Technical Report 006 • 2020

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UNIVERSITY OF WISCONSIN–MADISON

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Photo credits

Front: Mink River Estuary, Peter Chase
Back: Three Springs, David Hart

All other photos by David Hart, except figure 4a (p. 11) by Kari Hagenow, and the MR3 well (p. 22) and the Ridges (p. 43) by Peter Chase.

Contents

Figures

Tables

Introduction

Wetlands are areas where the water table is at or near the surface for much of the year with plant species adapted to wet soil conditions. Wetlands exist between terrestrial and aquatic systems and are important for water purification and providing plant and animal habitat. Door County, the narrow peninsula in eastern Wisconsin, is home to numerous wetlands, many of which are fed by groundwater. Poor-quality groundwater discharging to a wetland can alter the ecology of a wetland and harm native plant and animal communities. Protecting and sustaining these wetlands and the habitat they provide must include consideration of groundwater quality.

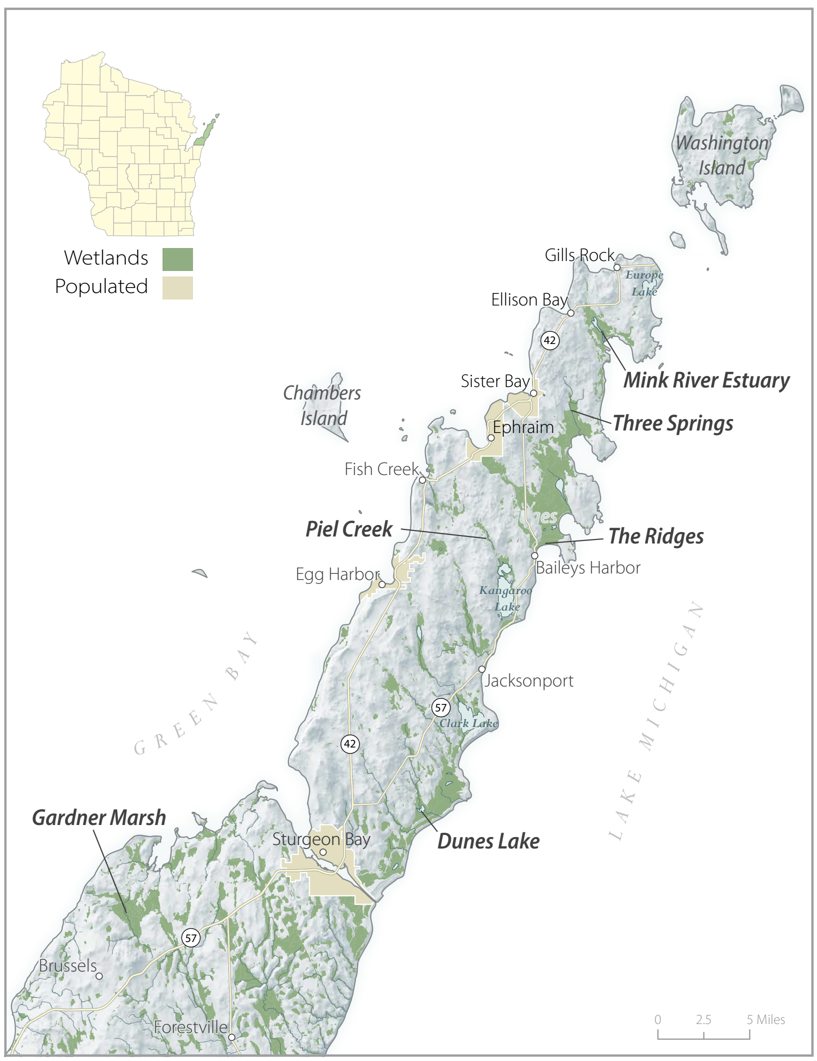
The addition, or loading, of nutrients and contaminants to Door County's coastal wetlands may support the invasion and spread of aggressive non-native plants (Surratt and others, 2012) and may harm the viability of the population of the endangered Hine's emerald dragonflies.

In most of Door County, private septic system effluent and landscape/agricultural chemicals have the potential to move through the thin soil layer into the underlying karst bedrock and groundwater aquifer. Once in the aquifer, this nonpoint source pollution (organic matter, nutrients, bacteria, viruses, herbicides, and various chemicals) has the potential to rapidly move down gradient, and discharge into a receiving lake, river, stream, or wetland with little filtration or attenuation.

We selected six representative wetlands for contaminant sampling and flow measurements made over the course of a year (September 2017–June 2018). Those wetlands are Mink River Estuary, Three Springs, Piel Creek, the Ridges, Dunes Lake, and Gardner Marsh (fig. 1). These wetlands ranged in ecological quality from high quality with a Ramsar designation (Ramsar Sites Information Service, 2015)—Mink River Estuary—to severely degraded by excess nutrients—Dunes Lake. Water samples were collected from springs discharging into each wetland. We also collected groundwater samples from wells and surface water samples from streams at locations near some of the wetlands.

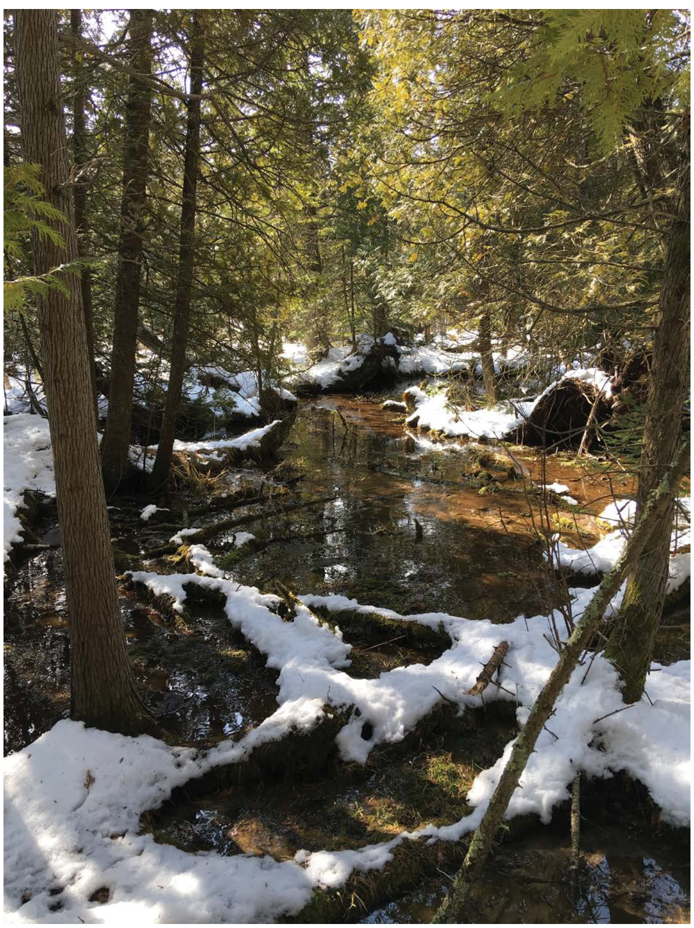
The six study wetlands were chosen because they had been previously studied or were important habitat. The Mink River Estuary, Three Springs, Piel Creek, the Ridges, and Gardner Marsh were all identified as habitat for the Hine's emerald dragonfly, an insect on the federal and Wisconsin

Figure 1. Wetlands, rivers, and streams in Door County. The six wetlands in the study are labeled.



endangered species lists. Cobb and Bradbury (2008) determined groundwater-contributing areas for these five wetlands. Groundwater flows and geology at the Mink River Estuary were studied by Bradbury and others (2012) and by Heimstead and Muldoon (2012). Evenson (2004) and Sager and others (2007) studied the surface and groundwater at the Ridges. Evenson (2004) found high chloride levels in some of the samples and considered whether the source was road salt or septic systems. Dunes Lake, the most degraded of all the wetlands was the subject of a comprehensive study by Johnson and others (2013) including groundwater contributing zone analysis and nutrient loading.

We designed this study to assist land managers of the six wetlands by (1) documenting the current state of water quality and quantity discharging to the wetlands and (2) linking land use to the contaminants found in the wetlands. For the first goal, we tested the wetlands for the presence of major ions (sodium, potassium, calcium, magnesium, chloride, sulfate, and bicarbonate), nitrate, phosphorus, metals, caffeine, artificial sweeteners, enterococci bacteria, and pesticides (including neonicotinoids). We also measured surface water flows into and out of the wetlands. These data provide a snapshot of water quality and flows that was not available for most of these wetlands before this study. The second goal was to link land use in areas contributing groundwater to the wetlands with the contaminants observed in the water discharging to the wetlands. Some contaminants, such as caffeine and artificial sweeteners, indicate a human source, most likely a septic system (Nitka and others, 2019). Other contaminants, such as ESA metolachlor, a metabolite of a common herbicide, indicate an agricultural source (Cook and others, 2017).



The Ridges | Distributed seeps near sample point

To link land use to potential nutrients and contaminants, we identified the zone of contribution (ZOC), or the land area that contributes water, for each of the sampled wetland springs. Within each ZOC we then used locations of housing/septic systems to determine residential densities and agricultural crop data to determine percent of cropland and within the cropland areas, the percent of corn in the ZOCs. The percent cropland and percent corn in a ZOC was averaged over 2015, 2016, and 2017 to account for variation in crops due to crop rotation schedules. We limited the average time to the three years before sampling due to the fast transport times expected in the dolomite. The correlations between water quality, human and agriculturally sourced contaminants, residential density, percent cropland, and percent corn were calculated.

All data and sampling locations, as well as this report have been submitted to the Wisconsin Department of Natural Resources Surface Water Integrated Monitoring System (SWIMS) database.

Study design and methods

Site descriptions

The six wetlands share a similar geologic setting. Silurian dolomite underlies the entire peninsula and dips to the east, often cropping out in the wetlands. Most wetlands in Door County form on low areas on the bedrock surface and extend east in bedrock valleys to Lake Michigan (fig. 1). The prevalence of wetlands on the east shore of Door County is likely due to the dipping bedrock. In this study, the two exceptions in wetland location and morphology are Gardner Marsh and the Ridges wetlands. Gardner Marsh is located in southwestern Door County and although it has no obvious coastal connection, it occupies a sediment-filled extension of the Ahnapee River valley (Carson and others, 2016). The Ridges wetlands are located in a series of sandy ridges and swales that formed during higher lake levels in Lake Michigan approximately 1,000 years ago (Johnson and others, 1990). The sample points for the Ridges are at the inland and west edge of the ridges and swales.

Springs and seeps often discharge into the wetlands at bedding plane fractures in the dolomite at multiple locations. For example, the springs sampled in this study at Mink River (Muldoon and others, 2001; Bradbury and others, 2012), Three Springs, and Gardner Marsh are all linked to bedding plane fractures in the dolomite. Organic and glacial sediments overlie the dolomite. The thickness of these sediments is generally less than 20 feet (ft) but varies over each wetland.

Figures 2a–f show aerial images of the wetlands, including locations of sampling sites and stream gaging.

Water sampling

We conducted four rounds of sampling (early fall, midwinter, spring during snowmelt, and early summer) to capture as much variation in groundwater flow patterns and land management practices as possible over the course of the study. We expected the results to show significant water quality variation over the sample year due to the fast travel times in the dolomite.

The following field collection protocol was used for all laboratory samples:

Each sample location had a dedicated peristaltic pump and tubing. Placement of the tubing depended on the type of site being sampled. For springs, tubing was placed at the spring vent (fig. 3a). For streams, the tubing was placed in the center third of the stream's width and the center third of the stream's depth (fig. 3b). For wells, the tubing was placed at the center of the well screen and pumped at a low level to achieve low-flow sampling rates (Sevee and others, 2000). Sample locations are shown in figures 2a–f.

Water was pumped into a flow-through cell until field parameters (temperature, pH, conductivity, and dissolved oxygen) stabilized, usually after 10–20 minutes. Parameters were measured using an Oakton Con 10 pH/conductivity meter and an Oakton DO6+ dissolved oxygen meter. The dissolved oxygen meter did not work at temperatures below –10°C; in those conditions, locations were pumped for at least 10 minutes after the temperature, pH, and conductivity had stabilized.

Samples were collected in lab-supplied bottles specific to the type of analysis, placed on ice, and shipped overnight to the appropriate laboratory. The University of Wisconsin–Stevens Point Water and Environmental Analysis Laboratory analyzed samples for major ions, low-level neonicotinoids, and pharmaceuticals and personal care products (PPCPs); the Wisconsin Department of Agriculture, Trade, and Consumer Protection laboratory analyzed samples for pesticides.

Because levels of detection for caffeine, artificial sweeteners, and neonicotinoids are measured in nanograms/liter (ng/L), we avoided the potential for contamination of samples by eliminating use of tobacco, caffeinated beverages, sunscreen, and insect repellents in the vehicle and during sampling. We also wore fresh latex gloves at each location. The dedicated tubing from each site was stored in labeled resealable bags that were, in turn, stored in a covered bin.

To assure quality control, field blanks for two of the four sampling rounds were submitted using Millipore water supplied by the laboratory; for the other two sampling rounds, duplicate samples were submitted. Test results for the field blanks and duplicates are included in the results section.

Figure 2a. Mink River Estuary and sampling points.

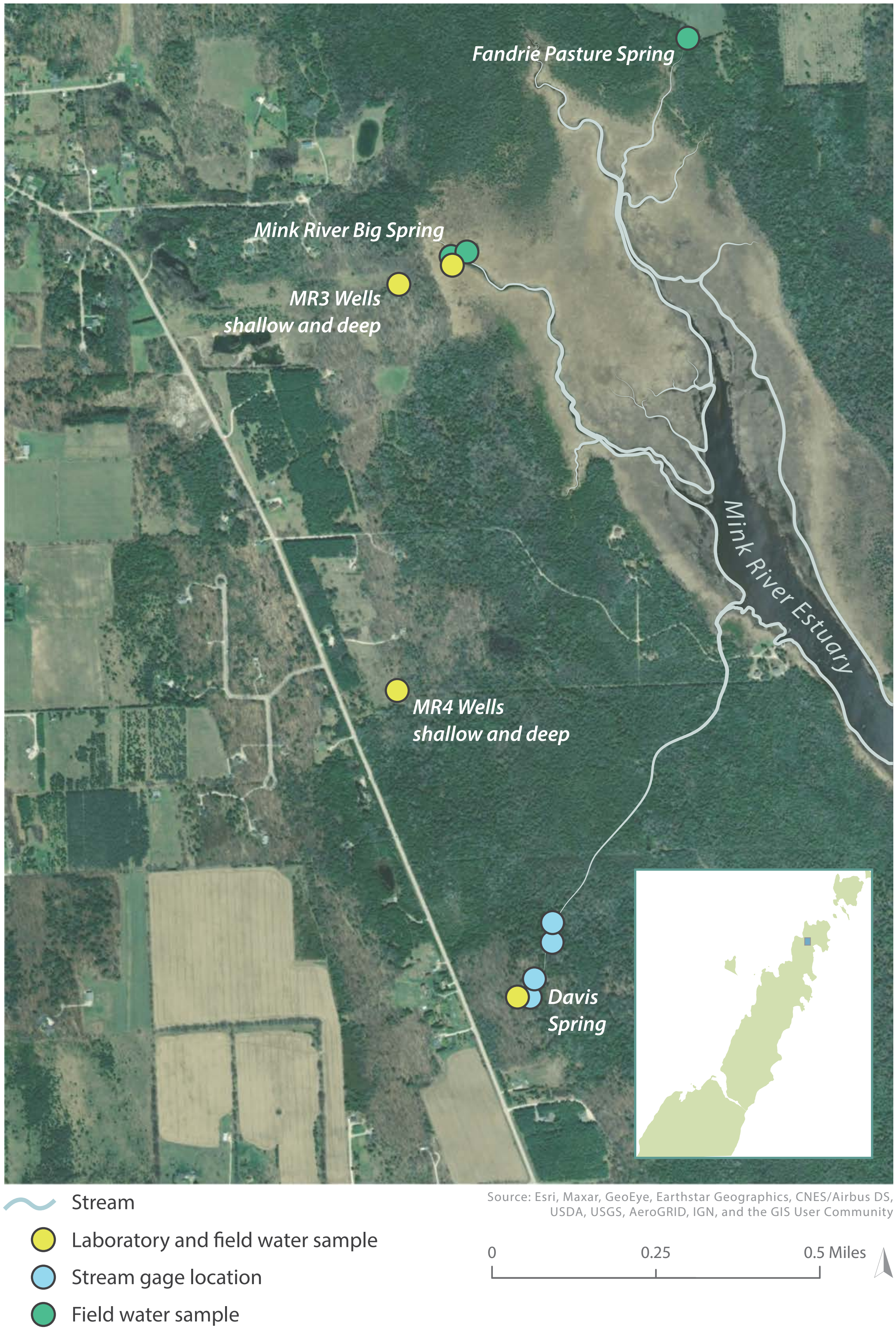


Figure 2b. Three Springs wetland and sampling points.

