	84.7	42%	27.4	55%
CTY D field duplicate				16.5		55.2		15.6	
				Average RPD	32%		23%		24%