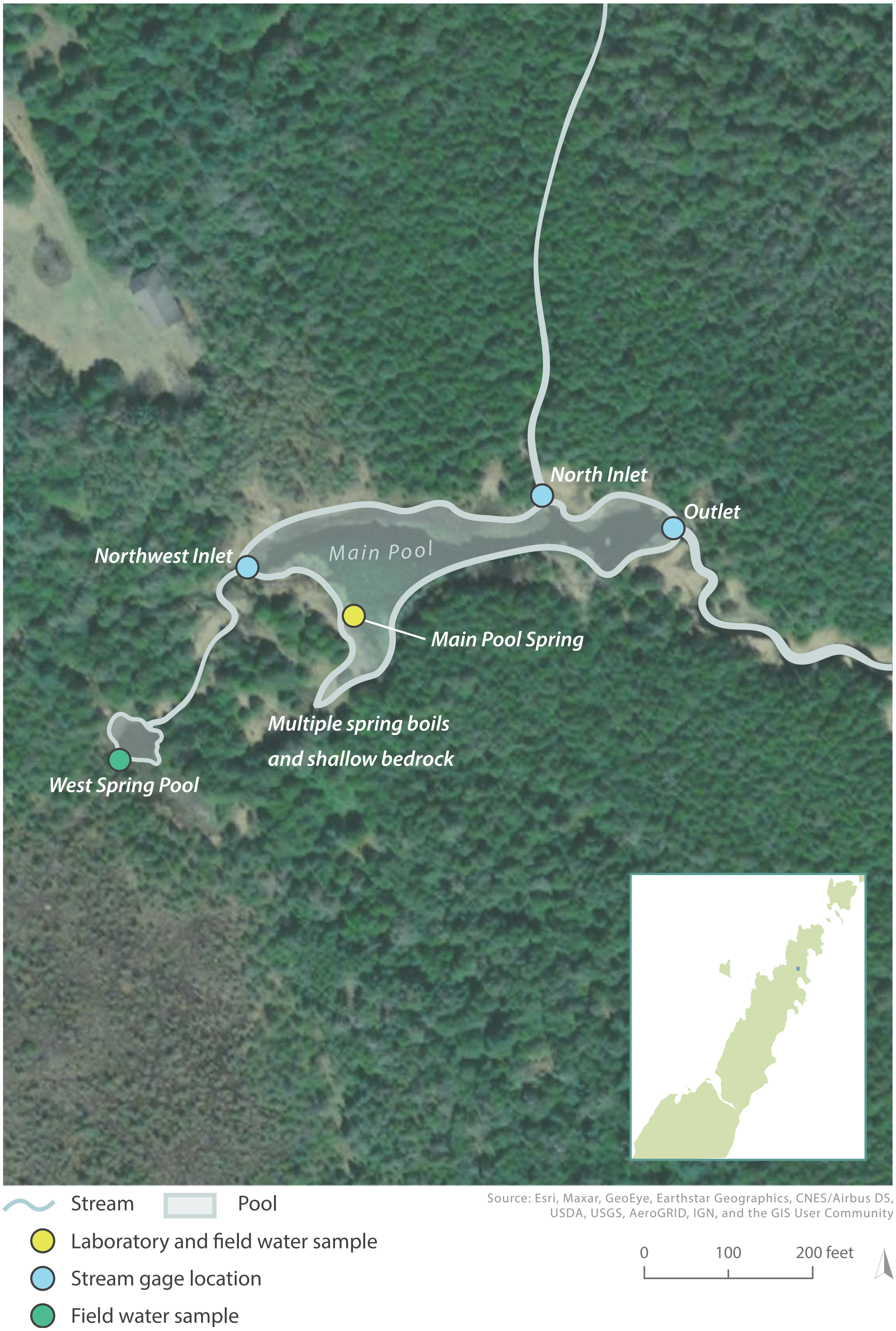


Figure 2c. Piel Creek wetland and sampling points.

Figure 2d. The Ridges Sanctuary wetland and sampling points.

Figure 2e. Dunes Lake, wetlands, and sampling points.

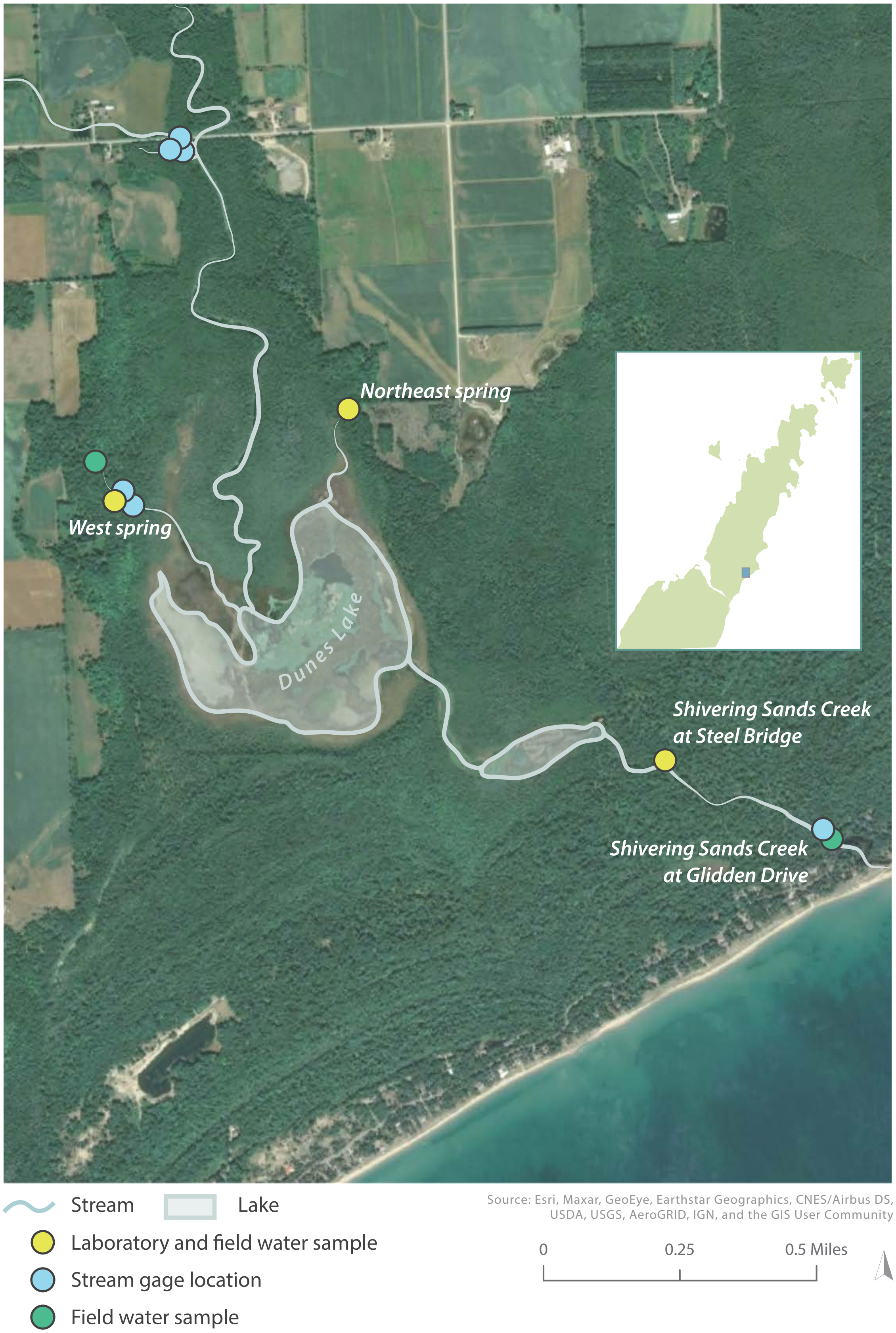


Figure 2f. Gardner Marsh and sampling points.

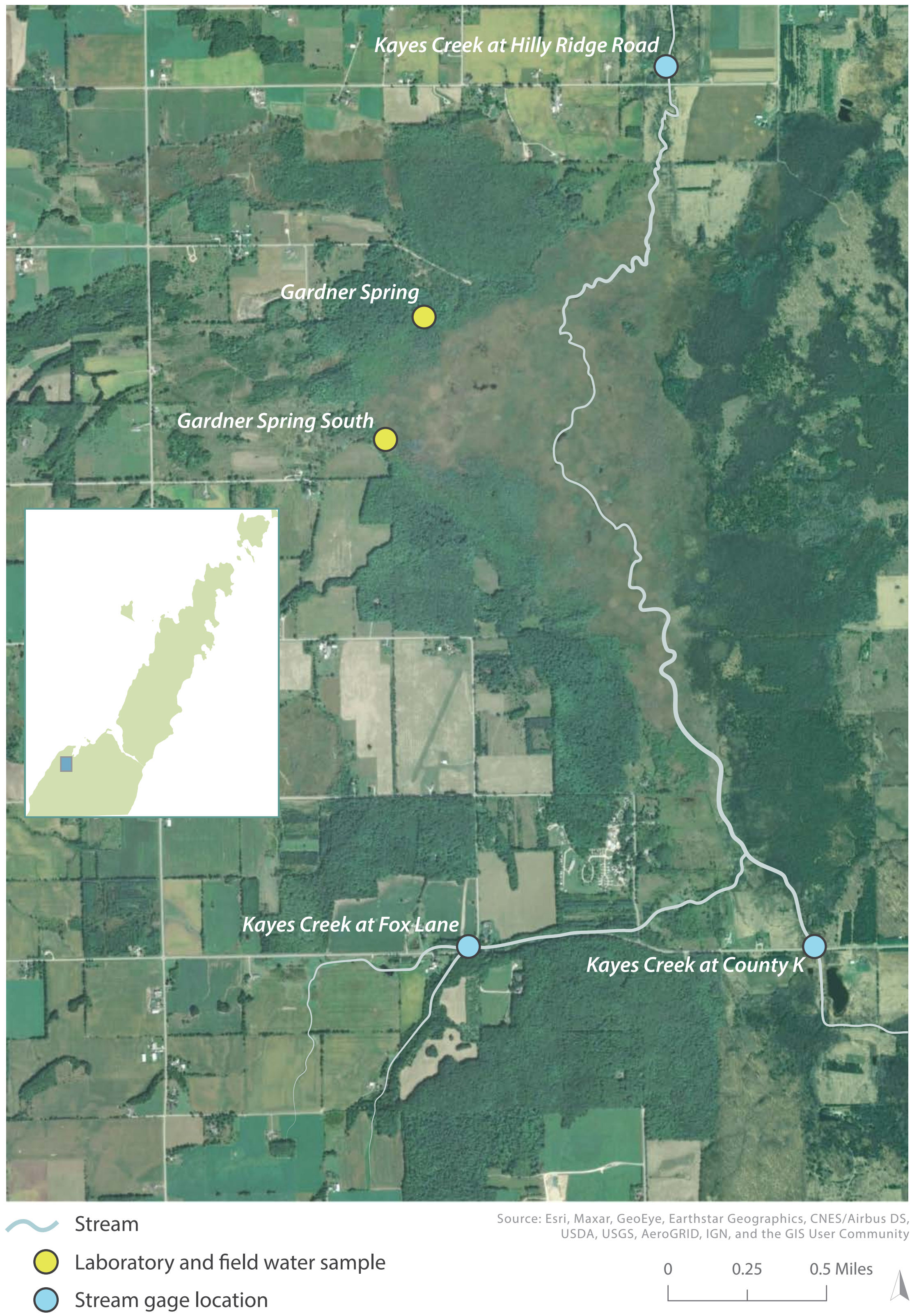


Figure 3a. For springs, tubing was placed at the vent.

Figure 3b. For streams, tubing was placed in the center third of the stream's width and the center third of the stream's depth.

Flow measurements

We collected flow measurements during each of the four sampling rounds to record seasonal variation in flows over the year. Figures 2a–f show the locations of the stream gage flow measurements for each wetland. We were unable to collect flow measurements in the Mink River due to high water levels in Lake Michigan. During the study period, the water levels were nearly the same as Lake Michigan and 1–2 ft above the wetland surface between the sedge tussocks. No flows were evident in the channel immediately downstream of the Mink River Big Spring vent. There was no sediment being transported or movement of aquatic plants in the channel. We do know there was discharge due to the existence of the spring vent and the difference in water temperatures and chemistry inside and outside of the spring vent. Figures 4a and b show contrasting water levels in the area around the Mink River Big Spring vent from years 2014 during lower water levels and 2018 during high water levels, respectively.

Due to frozen water, we were able to collect midwinter flow measurements at only two sites, Piel Creek and Three Springs. Davis Spring had no flow and the stream channel was dry during the fall and midwinter sampling events; it was gaged during the spring and summer sampling events when it was flowing again.

Figure 4a. Mink River Big Spring during low water levels in 2014.

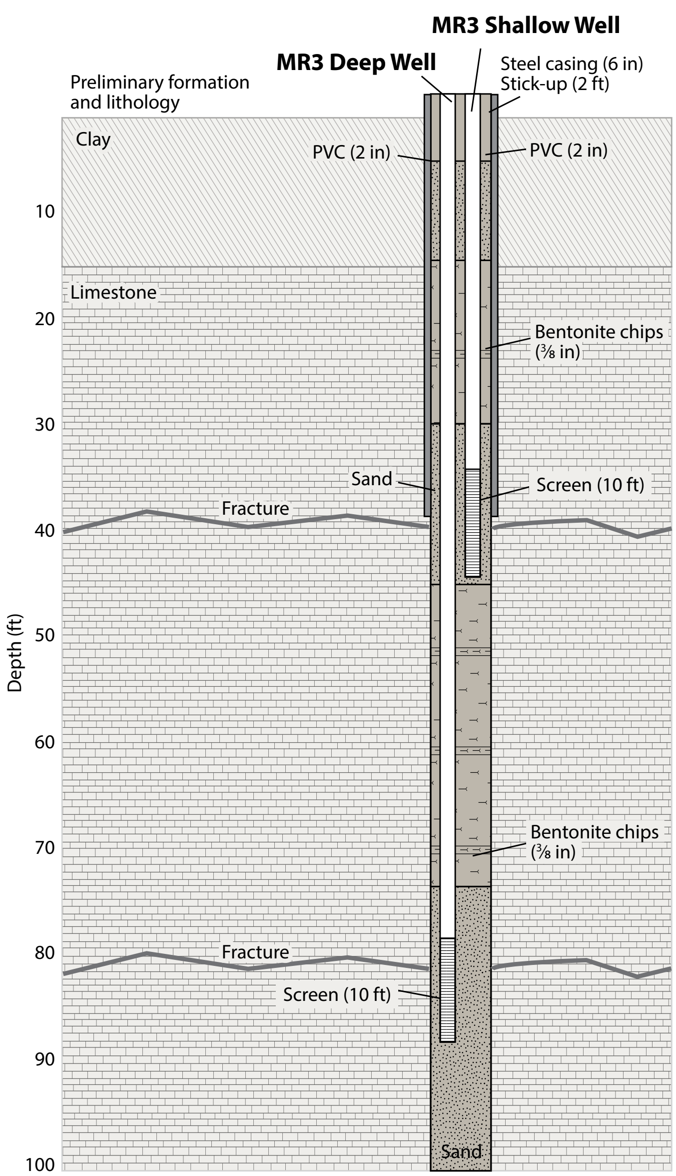
Figure 4b. Mink River Big Spring during high water levels in 2018. (The PVC pipe marks approximate location where figure 4a was taken.)

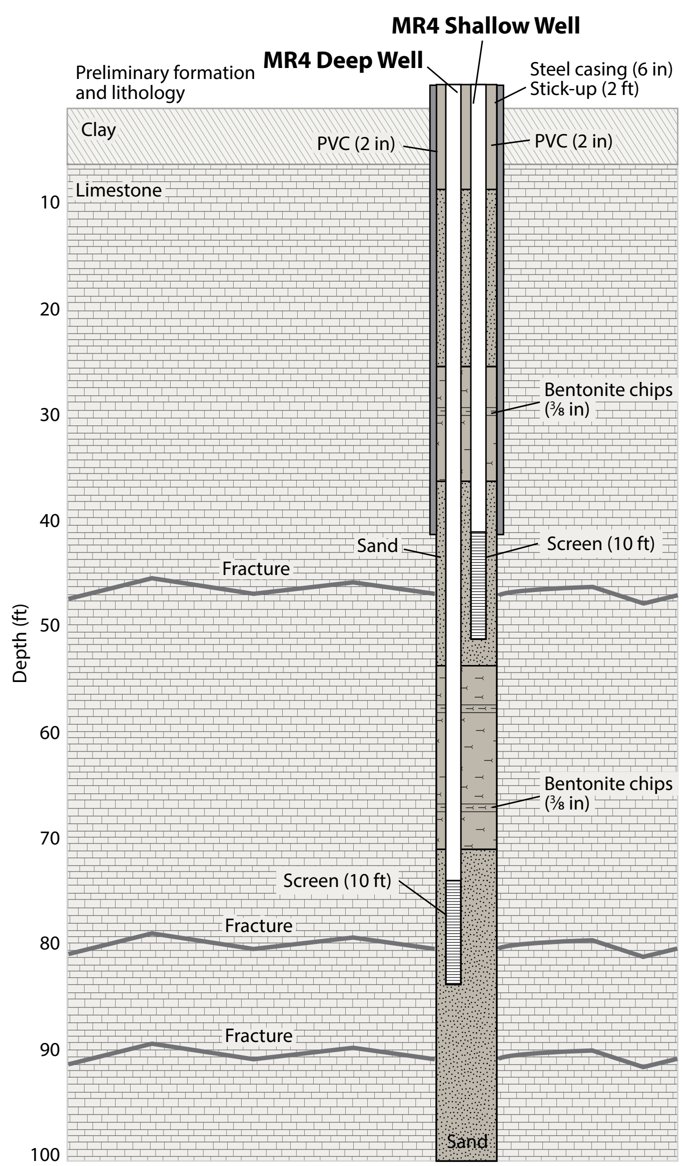
For most sites, we used the current meter midsection method (Turnipseed and Sauer, 2010) to calculate stream flow rates. We used a Marsh-McBirney electromagnetic meter and the six-tenths depth method to measure mean stream velocities in each cross section of the streams (Turnipseed and Sauer, 2010). For streams at least 4-ft wide, we made a minimum of 20 measurements; for narrower streams, we made measurements at 0.2-ft intervals. Figure 5 shows a stream flow measurement. In areas where it was not possible to wade into the stream, we used the float method to measure the velocity of an object (distance/time) in the stream. We generally made float measurements several times over different portions of the stream to get an average flow. Float measurements have large error associated with them, but they provide estimates of flows for streams that are otherwise difficult to measure.

Figure 5. Stream flow measurement downstream from Davis Spring.

Monitoring well reconstruction

In addition to sampling springs in the wetlands, we rebuilt two monitoring wells, MR3 and MR4, in the Mink River Estuary. Bradbury and others (2012) found that both wells intersected two or more fractures and that there was flow between fractures in the wells. This flow altered the heads and water chemistry of the fractures receiving the flows. We installed piezometers at two depths in each well—the shallow piezometer intersected the shallow fracture and the lower piezometer intersected the deeper fracture in MR3 and the deeper fractures in MR4. Reconstruction was successful, and the wells now provide reliable data on the heads and water chemistry of the fractures for future research and monitoring. Figure 6 shows the rebuilt well construction for wells MR 3 and 4.





Wetland capture zone analysis

One of the goals of this study was to link water chemistry of springs discharging into wetlands to land use surrounding those wetlands. To do that, we needed to estimate the area, or zone, that contributes flow to the springs discharging into the wetlands. A zone of groundwater contribution (ZOC) to a well or surface-water feature is defined as the land surface area beneath which all the groundwater, including recharge will ultimately discharge to the well or surface water feature. We estimated zones by modifying existing calibrated models. For Dunes Lake we used the model developed by Johnson and others (2013); for all other sites we used the models developed by Cobb and Bradbury (2008).

The groundwater flows were modeled using GFLOW (https://www.haitjema.com/). This groundwater modeling code simulates two-dimensional horizontal groundwater flows under steady-state or time constant conditions. GFLOW models have the advantage of easily representing streams and springs and are capable of delineating zones of contribution to a user-identified water feature. Cobb and Bradbury (2008) and Johnson and others (2013) determined ZOCs for the entire extent of the wetlands in our study.

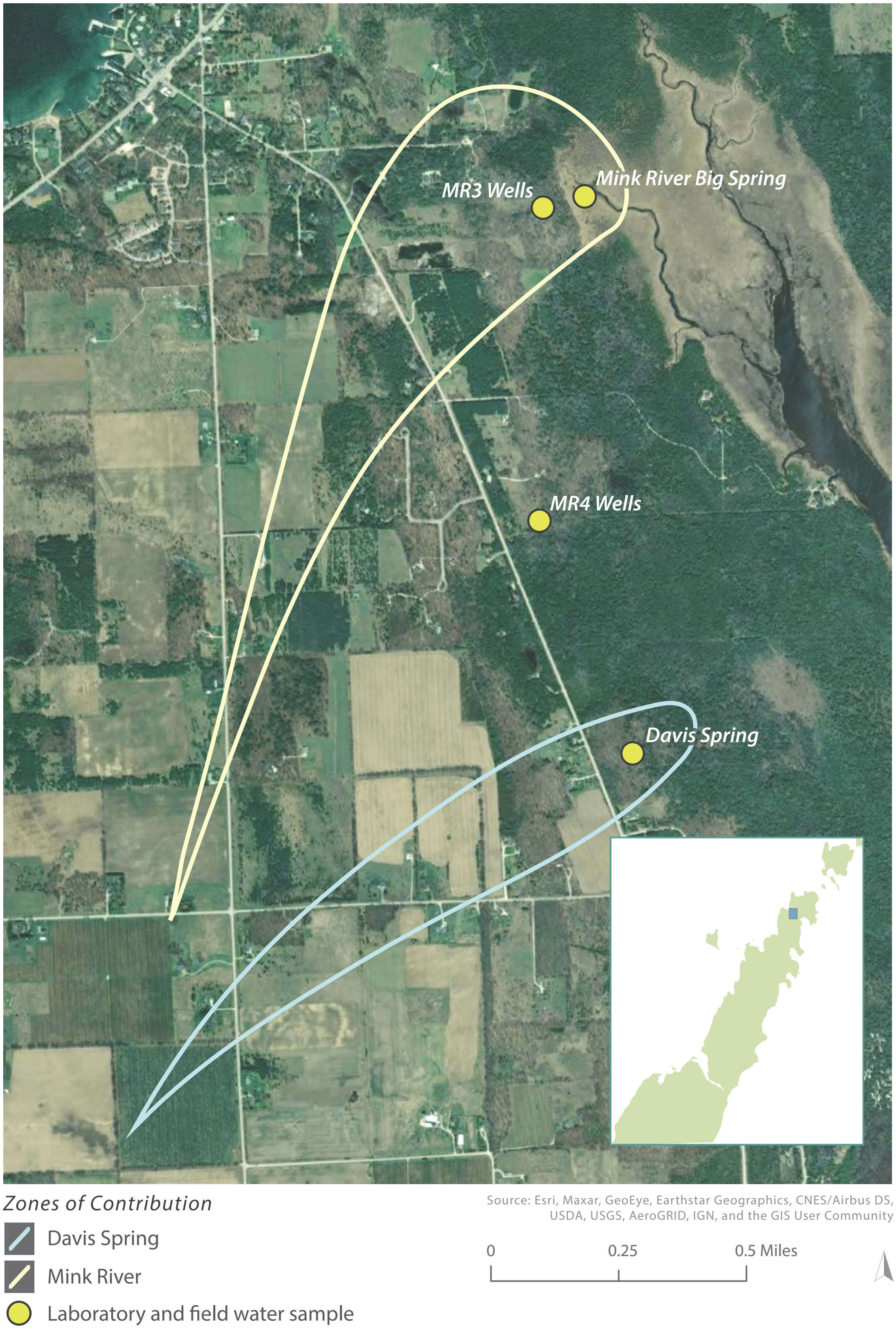
To improve our estimates of the correlation between land use and groundwater quality, we refined each ZOC using forward-particle tracking. Theses refinements improved the model's correspondence to the groundwater discharge areas. We included particles that discharged to the springs and seeps or to within approximately 1,000 ft of the springs. In most cases, the springs were not explicitly modeled by themselves but were part of a stream, either at the headwaters or along the stream reach.

Localized geology can play a large part in determining whether flow discharges to an individual spring or if it is more diffuse and distributed to many small springs and seeps. Although the samples were collected from the same location and spring, the sampled springs were all located within groundwater discharge areas with multiple springs and seeps.

With the exception of Davis Spring and the associated unnamed tributary to the Mink River Estuary, we used existing and calibrated flow models. Davis Spring and the associated tributary had not been included in these earlier studies. We modeled Davis Spring and the unnamed tributary by adding a line sink with the surface elevation of the spring and stream. The surface elevation was taken from a digital-elevation model derived from lidar (State Cartographer's Office, 2018). Figure 7 shows the ZOCs for Mink River Big Spring and Davis Spring in the Mink River Estuary.

Mink River Big Spring | Sampling from a canoe

Figure 7. ZOCs and sample locations for Mink River Big Spring and Davis Spring in the Mink River Estuary.



Results

Water quality—field and laboratory results

Field water sample parameters

We collected field water sample parameters at the same locations where laboratory samples were collected and where stream flow measurements were conducted (figs. 2a–f). Additional field water sample with parameter locations are shown in figures 2a-f. Table 1 lists the field water sample parameter measurements; appendix A provides a spreadsheet of the field water sample parameters, sample date, and precise sample location. The sample locations are listed in order from north to south in Door County with the measurement locations corresponding to flow measurements only listed at the bottom of the table. Photographs of each sample location are included in this report.

We make several simple observations from these data. The first is that groundwater temperatures changed less than surface water temperatures over the course of the year. The groundwater temperature changes seen over the year in wells MR3 and MR4 vary by 4.5˚C and 5.6˚C while the temperature change at Shivering Sands at Steel Bridge varies by 25˚C. Spring discharges show seasonal temperature responses as well. The Mink River Big Spring varied the most by 17.6˚C while Gardner Spring varied the least by only 3.8˚C. All spring discharge stayed cooler in the summer and warmer in the winter than the surface waters.

The fluid conductivity varies between sampling locations but does not seem to be strongly controlled by the source of the water. Conductivity in wells MR3 and MR4 depends on fracture depth. Shallow fractures intersected by wells MR3 shallow and MR4 shallow had conductivities of 534–659 microsiemens/centimeter (mS/cm) and 543–635 µS/cm, respectively, while the deeper fractures intersected by wells MR3 Deep and MR4 Deep have lower conductivities of 426–544 µS/cm and 506–530 µS/cm, respectively. There is also a significant upward hydraulic gradient between the shallow and deep fractures in both wells. In June 2018, MR3 Deep was a flowing well with the well top 2 ft above land surface. In contrast, the water level in MR3 Shallow was 7 ft lower. The water level in MR4 Deep was 3 ft above the water level in MR4 Shallow. These differences in fluid conductivity and heads between the shallow and deep fractures suggest that they are not well connected at either location. It also suggests that the recharge areas are different. It may be that the deep fracture subcrops and receives recharge at a higher elevation than the shallow fracture (fig. 8).

The dissolved oxygen concentration was measured as a percentage of air saturation. The wells MR3 and MR4 had the lowest dissolved oxygen concentrations with the piezometers located in the deep fractures recording lower concentrations than the piezometers in the shallow fractures. This is likely due to the water in the deeper fractures losing more oxygen as the water moves through the aquifer. The dissolved oxygen in the surface waters and spring waters

Figure 8. Conceptual model of differing heads and water chemistry observed in wells MR3 shallow and deep.

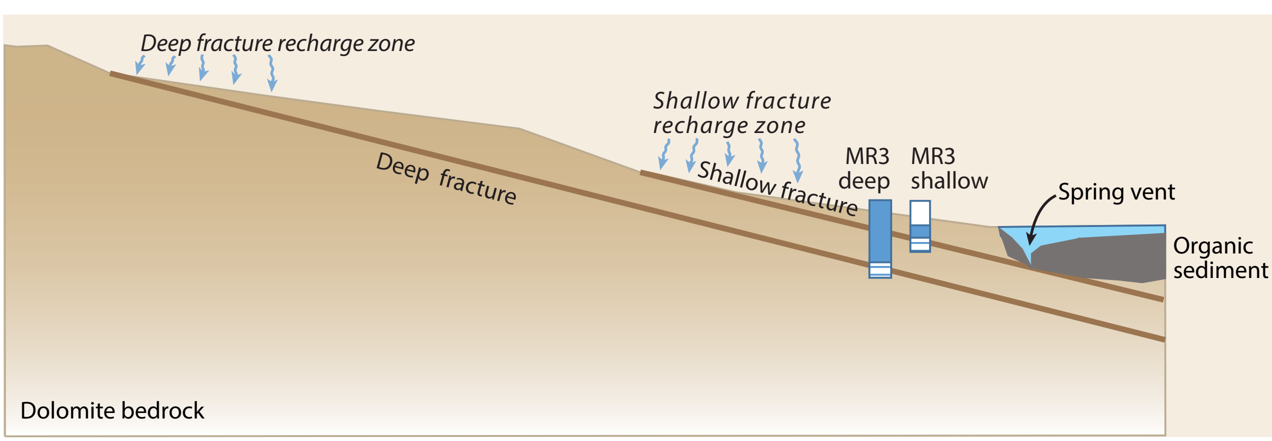


Table 1. Field parameters in sampled wetland springs, streams, and groundwater wells.

Wetland sample site name	Date	pH	Conductivity (mS/cm)	Temperature (°C)	Dissolved oxygen (%)
Mink River Estuary (fig. 2a)					
Mink River Big Spring	July 31, 2017	6.95	635	21.2	—
Mink River Big Spring	Sept. 20, 2017	6.78	613	10.4	—
Mink River Big Spring	Jan. 31, 2018	7.05	722	3.6	—
Mink River Big Spring	Apr. 10, 2018	7.18	741	5.5	48.6
Mink River Big Spring	June 12, 2018	7.13	629	11.2	38.4
MR3 Well (before rebuild)	Sept. 20, 2017	6.89	496	10.3	14.6
MR3 Deep Well	Nov. 8, 2017	7.41	544	8.0	—
MR3 Deep Well	Jan. 31, 2018	7.11	499	5.8	8.6
MR3 Deep Well	Apr. 10, 2018	7.42	426	7.9	21.3
MR3 Deep Well	June 12, 2018	7.38	499	9.1	19.7
MR3 Shallow Well	Nov. 8, 2017	7.24	659	8.2	—
MR3 Shallow Well	Jan. 31, 2018	7.07	633	6.3	48.6
MR3 Shallow Well	Apr. 10, 2018	7.19	534	7.9	48.5
MR3 Shallow Well	June 12, 2018	7.14	548	9.1	57.1
MR4 Well (before rebuild)	Sept. 20, 2017	6.87	490	11.7	—
MR4 Deep Well	Nov. 9, 2017	7.46	530	8.6	—
MR4 Deep Well	Feb. 1, 2018	—	521	6.6	—
MR4 Deep Well	Apr. 10, 2018	7.40	506	8.0	15.8
MR4 Deep Well	June 12, 2018	7.37	514	10.4	13.6
MR4 Shallow Well	Nov. 9, 2017	7.50	635	8.4	—
MR4 Shallow Well	Feb. 1, 2018	—	593	6.1	16.6
MR4 Shallow Well	Apr. 10, 2018	7.41	570	7.8	26.4
MR4 Shallow Well	June 12, 2018	7.31	543	10.3	27.1
Davis Spring	Apr. 10, 2018	7.15	696	6.8	61.7
Davis Spring	June 12, 2018	7.13	619	9.1	62.2
Fandrie Pasture spring	July 31, 2017	6.71	589	10.4	—
Three Springs Wetland (fig. 2b)					
Three Springs Main Pool Spring	July 31, 2017	7.69	568	10.9	—
Three Springs Main Pool Spring	Sept. 19, 2017	6.78	596	12.6	27.3
Three Springs Main Pool Spring	Jan. 31, 2018	6.97	625	6.8	57.0
Three Springs Main Pool Spring	Apr. 11, 2018	7.11	609	6.3	57.0
Three Springs Main Pool Spring	June 13, 2018	7.20	568	10.2	47.1
Three Springs West Spring Pool	July 31, 2017	7.13	552	19.3	—
Piel Creek Wetland (fig. 2c)					
Piel Creek at culvert	Aug. 1, 2017	7.24	531	20.5	—
Piel Creek at culvert	Sept. 19, 2017	7.07	578	16.9	54.5
Piel Creek at culvert	Feb. 1, 2018	7.03	692	0.0	—
Piel Creek at culvert	Apr. 11, 2018	7.52	554	5.9	78.1
Piel Creek at culvert	June 13, 2018	7.52	569	19.9	37.2

Abbreviations: ft = feet; std = standard deviation

Table 1. *(continued)*

Wetland sample site name	Date	pH	Conductivity (mS/cm)	Temperature (°C)	Dissolved oxygen (%)
Ridges Sanctuary Wetland (fig. 2d)					
Ridges Spring	Aug. 1, 2017	7.27	530	15.4	—
Ridges Spring	Sept. 19, 2017	7.23	558	14.2	20.4
Ridges Spring	Feb. 1, 2018	7.63	621	4.1	84.2
Ridges Spring	Apr. 11, 2018	7.62	589	2.3	79.9
Ridges Spring	June 13, 2018	7.62	543	11.7	40.3
Dunes Lake and Wetland (fig. 2e)					
Dunes Lake NE Spring	Aug. 1, 2017	6.83	530	9.9	—
Dunes Lake NE Spring	Sept. 18, 2017	6.95	544	11.1	23.0
Dunes Lake NE Spring	Jan. 30, 2018	7.12	550	7.1	34.8
Dunes Lake NE Spring	Apr. 12, 2018	7.27	559	5.1	49.6
Dunes Lake NE Spring	June 14, 2018	7.32	589	8.5	29.7
Dunes Lake West Spring	Sept. 19, 2017	6.77	683	10.5	36.6
Dunes Lake West Spring	Jan. 30, 2018	6.97	701	7.0	50.4
Dunes Lake West Spring	Apr. 12, 2018	7.11	779	6.0	37.1
Shivering Sands Creek at Steel Bridge	Sept. 19, 2017	7.47	540	18.3	56.6
Shivering Sands Creek at Steel Bridge	Jan. 30, 2018	7.21	626	0.0	—
Shivering Sands Creek at Steel Bridge	Apr. 11, 2018	8.14	545	8.4	115.0
Shivering Sands Creek at Steel Bridge	June 13, 2018	8.00	583	25.0	79.3
Gardner Marsh (fig. 2f)					
Gardner Spring	Aug. 1, 2017	7.07	553	9.3	—
Gardner Spring	Sept. 18, 2017	6.89	589	10.8	19.1
Gardner Spring	Jan. 30, 2018	7.14	610	7.2	16.4
Gardner Spring	Apr. 12, 2018	7.30	688	7.0	35.5
Gardner Spring	June 14, 2018	7.44	601	8.3	34.8
Gardner Spring South	June 14, 2018	7.19	722	10.8	47.6
Kayes Creek at Fox Ln	Sept. 18, 2017	7.91	626	23.2	97.0
Kayes Creek at Fox Ln	Apr. 11, 2018	7.40	509	4.6	78.1
Kayes Creek at Fox Ln	June 14, 2018	8.22	632	25.7	123.0
Kayes Creek at County K	Sept. 18, 2017	7.77	678	22.8	30.5
Kayes Creek at County K	Apr. 11, 2018	7.95	570	11.8	109.0
Kayes Creek at County K	June 14, 2018	8.38	574	27.1	104.4
Kayes Creek at Hilly Ridge Road	Sept. 18, 2017	7.31	748	12.2	78.5
Kayes Creek at Hilly Ridge Road	Apr. 11, 2018	7.65	826	8.1	104.0
Kayes Creek at Hilly Ridge Road	June 14, 2018	7.98	696	15.9	96.9

Abbreviations: ft = feet; std = standard deviation was generally higher. It appears that springs with more constant temperatures such as Gardner Marsh also have lower concentrations of dissolved oxygen and higher conductivities. Springs with greater temperature variation, such as the spring discharging in the Ridges Sanctuary, also have a larger range in dissolved oxygen concentrations and lower conductivities. These differences are possibly due to longer groundwater flow paths in more constant temperature springs and shorter groundwater flow paths in the more variable springs.

Major ion chemistry

We collected laboratory water samples from 14 different field points in Door County (figs. 2a-f). Eight of the sample locations (Gardner Spring, Gardner Spring South, Dunes Lake NE Spring, Dunes Lake West Spring, Ridges Spring, Three Springs, Mink River Big Spring, and Davis Spring) were at well-defined spring discharge points. The Piel Creek sample was collected at a culvert located in the wetlands and near groundwater discharge as seep. The Shivering Sands Steel Bridge sample was a surface water sample. The rest of the points were well water samples. Photos of each of the sample locations are shown throughout this report.

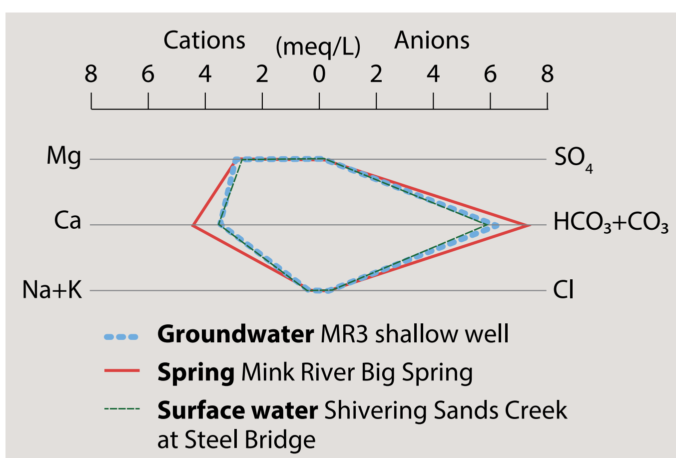
We sampled eight of the 14 points four times: September 2017, January/February 2018, April 2018, and June 2018. The two wells, MR3 and MR4 in the Mink River Estuary, were sampled fewer times due to reconstruction. The other two points, Davis Spring and Gardner Spring South, were added later to the study to aid our understanding of groundwater quality to the Mink River Estuary and Gardner Marsh, respectively. Davis Spring, sampled twice, was overlooked in previous studies due to its ephemeral flow. Gardner Spring South, sampled once, was chosen to provide a check on whether the more accessible Gardner Spring was providing representative samples.

We tested each sample for water chemistry, enterococci bacteria, pharmaceuticals and personal care products (PPCPs), and pesticides. The basic water chemistry had 22 analytes that included major ions, metals, pH, turbidity, and color. The PPCPs included acesulfame, sucralose, caffeine, paraxanthine, cotinine, sulfamethoxazole, and sulfamethazine. We tested for 102 different pesticides including five neonicotinoids. Because neonicotinoids are of special concern to bees and other pollinators as well as aquatic species, they were tested at very low detection limits (0.0017 µg/L) in the final sampling round.

The water chemistry of all the samples can be classified as calcium-magnesium bicarbonate. Figure 9 shows Stiff diagrams of a surface-water sample (Shivering Sands Creek), a groundwater sample (MR3 shallow), and a spring sample (Mink River Big Spring), all collected in January 2018. Water samples from all sites produced similar Stiff diagrams.

Major ion water chemistry results for all the sample locations and events are shown in table 2. Sample point locations are shown in figures 2a–f. In general, the cation/anion charge balance, a measure of the accuracy of the chemical analysis, was less than 5 percent, although four of the samples had charge balances greater than 5 percent but less than 10 percent, signaling potential issues with concentrations for those four samples. Because all of the samples are calcium-magnesium bicarbonate, their conductivity is related to the concentrations of these ions. Figure 10 is a cross plot showing the correlation between calcium concentrations

Figure 9. Stiff diagrams for surface water, groundwater, and spring discharge samples. Sampling occurred in January 2018.



and laboratory measured conductivity for all sample locations and events. To provide a more direct comparison of the two parameters, the plot uses conductivity values measured in the laboratory listed in table 2 rather than the field values that were reported in table 1. Since calcium and conductivity are correlated, and the Stiff diagrams have similar shapes or ion ratios, conductivity can be used as proxy to identify the different chemistry of the springs, potentially reducing the need to collect and analyze all samples for major ions.

There are two anomalous readings called out on the plot, one for MR4 Shallow on February 1, 2018, and the other for Mink River Big Spring on April 10, 2018. As can be seen in table 2, there is nothing apparent in their chemistry to differentiate them from the other samples collected at those locations, making it difficult to understand why the correlation between conductivity and calcium is different in those samples on those two dates. These two readings were not included in the linear best-fit equation shown on the plot. The major ion water chemistry results, sample date, and sample location in latitude and longitude are available in the "Laboratory Water Chemistry Results" spreadsheet in appendix A.

Figure 10. Cross plot showing correlation between calcium concentrations and conductivity.

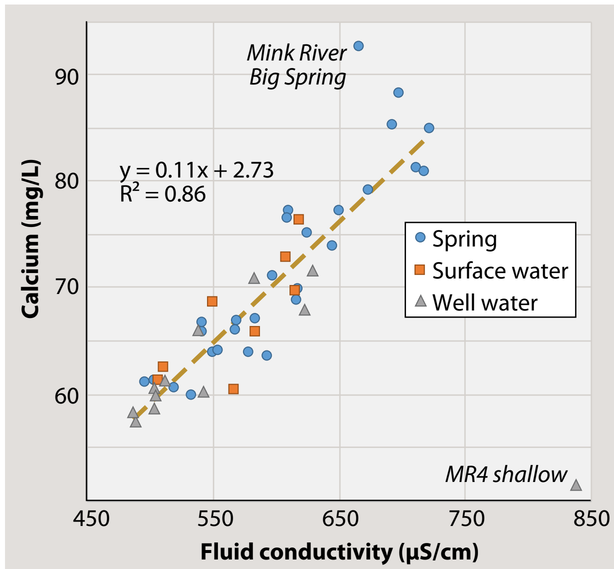


Table 2. Major ions in sampled wetland springs, surface waters, and groundwater.

Wetland sample name	Sample date	Alkalinity mg/L	Calcium mg/L	Chloride mg/L	Magnesium mg/L	Potassium mg/L	Sodium mg/	Sulfate mg/L	Conductivity mS/cm
Limit of detection		**20**	**0.05**	**0.5**	**0.05**	**0.05**	**0.5**	**0.2**	**1**
Mink River Estuary (fig. 2a)									
Mink River Big Spring	Sept. 20, 2017	325	77.3	12.6	36.2	1.0	5.9	10.8	618
Mink River Big Spring	Jan. 31, 2018	366	88.3	10.3	34.9	0.9	5.6	9.2	610
Mink River Big Spring	Apr. 10, 2018	350	92.7	8.9	33.9	0.7	4.3	11.8	569
Mink River Big Spring	June 12, 2018	338	75.1	9.6	34.7	0.8	5.1	10.9	542
MR3 Well (before rebuild)	Sept. 20, 2017	251	63.7	3.7	30.8	1.1	1.3	20.1	522
MR3 Deep Well	Jan. 31, 2018	252	60.6	2.3	27.7	1.5	1.2	23.2	504
MR3 Deep Well	Apr. 10, 2018	248	61.4	3.2	29.9	1.1	0.9	21.0	512
MR3 Deep Well	June 12, 2018	261	59.9	2.5	28.7	1.1	0.9	20.7	505
MR3 Shallow Well	Jan. 31, 2018	314	68.0	12.9	34.7	1.0	6.7	8.6	623
MR3 Shallow Well	Apr. 10, 2018	314	71.6	10.6	35.6	0.9	5.7	9.0	629
MR3 Shallow Well	June 12, 2018	330	70.9	11.6	34.8	0.8	6.0	7.8	583
MR4 Well (before rebuild)	Sept. 20, 2017	254	60.6	2.7	31.6	0.9	0.9	13.2	519
MR4 Deep Well	Feb. 1, 2018	253	57.6	2.5	30.0	1.0	0.8	12.5	489
MR4 Deep Well—duplicate	Feb. 1, 2018	261	58.1	2.4	30.2	1.0	1.0	12.5	498
MR4 Deep Well	Apr. 10, 2018	255	58.7	2.9	30.2	0.9	0.9	13.1	503
MR4 Deep Well	June 12, 2018	267	58.3	2.7	29.7	0.9	1.1	13.0	487
MR4 Shallow Well	Feb. 1, 2018	273	51.6	2.7	23.9	1.4	27.8	25.8	838
MR4 Shallow Well	Apr. 10, 2018	272	60.3	3.3	30.7	0.9	10.1	21.0	543
MR4 Shallow Well	June 12, 2018	290	66.1	2.8	32.8	0.9	4.6	20.0	538
Davis Spring	Apr. 10, 2018	314	73.9	12.9	37.5	3.2	5.3	10.3	645
Davis Spring	June 12, 2018	315	67.1	8.5	35.0	3.5	3.4	10.2	584
Three Springs Wetland (fig. 2b)									
Three Springs Main Pool Spring	Sept. 19, 2017	297	69.9	14.3	33.2	1.2	6.3	12.0	618
Three Springs Main Pool Spring	Jan. 31, 2018	297	77.3	14.2	38.4	1.1	6.7	14.2	610
Three Springs Main Pool Spring	Apr. 11, 2018	270	66.8	10.8	31.6	1.0	5.4	15.2	569
Three Springs Main Pool Spring	June 13, 2018	278	65.8	10.5	30.5	1.0	4.3	10.6	542
Piel Creek Wetland (fig. 2c)									
Piel Creek at culvert	Sept. 19, 2017	319	72.9	5.8	33.5	0.8	2.8	3.8	608
Piel Creek at culvert	Feb. 1, 2018	338	76.3	5.0	34.2	0.8	2.6	4.6	619
Piel Creek at culvert	Apr. 11, 2018	272	62.5	5.6	29.9	0.6	3.3	5.6	511
Piel Creek at culvert	June 13, 2018	308	68.8	8.3	33.0	0.8	3.9	13.9	550

*Cation/anion charge balance was greater than 5%, signaling a potential issue with concentrations.

Abbreviations: mg/L = milligram/liter; mS/cm = microsiemens/centimeter.

Table 2. *(continued)*

Wetland sample name	Sample date	Alkalinity mg/L	Calcium mg/L	Chloride mg/L	Magnesium mg/L	Potassium mg/L	Sodium mg/	Sulfate mg/L	Conductivity mS/cm
Limit of detection		**20**	**0.05**	**0.5**	**0.05**	**0.05**	**0.5**	**0.2**	**1**
*Cation/anion charge balance was greater than 5%, signaling a potential issue with concentrations.									
Abbreviations: mg/L = milligram/liter; mS/cm = microsiemens/centimeter.									
Ridges Sanctuary Wetland (fig. 2d)									
Ridges Spring	Sept. 19, 2017	286	63.6	12.9	32.5	2.3	6.4	7.6	593
Ridges Spring	Feb. 1, 2018	286	64.0	13.2	34.1	1.8	6.5	7.7	579
Ridges Spring	Apr. 11, 2018	256	60.0	15.1	30.9	1.6	6.9	8.7	533
Ridges Spring	June 13, 2018	264	60.6	15.9	29.4	1.7	7.1	6.2	519
Dunes Lake Wetland (fig. 2e)									
Dunes Lake NE Spring	Sept. 18, 2017	264	66.0	9.7	31.0	1.8	3.2	15.6	568
Dunes Lake NE Spring	Jan. 30, 2018	258	63.9	7.4	31.1	1.8	2.5	12.4	550
Dunes Lake NE Spring	Apr. 12, 2018	234	61.1	6.2	29.6	1.7	2.2	10.7	496
Dunes Lake NE Spring—duplicate	Apr. 12, 2018	236	61.4	6.2	29.7	1.7	2.1	10.7	503
Dunes Lake NE Spring	June 14, 2018	265	66.8	7.2	31.1	1.6	3.2	15.5	542
Dunes Lake West Spring*	Sept. 19, 2017	285	81.3	11.3	36.7	3.6	3.9	13.1	712
Dunes Lake West Spring	Jan. 30, 2018	296	80.9	11.1	37.8	3.3	4.4	11.9	718
Dunes Lake West Spring*	Apr. 12, 2018	294	85.3	9.2	38.9	2.8	4.7	12.1	693
Dunes Lake West Spring*	June 14, 2018	300	84.9	9.8	38.2	2.8	4.8	12.3	722
Shivering Sands Creek at Steel Bridge	Sept. 19, 2017	276	60.4	15.8	33.5	3.4	6.0	6.0	567
Shivering Sands Creek at Steel Bridge	Jan. 30, 2018	296	69.8	16.5	32.4	5.8	5.3	12.7	615
Shivering Sands Creek at Steel Bridge	Apr. 11, 2018	244	61.3	12.4	27.4	2.9	4.7	10.6	507
Shivering Sands Creek at Steel Bridge	June 13, 2018	294	65.9	21.8	34.2	2.7	9.5	7.2	584
Gardner Marsh (Figure 2f)									
Gardner Spring	Sept. 18, 2017	306	68.9	15.3	33.9	1.8	6.4	7.6	616
Gardner Spring	Jan. 30, 2018	315	71.1	16.2	35.7	2.1	7.1	8.1	598
Gardner Spring	Apr. 12, 2018	320	76.6	14.3	37.8	1.9	6.7	11.8	609
Gardner Spring	June 14, 2018	288	64.2	8.5	32.2	1.6	4.2	11.4	554
Gardner Spring South*	June 14, 2018	615	79.1	15.7	38.4	3.6	5.6	13.4	674

*Cation/anion charge balance was greater than 5%, signaling a potential issue with concentrations.

Abbreviations: mg/L = milligram/liter; mS/cm = microsiemens/centimeter.

Pharmaceuticals and personal care products

The samples were analyzed for 12 pharmaceuticals and personal care products (PPCPs). Of those, only six were detected: two artificial sweeteners (acesulfame and sucralose), caffeine and a caffeine metabolite (paraxanthine), a nicotine metabolite (cotinine), and a human antibiotic (sulfamethoxazole). These analytes indicate a human source, which in this environment most likely originate as discharge from septic drain fields. The results are shown in table 3. The detection limit for these analytes is low, between 3 and 25 ng/L. Because the detection limit is so low, and these analytes are common, we used blanks and duplicates to confirm our results. No detects were found in the blanks. For analytes with no detects in the original sample, there were no detects in the duplicate samples. These results provide evidence that our sampling protocol eliminated contamination of the samples. Appendix A2 provides full PPCP results, sample dates, and sample locations in latitude and longitude.

Acesulfame was the most commonly detected analyte, an artificial sweetener with the trade names of Sweet One and Sunett. It is commonly found in soft drinks such as Coca-Cola Zero Sugar and Pepsi One. Acesulfame was detected in 36 percent of all samples and at 9 of the 14 sampling locations. Paraxanthine, a metabolite of caffeine, was the next most commonly detected analyte, seen in 17 percent of all samples and at 8 of the 14 sampling points. We found that other contaminants were detected without acesulfame only four times out of the 47 samples. This suggests that acesulfame by itself might serve as a usable indicator of human-sourced contaminants if analysis of a full list of these analytes is not feasible. Adding sucralose, caffeine, and its metabolite, paraxanthine, as a reduced set of PPCP indicators would further increase the accuracy of PPCP detection without the need to analyze the full suite of 12 PPCPs tested for in this study.

Using acesulfame as an example, a simple calculation provides insight into the concentrations of the PPCPs seen in table 3. Twelve ounces of some common diet sodas have approximately 30 milligrams (mg) of acesulfame. A daily discharge of one serving of diet soda then releases 30 mg of acesulfame into the ZOC of the spring. If the spring is discharging at 1 cubic foot per second or 2,400,000 liters/day, the concentration of acesulfame in the spring discharge will be (30 mg/day ÷ 2,400,000 liter/day) = 0.0000125 mg/L or 12.5 ng/L.

These are low levels of both detection and quantities of analytes released into the groundwater system. As a result, these PPCPs are effective tracers for indicating human sources (Nitka and others, 2019).

MR3 shallow and deep wells | Winter water sample collection

Pesticides and bovine antibiotics

All water samples were analyzed for 107 pesticides and their breakdown products and a bovine antibiotic. These analytes were used to indicate an agricultural source of the groundwater contaminant. Of those 107 analytes, only five were detected: sulfamethazine (a bovine antibiotic), metolachlor ESA (a breakdown product of the herbicide metolachlor), trifluralin and fomesafen (herbicides), and clothianidin (a neonicotinoid insecticide). Of these five products, only metolachlor ESA was detected in multiple samples and sites. The results are summarized in table 4 and complete test results are presented in appendix A2.

As has been observed elsewhere in Wisconsin, metolachlor ESA is the most commonly detected pesticide (Cook and others, 2017). It was detected in 32 percent of the water samples and at six of the 14 sample locations. At Dunes Lake Wetland, metolachlor ESA was detected at all three sampling sites and during all four sampling rounds with no apparent trends in concentrations over time: At the Dunes Lake NE Spring, concentrations were low in the fall, nearly doubled in the winter, nearly doubled again in the spring, then dropped back down in the summer (0.13, 0.25, 0.40, 0.14 micrograms/liter (μg/L)). By contrast, at Shivering Sands Creek at Steel Bridge, concentrations were low in the fall, dropped by half in the winter, remained steady in the spring, then doubled in the summer (0.16, 0.07, 0.06, and 0.12 μg/L). And at Dunes Lake West Spring, concentrations remained steady throughout the year (0.18, 0.16, 0.15, and 0.22 μg/L).

Neonicotinoids, such as clothianidin, are of special concern in wetland environments because they harm non-target insects, even at low concentrations. This concern is heightened due to the presence of the endangered Hine's emerald dragonflies in the wetlands that receive discharge from the springs in this study. Clothianidin was detected only once and at a low concentration of 0.0065 μg/L in the Dunes Lake NE spring. We also tested for four other neonicotinoids (acetamiprid, dinotefuran, imidacloprid, and thiamethoxam), but they were not detected, even when tested at 2.4 ng/L and lower detection limits.

MR4 shallow and deep wells | Winter water sample collection

Table 3. Concentrations of pharmaceuticals and personal care products in sampled wetland springs, surface waters, and groundwater.

Wetland sample name	Sample date	Acesulfame (artificial sweetener) ng/L	Sucralose (artificial sweetener) ng/L	Caffeine (stimulant) ng/L	Paraxanthine (caffeine metabolite) ng/L	Cotinine (nicotine metabolite) ng/L	Sulfa methoxazole (human antibiotic) ng/L
Limit of detection		**5**	**25**	**12**	**5**	**3**	**5**
Mink River Estuary (fig. 2a)							
Mink River Big Spring	Sept. 20, 2017	—[a]	89.60	—	—	—	—
Mink River Big Spring	Jan. 31, 2018	—	—	—	—	—	—
Mink River Big Spring	Apr. 10, 2018	—	—	—	—	—	—
Mink River Big Spring	June 12, 2018	15.10	—	—	—	—	—
MR3 Deep Well	Jan. 31, 2018	—	—	—	—	—	—
MR3 Deep Well	Apr. 10, 2018	—	—	—	—	—	—
MR3 Deep Well	June 12, 2018	—	—	—	—	—	—
MR3 Shallow Well	Jan. 31, 2018	15.00	120.50	—	—	—	—
MR3 Shallow Well	Apr. 10, 2018	14.10	—	—	—	—	—
MR3 Shallow Well	June 12, 2018	12.70	—	—	13.80	—	—
MR4 Deep Well	Feb. 1, 2018	—	—	—	—	—	—
MR4 Deep Well (duplicate)	Feb. 1, 2018	—	—	—	—	—	—
MR4 Deep Well	Apr. 10, 2018	—	—	—	—	—	—
MR4 Deep Well	June 12, 2018	—	—	12.10	13.20	—	—
MR4 Shallow Well	Feb. 1, 2018	—	—	12.60	7.10	—	—
MR4 Shallow Well	Apr. 10, 2018	—	—	—	—	—	—
MR4 Shallow Well	June 12, 2018	—	—	—	—	—	—
Davis Spring	Apr. 10, 2018	211.00	969.00	—	—	—	5.00
Davis Spring	June 12, 2018	14.70	—	—	—	—	—
Three Springs Wetland (fig. 2b)							
Three Springs Main Pool Spring	Sept. 19, 2017	—	—	—	—	—	—
Three Springs Main Pool Spring	Jan. 31, 2018	—	—	—	—	—	—
Three Springs Main Pool Spring	Apr. 11, 2018	—	—	—	—	—	—
Three Springs Main Pool Spring	June 13, 2018	8.20	—	—	11.70	—	—
Piel Creek Wetland (fig. 2c)							
Piel Creek at culvert	Sept. 19, 2017	—	—	—	—	—	—
Piel Creek at culvert	Feb. 1, 2018	—	—	—	—	—	—
Piel Creek at culvert	Apr. 11, 2018	—	—	—	—	—	—
Piel Creek at culvert	June 13, 2018	—	—	—	—	—	—
Ridges Sanctuary Wetland (fig. 2d)							
Ridges Spring	Sept. 19, 2017	9.00	—	—	—	—	—
Ridges Spring	Feb. 1, 2018	9.50	—	—	—	—	—
Ridges Spring	Apr. 11, 2018	11.50	—	—	—	—	—
Ridges Spring	June 13, 2018	—	—	—	—	—	—

Abbreviation: ng/L = nanogram/liter

[a]— = Amount present in sample was below the limit of detection.

Table 3. *(continued)*

Wetland sample name	Sample date	Acesulfame (artificial sweetener) ng/L	Sucralose (artificial sweetener) ng/L	Caffeine (stimulant) ng/L	Paraxanthine (caffeine metabolite) ng/L	Cotinine (nicotine metabolite) ng/L	Sulfa methoxazole (human antibiotic) ng/L
Limit of detection		**5**	**25**	**12**	**5**	**3**	**5**
Dunes Lake Wetland (fig. 2e)							
Dunes Lake NE Spring	Sept. 18, 2017	—	—	—	6.86	—	—
Dunes Lake NE Spring	Jan. 30, 2018	—	—	—	—	—	—
Dunes Lake NE Spring	Apr. 12, 2018	—	—	—	—	—	—
Dunes Lake NE Spring (duplicate)	Apr. 12, 2018	—	—	—	—	—	—
Dunes Lake NE Spring	June 14, 2018	—	—	—	—	—	—
Dunes Lake West Spring	Sept. 19, 2017	9.10	—	—	—	—	—
Dunes Lake West Spring	Jan. 30, 2018	—	—	—	—	—	—
Dunes Lake West Spring	Apr. 12, 2018	—	—	—	—	—	—
Dunes Lake West Spring	June 14, 2018	—	—	12.90	14.00	—	—
Shivering Sands Creek at Steel Bridge	Sept. 19, 2017	36.10	—	—	—	—	—
Shivering Sands Creek at Steel Bridge	Jan. 30, 2018	18.30	—	—	—	—	—
Shivering Sands Creek at Steel Bridge	Apr. 11, 2018	11.90	—	—	—	—	—
Shivering Sands Creek at Steel Bridge	June 13, 2018	56.30	840.40	21.20	18.00	6.60	—
Gardner Marsh (fig. 2f)							
Gardner Spring	Sept. 18, 2017	9.91	—	12.88	15.84	—	—
Gardner Spring	Jan. 30, 2018	—	—	—	—	—	—
Gardner Spring	Apr. 12, 2018	—	—	—	—	—	—
Gardner Spring	June 14, 2018	—	—	—	—	—	—
Gardner Spring South	June 14, 2018	13.10	—	—	—	—	—
Blank	Sept. 17, 2017	—	—	—	—	—	—
Blank	June 14, 2018	—	—	—	—	—	—

Abbreviation: ng/L = nanogram/liter

[a]— = Amount present in sample was below the limit of detection.

Table 4. Concentrations of pesticides in sampled wetland springs, surface waters, groundwater.

Wetland sample name	Sample date	Sulfamethazine (bovine antibiotic) ng/L	Metolachlor ESA (herbicide breakdown product) µg/L	Trifluralin (herbicide) µg/L	Fomesafen (herbicide) µg/L	Clothianidin (neonicotinoid insecticide) µg/L
Limit of detection		**1**	**0.05**	**0.05**	**0.061**	**0.5/0.0017***
Mink River Estuary (fig. 2a)						
Mink River Big Spring	Sept. 20, 2017	—[a]	—	—	—	—
Mink River Big Spring	Jan. 31, 2018	—	—	—	—	—
Mink River Big Spring	Apr. 10, 2018	—	—	—	—	—*
Mink River Big Spring	June 12, 2018	—	—	—	—	—*
MR3 Deep Well	Jan. 31, 2018	—	—	—	—	—
MR3 Deep Well	Apr. 10, 2018	—	—	—	—	—
MR3 Deep Well	June 12, 2018	—	—	—	—	—
MR3 Shallow Well	Jan. 31, 2018	—	—	—	—	—
MR3 Shallow Well	Apr. 10, 2018	—	—	—	—	—
MR3 Shallow Well	June 12, 2018	—	—	—	—	—
MR4 Deep Well	Feb. 1, 2018	—	—	—	—	—
MR4 Deep Well	Apr. 10, 2018	—	—	—	—	—
MR4 Deep Well	June 12, 2018	—	—	—	—	—
MR4 Shallow Well	Feb. 1, 2018	—	—	0.06	—	—
MR4 Shallow Well	Apr. 10, 2018	—	—	—	—	—
MR4 Shallow Well	June 12, 2018	—	—	—	—	—
Davis Spring	Apr. 10, 2018	—	—	—	—	—
Davis Spring	June 12, 2018	—	—	—	—	—
Three Springs Wetland (fig. 2b)						
Three Springs Main Pool Spring	Sept. 19, 2017	—	—	—	—	—
Three Springs Main Pool Spring	Jan. 31, 2018	—	—	—	—	—
Three Springs Main Pool Spring	Apr. 11, 2018	—	—	—	—	—
Three Springs Main Pool Spring	June 13, 2018	5.80	—	—	—	—*
Piel Creek Wetland (fig. 2c)						
Piel Creek at culvert	Sept. 19, 2017	—	0.06	—	—	—
Piel Creek at culvert	Feb. 1, 2018	—	—	—	—	—
Piel Creek at culvert	Apr. 11, 2018	—	—	—	—	—*
Piel Creek at culvert	June 13, 2018	—	—	—	—	—*
Ridges Sanctuary Wetland (fig. 2d)						
Ridges Spring	Sept. 19, 2017	—	—	—	—	—
Ridges Spring	Feb. 1, 2018	—	—	—	—	—
Ridges Spring	Apr. 11, 2018	—	—	—	—	—
Ridges Spring	June 13, 2018	—	—	—	—	—

Abbreviations: µg/L = microgram/liter; ng/L = nanogram/liter.

* Sample tested at the lower limit of detection (0.0017 µg/L).

[a] — = Amount present in sample was below the limit of detection.

Table 4. *(continued)*

Wetland sample name	Sample date	Sulfamethazine (bovine antibiotic) ng/L	Metolachlor ESA (herbicide breakdown product) µg/L	Trifluralin (herbicide) µg/L	Fomesafen (herbicide) µg/L	Clothianidin (neonicotinoid insecticide) µg/L
Limit of detection		**1**	**0.05**	**0.05**	**0.061**	**0.5/0.0017***
Dunes Lake Wetland (fig. 2e)						
Dunes Lake NE Spring	Sept. 18, 2017	—	0.13	—	—	—
Dunes Lake NE Spring	Jan. 30, 2018	—	0.25	—	—	—
Dunes Lake NE Spring	Apr. 12, 2018	—	0.40	—	0.11	0.0065*
Dunes Lake NE Spring	June 14, 2018	—	0.14	—	—	—*
Dunes Lake West Spring	Sept. 19, 2017	—	0.18	—	—	—
Dunes Lake West Spring	Jan. 30, 2018	—	0.16	—	—	—
Dunes Lake West Spring	Apr. 12, 2018	—	0.15	—	—	—
Dunes Lake West Spring	June 14, 2018	—	0.22	—	—	—
Shivering Sands Creek at Steel Bridge	Sept. 19, 2017	—	0.16	—	—	—
Shivering Sands Creek at Steel Bridge	Jan. 30, 2018	—	0.07	—	—	—
Shivering Sands Creek at Steel Bridge	Apr. 11, 2018	—	0.06	—	—	—
Shivering Sands Creek at Steel Bridge	June 13, 2018	—	0.12	—	—	—
Gardner Marsh (fig. 2f)						
Gardner Spring	Sept. 18, 2017	—	0.07	—	—	—
Gardner Spring	Jan. 30, 2018	—	—	—	—	—
Gardner Spring	Apr. 12, 2018	—	—	—	—	—
Gardner Spring	June 14, 2018	—	—	—	—	—*
Gardner Spring South	June 14, 2018	—	0.15	—	—	—

Abbreviations: µg/L = microgram/liter; ng/L = nanogram/liter.
* Sample tested at the lower limit of detection (0.0017 µg/L).
[a] — = Amount present in sample was below the limit of detection.

Water-quality indicators

Many wetlands are nutrient poor and have plant and animal species that fill specialized niches within those environments. Nutrient-rich water can alter the ecology significantly so that the original plant community is lost (Surratt and others, 2012). Nitrate and phosphorus are the nutrients most commonly applied in agriculture as chemical fertilizer or in manures. Discharge from septic systems also contains nitrate and phosphorus. Excess chloride can also affect wetland ecology. Manure, septic system discharge, and road salt are all potential sources of chloride in groundwater and spring discharge. Table 5 lists the concentrations of chloride, nitrate plus nitrite as nitrogen ($NO_3 + NO_2$–N), and total phosphorus in the samples; complete test results are presented in appendix A2. In the environment, nitrate (NO_3) is much more common than nitrite (NO_2) since nitrite is easily and rapidly oxidized to nitrate. For this reason, when we discuss nitrate concentrations, we are talking about the concentrations of nitrogen as nitrate and nitrite in laboratory tests.

Enterococci bacteria in the environment are most often due to fecal contamination from warm-blooded animals. It can be sourced from farm animals, people, and wildlife including birds. While we would expect to encounter some enterococci in natural systems, elevated numbers might be due to a more concentrated fecal source than is generally found naturally.

Table 5. Water-quality indicators in sampled wetland springs, surface waters, and groundwater.

Wetland sample name	Sample date	Chloride mg/L	Enterococci MPN/100 mL	NO_3+NO_2–N mg/L	Total phosphorus mg/L
Limit of detection		**0.5**	**1.0**	**0.1**	**0.00**
Mink River Estuary (fig. 2a)					
Mink River Big Spring	Sept. 20, 2017	12.6	19.9	0.1	0.018
Mink River Big Spring	Jan. 31, 2018	10.3	8.2	0.3	0.037
Mink River Big Spring	Apr. 10, 2018	8.9	1.0	—	0.018
Mink River Big Spring	June 12, 2018	9.6	—	0.7	0.032
MR3 Deep Well	Jan. 31, 2018	2.3	—	0.7	0.01
MR3 Deep Well	Apr. 10, 2018	3.2	—	0.8	—
MR3 Deep Well	June 12, 2018	2.5	—	1.2	—
MR3 Shallow Well	Jan. 31, 2018	12.9	—	1.0	—
MR3 Shallow Well	Apr. 10, 2018	10.6	—	0.9	0.008
MR3 Shallow Well	June 12, 2018	11.6	—	0.9	0.008
MR4 Deep Well	Feb. 1, 2018	2.5	—	1.4	0.028
MR4 Deep Well	Apr. 10, 2018	2.9	—	1.4	0.02
MR4 Deep Well	June 12, 2018	2.7	—	1.7	0.013
MR4 Shallow Well	Feb. 1, 2018	2.7	—	0.8	0.009
MR4 Shallow Well	Apr. 10, 2018	3.3	—	0.8	0.007
MR4 Shallow Well	June 12, 2018	2.8	—	1.0	0.018
Davis Spring	Apr. 10, 2018	12.9	—	3.1	0.031
Davis Spring	June 12, 2018	8.5	—	4.2	0.021
Three Springs Wetland (fig. 2b)					
Three Springs Main Pool Spring	Sept. 19, 2017	14.3	—	0.9	0.019
Three Springs Main Pool Spring	Jan. 31, 2018	14.2	—	1.2	0.018
Three Springs Main Pool Spring	Apr. 11, 2018	10.8	3.0	1.7	0.006
Three Springs Main Pool Spring	June 13, 2018	10.5	13.5	1.7	0.009
Piel Creek Wetland (fig. 2c)					
Piel Creek at culvert	Sept. 19, 2017	5.8	227.9	0.3	0.009
Piel Creek at culvert	Feb. 1, 2018	5.0	—	0.2	—
Piel Creek at culvert	Apr. 11, 2018	5.6	4.1	—	—
Piel Creek at culvert	June 13, 2018	8.3	240	—	0.008
Ridges Sanctuary Wetland (fig. 2d)					
Ridges Spring	Sept. 19, 2017	12.9	30.5	0.6	0.012
Ridges Spring	Feb. 1, 2018	13.2	4.1	1.1	0.007
Ridges Spring	Apr. 11, 2018	15.1	—	0.2	—
Ridges Spring	June 13, 2018	15.9	18.5	0.3	0.033
Dunes Lake Wetland (fig. 2e)					
Dunes Lake NE Spring	Sept. 18, 2017	9.7	88.2	4.1	0.012
Dunes Lake NE Spring	Jan. 30, 2018	7.4	—	5.2	—
Dunes Lake NE Spring	Apr. 12, 2018	6.2	20.1	5.9	—
Dunes Lake NE Spring	June 14, 2018	7.2	—	4.0	0.01

Abbreviations: mg/L = milligrams/liter; MPN/100 mL = most probable number/100 milliliters; — = less than limit of detection

Table 5. *(continued)*

Wetland sample name	Sample date	Chloride mg/L	Enterococci MPN/100 mL	NO_3+NO_2–N mg/L	Total phosphorus mg/L
Limit of detection		**0.5**	**1.0**	**0.1**	**0.00**
Dunes Lake West Spring	Sept. 19, 2017	11.3	6.3	15.5	0.019
Dunes Lake West Spring	Jan. 30, 2018	11.1	3.0	16.4	0.016
Dunes Lake West Spring	Apr. 12, 2018	9.2	—	18.9	0.01
Dunes Lake West Spring	June 14, 2018	9.8	—	19.2	0.016
Shivering Sands Creek at Steel Bridge	Sept. 19, 2017	15.8	210.5	0.3	0.014
Shivering Sands Creek at Steel Bridge	Jan. 30, 2018	16.5	21.3	1.2	0.025
Shivering Sands Creek at Steel Bridge	Apr. 11, 2018	12.4	2.0	0.5	0.02
Shivering Sands Creek at Steel Bridge	June 13, 2018	21.8	88.4	—	0.026
Gardner Marsh (fig. 2f)					
Gardner Spring	Sept. 18, 2017	15.3	—	—	0.01
Gardner Spring	Jan. 30, 2018	16.2	—	0.2	—
Gardner Spring	Apr. 12, 2018	14.3	—	0.4	—
Gardner Spring	June 14, 2018	8.5	—	0.7	0.011
Gardner Spring South	June 14, 2018	15.7	—	4.8	0.014

Abbreviations: mg/L = milligrams/liter; MPN/100 mL = most probable number/100 milliliters; — = less than limit of detection

The enterococci values are given in most probable number (MPN) per 100 ml of sample. The MPN is the most probable number of viable enterococci bacteria or colonies in a sample of 100 ml water. None of the groundwater samples, MR3 and MR4 shallow and deep, had any detects of enterococci. Davis Spring and the Gardner Marsh springs had no detects either. The two locations with surface waters, Shivering Sands Steel Bridge and Piel Creek, had the highest concentrations, above 200 MPN; the rest of the springs had concentrations below 90 MPN.

The chloride concentrations are lowest in the wells MR3 deep and MR4 shallow and deep, varying between 2.3 and 3.3 mg/L. The chloride concentration in MR3 shallow is significantly higher, varying between 10.6 and 12.9 mg/L, suggesting some additional source of chloride to that shallow fracture, possible septic system effluent or road salt. Shivering Sands Steel Bridge, the Ridges, and both Gardner Marsh Springs had the highest chloride concentrations, each with at least one reading above 15 mg/L. The rest of the samples and locations had concentrations between 5 and 15 mg/L.

Nitrate concentrations above 2 mg/L are above background natural concentrations (Wisconsin Groundwater Coordinating Council, 2018). Nitrate concentrations above 10 mg/L exceed drinking water health standards set by the state of Wisconsin. Davis Spring, Dunes Lake NE Spring, and Gardner Marsh Spring South had nitrate levels between 2 and 10 mg/L, indicating anthropogenic sources. Dunes Lake West Spring had nitrate concentrations between 15.5 and 19.2 mg/L, well above the health standard. Although Shivering Sands Steel Bridge is downstream from Dunes Lake NE Spring and Dunes Lake West Spring, it has nitrate concentrations below 2 mg/L. We suspect the lower nitrate concentrations are a result of denitrification by bacteria and plants. The rest of the sample locations did not exceed 2 mg/L.

Phosphorus enters groundwater through the soil column from the surface or septic drain field or by geochemical weathering of the soil or bedrock. Phosphorus has a low mobility in groundwater since it is likely to bind with, or sorb onto, soil and rock. However, as sorption sites on the soil and rock fill with phosphorus, a plume of unattached phosphorus can develop. In this case, additional phosphorus moves through the plume until it reaches a site where it can be sorbed. Groundwater flow through fractures can also aid in transport of phosphorus if the phosphorus sorbs onto small rock and soil particles. These particles with sorbed phosphorus can be carried by groundwater through the fracture.

In an agricultural setting in southwest Wisconsin, McGinley and others (2016) measured groundwater phosphorus concentrations of less than 0.005 mg/L to 2.4 mg/L. They found that carbonate-rich aquifers, such as the Silurian dolomite in Door County, tended to buffer the recharge waters and limit dissolution of phosphate-rich minerals while the older sandstones had elevated concentrations of phosphorus.

Surface waters can be affected by phosphorus from septic systems. Although effluent from septic tanks can contain phosphorus at concentrations of 7–16 mg/L, most shallow groundwater concentrations range from 0.005 to 0.1 mg/L (Lusk and others, 2017).

Lakes with total phosphorus concentrations above 0.03 mg/L are listed as eutrophic with high aquatic plant growth potential (Lillie and others, 1983). Mink River Big Spring, Davis Spring, and Ridges Spring had samples with concentrations above 0.03 mg/L; Shivering Sands Steel Bridge and MR4 Deep each had samples with concentrations at or above 0.02 mg/L; and the rest had concentrations below 0.02 mg/L.

Flow measurements

We measured flows at many of the streams associated with the springs and wetlands when and where possible. The flow measurement locations are shown for each wetland in figures 2a–f and stream flow data are provided with latitude and longitude in appendix A3 for use with GIS. We were able to collect multiple measurements at Davis Spring, Three Springs, Piel Creek, Dunes Lake, and Gardner Marsh. High water levels in Lake Michigan caused flooding in the Mink River Estuary, preventing measurable flows in the stream channels. Only one flow estimate was made at the Ridges Sanctuary springs because those springs had no well-defined discharge channel.

Flow measurements help constrain the water budget for the wetlands. The difference between stream inflows and outflows can be caused by spring discharge directly to the wetland, precipitation into the wetland, and evaporation and transpiration out of the wetland. Table 6 lists stream flows entering and exiting the Three Springs Main Pool (fig. 2b) and Gardner Marsh (fig. 2f). The difference between stream outflows and inflows is also given. At Three Springs, the difference between the outflows and inflows is always positive, meaning that additional water is entering the main pool to make up the difference. We know that the additional water

Table 6. Stream flows into and out of Three Springs and Gardner Marsh

Flow, by location	Flow rate (cfs), by date sampled		
	Sept. 2017	April 2018	June 2018
Three Springs			
Inflow			
Northwest inlet	—	0.30	1.00
North inlet	—	0.94	1.77
Total inflow	—	1.24	2.77
Outflow			
Outlet	—	2.52	4.01
Difference (Inflow–outflow)	—	1.28	1.24
Gardner Marsh			
Inflow			
Kayes Creek at Fox Lane	0.46	0.50	1.77
Kayes Creek at County K	0.25	1.53	0.46
Total inflow	0.71	2.03	2.23
Outflow			
Kayes Creek at Hilly Ridge Road	0.39	10.56	1.47
Difference (inflow–outflow)	–0.32	8.53	–0.76

Abbreviations: — = no samples taken; cfs = cubic feet per second.

Table 7. Areas, number of residences, and percent area in crops in ZOCs for the study wetlands.

ZOC, by location	Number of residences	Area (mi^2)	Residences/ mi^2	Cropland (%)	Corn (%)
Mink River Estuary (fig. 11a)					
Mink River Big Spring	12	0.32	37.9	11.3	4.2
Davis Spring	9	0.16	54.6	21.4	17.3
Three Springs Wetland (fig. 11b)					
Three Springs Main Point	2	0.20	9.8	12.3	4.3
Piel Creek Wetland (fig. 11c)					
Piel Creek culvert	10	0.83	12.1	32.7	10.3
Ridges Sanctuary Wetland (fig. 11d)					
Ridges Spring	32	0.48	66.8	0.5	0.1
Dunes Lake Wetland (fig. 11e)					
Dunes Lake NE Spring	1	0.11	8.7	33.4	19.4
Dunes Lake West Spring	6	0.52	11.6	52.4	27.7
Shivering Sands Steel Bridge	164	9.30	17.6	53.6	18.2
Gardner Marsh (fig. 11f)					
Gardner Marsh Spring	20	0.96	20.9	42.1	13.5
Gardner Marsh Spring South	20	0.96	20.9	42.1	13.5

Abbreviations: % = percent; mi^2 = square miles; ZOC = zone of contribution.

is spring discharge because we can see spring boils distributed along the west edge of the pool. In this case, stream-flow measurements provide a measure of the added groundwater discharge to the main pool. By contrast, at Gardner Marsh the outflow was less than the inflows in June and September. This indicates that during these times the marsh was losing more water than it gained. In April, the situation was reversed with the outflow being greater than the inflow. We suspect that this difference is due to a combination of plant transpiration, evaporation, and quantity of spring discharge. Gardner Marsh has a larger surface area than Three Springs and much more vegetation. During the growing season (as captured during the June and September measurements), plants remove water from the system; during spring snowmelt (as captured in the April measurement), most plants are still dormant, allowing larger flows to exit the marsh. Three Springs has little vegetation and, unlike Gardner Marsh, does not freeze solid due to its larger spring discharge compared to its surface area, so no snowpack is stored for spring melt as it is at Gardner Marsh.

Zones of contribution and land-use analysis

We used GIS to overlay the area of the ZOCs determined by the GFLOW models with land-use layers to determine the number of homes present and the percentage in agriculture. We used address points provided by the Door County Planning Department (Door County Web Map, 2018) to estimate the total number and density of housing in each ZOC. The percent in agricultural production was determined using the USDA Cropscape data averaged over three years (2015–2017). We used the average Cropscape data from the previous three years to water sampling. This choice is a tradeoff between the shorter travel times observed in Door County's groundwater systems (Borchardt and others, 2011) and the variability of crop rotation. Using the three-year average also allowed us to account for higher applications of nitrogen and phosphorus when corn was part of the crop rotation (Laboski and Peters, 2012).

Figures 11a–f show 2017 land use and residences data for each wetland. Also shown are ZOCs for the entire wetland and for the individual sampling points. A geodatabase with all sampling locations, land use layers, septic density, base maps, zones of contribution and associated shapefiles is linked to appendix B.

Table 7 shows the number of residences, residential density per square mile (mi^2), the three-year average percent in cropland and three-year average percent in corn for all spring discharge ZOCs and for Shivering Sands Creek. Of the spring discharge ZOCs, Dunes Lake West Spring had the highest percentage of cropland and corn at 52.4 percent and 27.7 percent, respectively. Ridges Spring had the lowest percentage of cropland (0.5 percent) but the highest residential housing density (66.8 residences/mi^2). Dunes Lake NE Spring had the lowest residential density at 8.7 residences/mi^2.

Piel Creek | Location for flow measurement and water sample collection

Figure 11a. Mink River Estuary, showing zones of contribution, land use, and residences (2017).

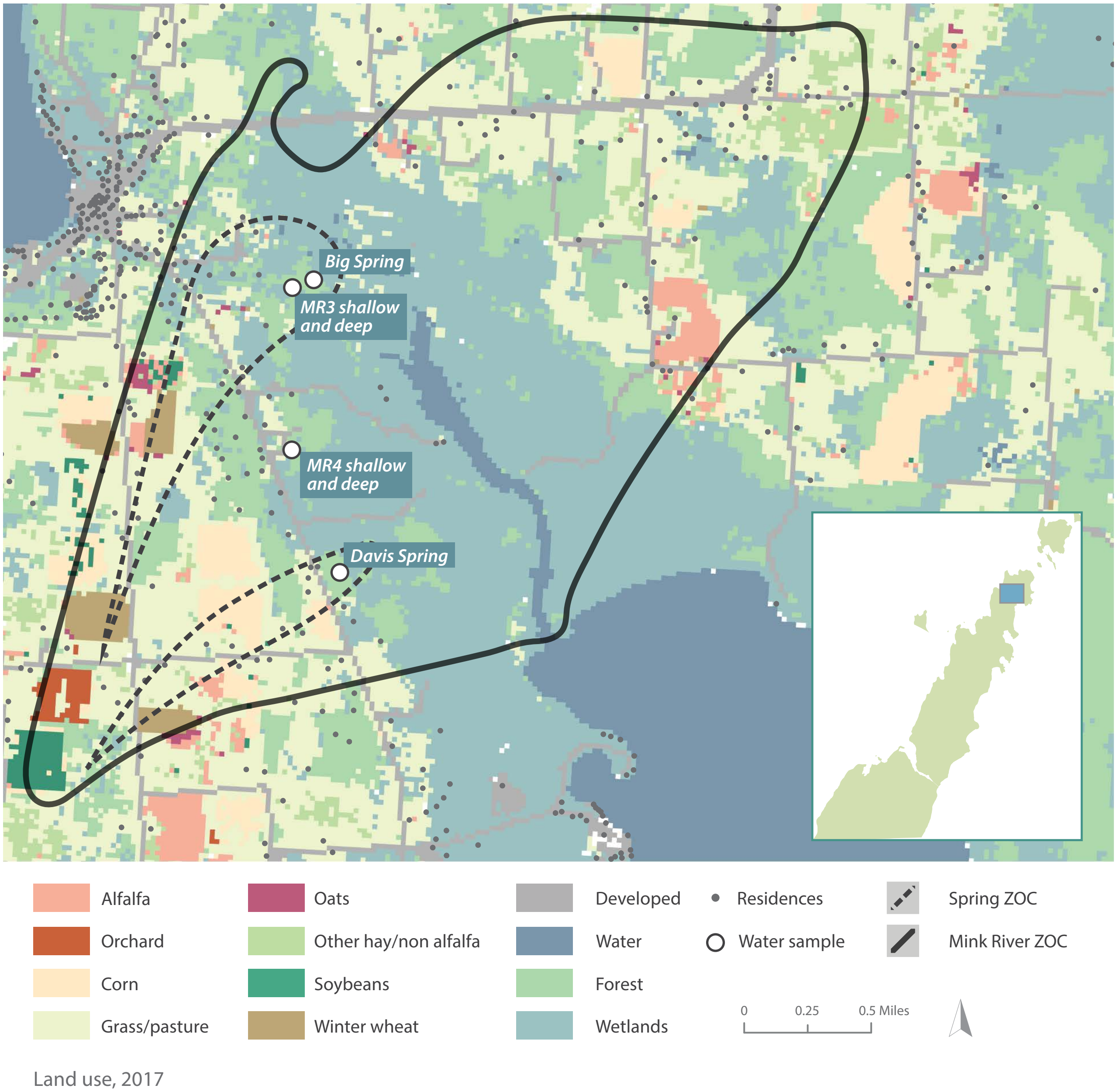


Figure 11b. Three Springs, showing zones of contribution, land use, and residences (2017).

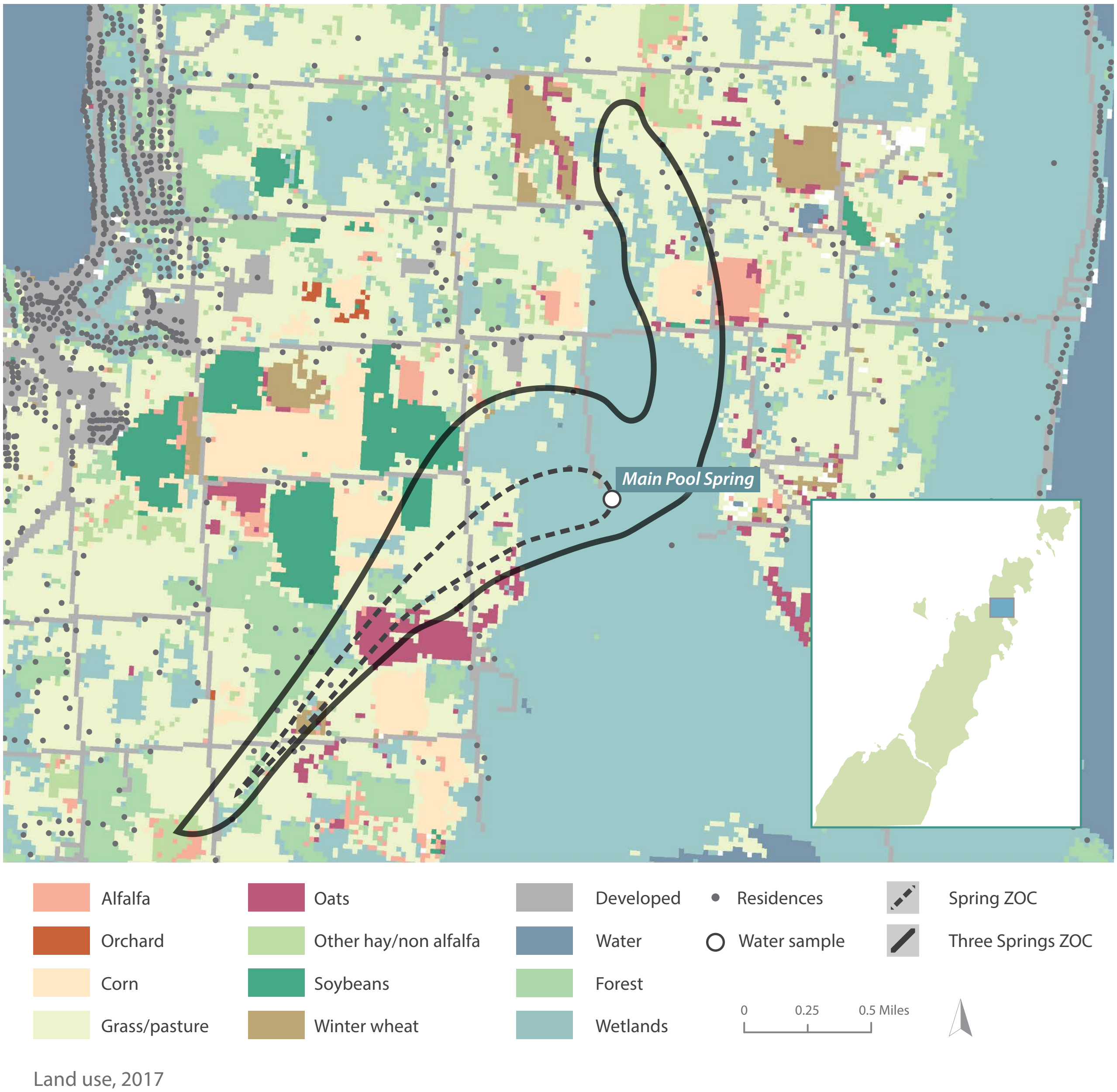


Figure 11c. Piel Creek, showing zones of contribution, land use, and residences (2017).

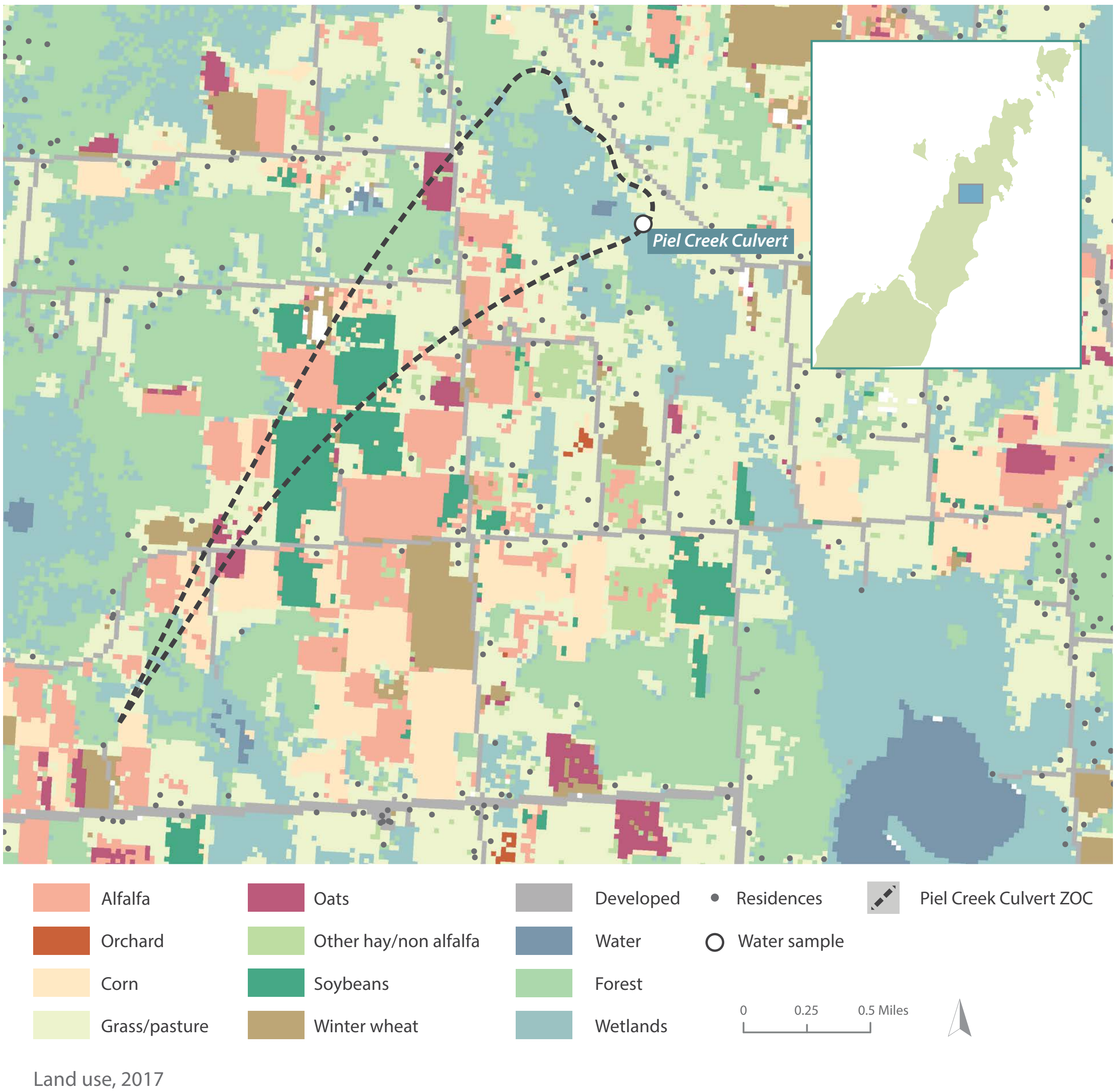


Figure 11d. The Ridges wetlands, showing zones of contribution, land use, and residences (2017).

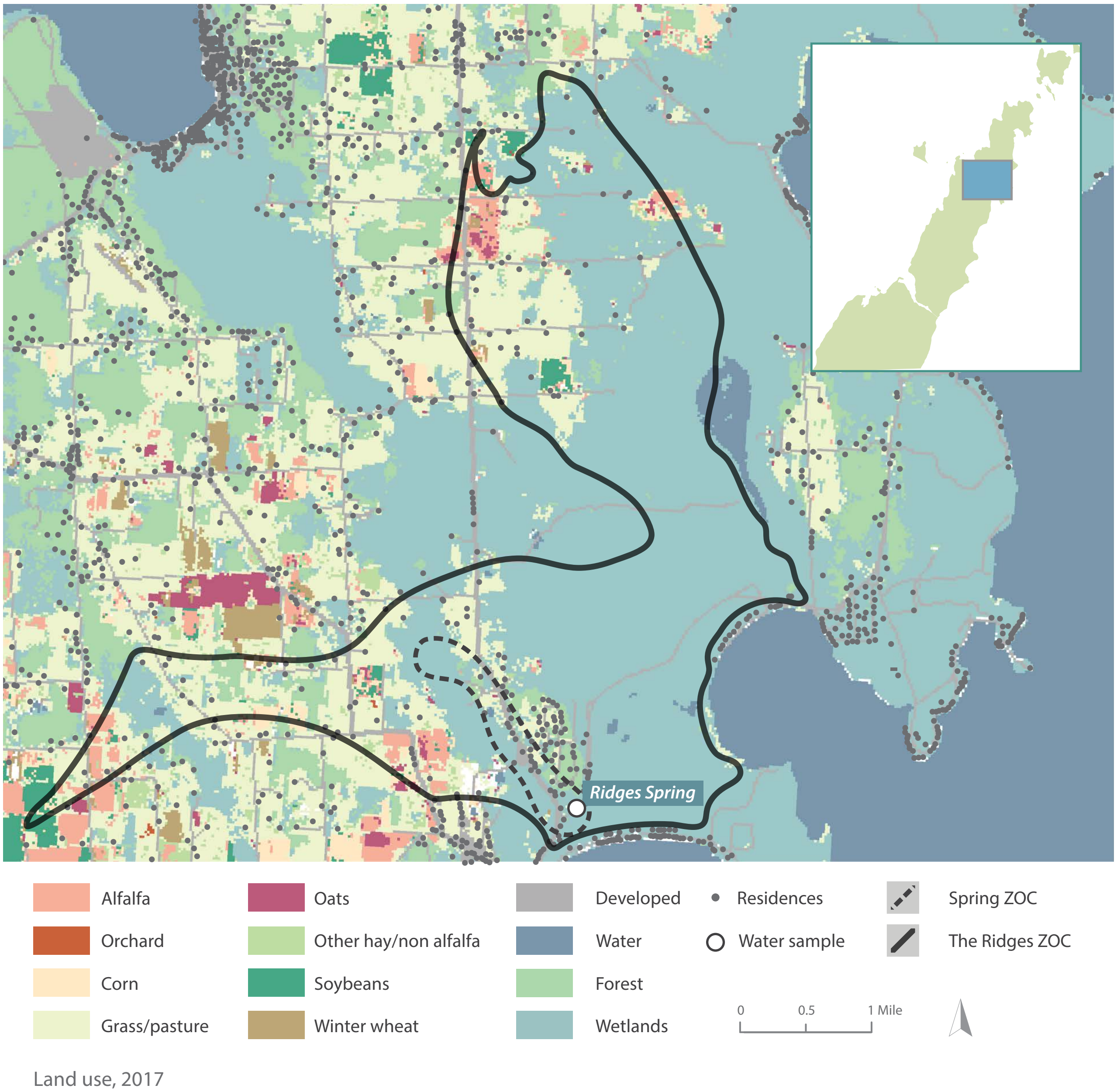


Figure 11e. Dunes Lake, showing zones of contribution, land use, and residences (2017).

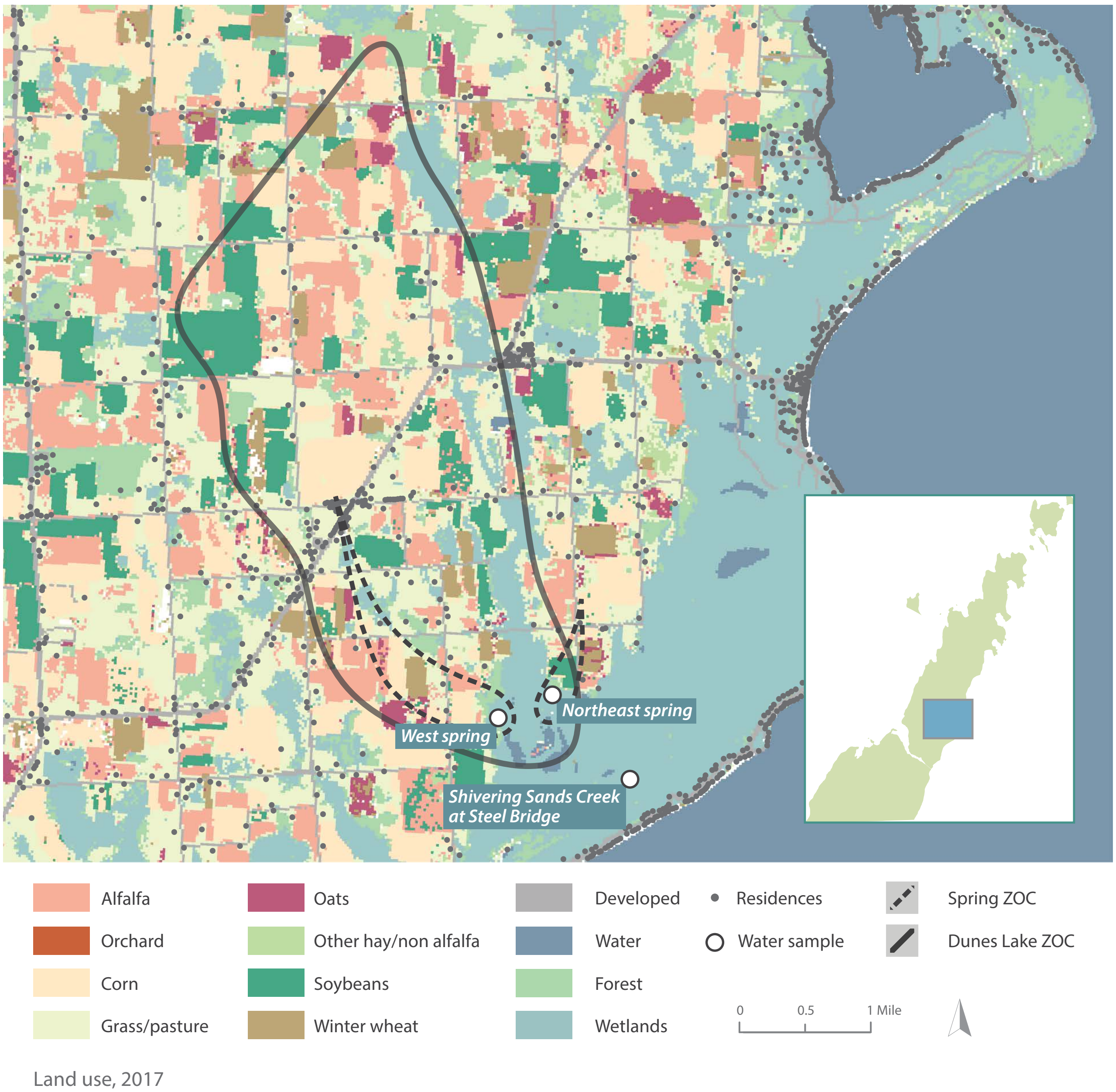
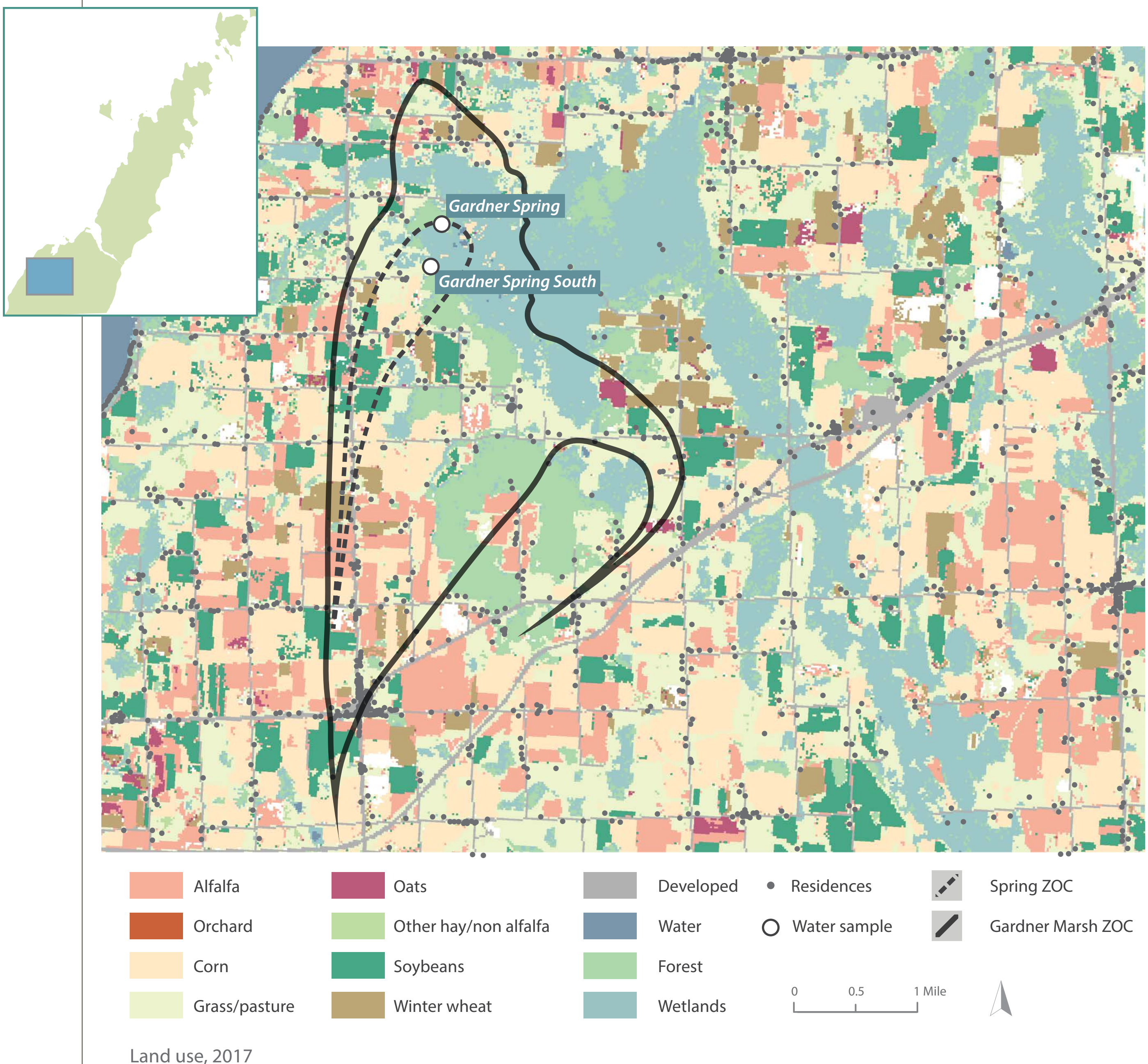


Figure 11f. Gardner Marsh, showing zones of contribution, land use, and residences (2017).



Discussion

Understanding the connections between land use and the water quality of the groundwater discharge to wetlands is essential for planning that maintains healthy coastal wetlands in Door County. To measure impacts to water quality of spring discharge to the wetlands we averaged the concentrations in table 5 over all the sampling events for each location for chloride, nitrogen as nitrate and nitrite, total phosphorus, and enterococci bacteria. We also used the percentage of detects at a sampling location for all detected human indicators listed in table 3 and for all agricultural indicators listed in table 4. For example, the average chloride level in Mink River Big Spring was 10.4 mg/L. After four rounds of sampling at the site (six parameters measured during each round), there were two detects resulting in an 8 percent detection rate (i.e., two detects out of 24 possible). No pesticides or bovine antibiotics were detected over the four sample rounds.

We used the percentage of detects rather than an average concentration since most of the time no PPCPs or pesticides or bovine antibiotics were detected. When many readings are below the detection limit, using percent detects tends to show greater variation in the samples than using average readings. Table 8 summarizes the impacts to water quality of the different springs based on these metrics.

Table 8. Summary of water-quality indicators in spring discharge and surface water samples.

Sample site, by location	Chloride (mg/L)	Enterococci (MPN)	NO_3+NO_2–N (mg/L)	Total phosphorus (mg/L)	Human indicators (% detects)	Ag indicators (% detects)
Mink River Estuary						
Mink River Big Spring	10.4	9.7	0.4	0.03	8	0
MR3 Deep Well	2.7	0.0	0.9	0.01	0	0
MR3 Shallow Well	2.9	0.0	0.9	0.01	28	0
MR4 Deep Well	2.7	0.0	1.5	0.02	11	0
MR4 Shallow Well	2.9	0.0	0.9	0.01	11	7
Davis Spring	10.7	0.0	3.7	0.03	25	0
Three Springs Wetland						
Three Springs Main Pool Vent	12.5	8.3	1.4	0.01	8	5
Piel Creek Wetland						
Piel Creek at culvert	6.2	157.3	0.3	0.01	0	5
Ridges Sanctuary Wetland						
Ridges Spring	14.3	17.7	0.5	0.02	13	0
Dunes Lake Wetland						
Dunes Lake NE Spring	7.6	54.2	4.8	0.01	4	30
Dunes Lake West Spring	10.4	4.7	17.5	0.02	13	20
Shivering Sands Steel Bridge	16.6	80.6	0.7	0.02	33	20
Gardner Marsh						
Gardner Spring	13.6	0.0	0.4	0.01	13	25
Gardner Spring South	15.7	0.0	4.8	0.01	17	20

Abbreviations: MPN = most probable number; mg/L = milligrams/liter.

We looked for correlations using Pearson's correlation coefficient (r) between all the variables except area in table 6 and all the sites in table 7 except the shallow and deep wells at MR3 and MR4 and Shivering Sands Steel Bridge. Those sites were not included since they are not spring discharge areas. Although Piel Creek is a surface water, it was included because the sample location is at the headwaters in a wetland and within 50 ft of an area of groundwater seepage.

Pearson's correlation coefficient varies between 1 and −1. A value of 1 means that the variables being compared have a one-to-one positive correlation, a value of zero means that the two variables are not correlated, and a value of −1 means the variables are inversely or negatively correlated. Table 8 shows the correlation coefficients between the variables. Each variable is listed in the columns and the rows. To identify the correlation between two of the variables, choose the column of the first variable of interest and the row of the second variable of interest. The intersected cell shows the correlation coefficient for the two variables. The statistical significance of the correlations was tested by calculating the probability that the variables are not correlated, the null hypothesis. That probability, p, is listed in parentheses. The degrees of freedom for the analysis is 7.

Table 9. Correlation coefficients (r) for land-use parameters and water-quality indicators. Shading represents the strength of correlation. The significance p-value is shown in parentheses. This value is an estimate of the probability that the indicators and parameters are not correlated.

	Correlation coefficient, r (p-value significance)									
Variable	**Residences**	**Residences/mi^2**	**Corn (%)**	**Cropland (%)**	**Chloride (mean)**	**Enterococci (mean)**	**Nitrate (mean)**	**Total phosphorus (mean)**	**Human indicators (% present)**	**Ag indicators (% present)**
Residences	1.00									
Residences/mi^2	0.65	1.00								
	(0.06)									
Corn (%)	−0.47	−0.44	1.00							
	(0.20)	(0.23)								
Cropland (%)	−0.26	−0.65	0.84	1.00						
	(0.50)	(0.06)	(0.005)							
Chloride (mean)	0.65	0.36	−0.30	−0.13	1.00					
	(0.06)	(0.34)	(0.44)	(0.75)						
Enterococci (mean)	−0.19	−0.31	−0.06	0.07	−0.74	1.00				
	(0.62)	(0.41)	(0.88)	(0.86)	(0.02)					
Nitrate (mean)	−0.33	−0.31	0.81	0.63	−0.08	−0.24	1.00			
	(0.38)	(0.41)	(0.01)	(0.07)	(0.84)	(0.54)				
Total phosphorus (mean)	0.08	0.69	−0.15	−0.47	0.13	−0.49	−0.02	1.00		
	(0.83)	(0.04)	(0.70)	(0.20)	(0.74)	(0.18)	(0.96)			
Human indicators (% present)	0.28	0.56	0.20	0.00	0.58	−0.72	0.19	0.59	1.00	
	(0.47)	(0.12)	(0.61)	(0.99)	(0.10)	(0.03)	(0.62)	(0.10)		
Ag indicators (% present)	−0.21	−0.63	0.64	0.77	0.01	−0.08	0.41	−0.60	−0.15	1.00
	(0.60)	(0.07)	(0.06)	(0.01)	(0.99)	(0.84)	(0.28)	(0.09)	(0.70)	

Correlation coefficient

- 0.70 to 0.95 Strong
- 0.55 to 0.70 Moderate
- −0.55 to 0.55 Weak to weak negative
- −0.70 to −0.55 Moderate negative
- −0.95 to −0.70 Strong negative

Example 1: The correlation of the number of residences/mi^2 and nitrate concentration has a correlation coefficient of –0.31. This inverse correlation would suggest that a higher housing density in a ZOC is correlated with a lower nitrate concentration. However, the significance probability, p, that they are not correlated is 0.41. Based on the high probability of no correlation, nitrate and number of residences should not be considered to be correlated.

Example 2: The percent corn in a ZOC and nitrate have a positive correlation coefficient of 0.81 and a low significance probability of no correlation, p=0.01. The percent corn in a ZOC and nitrate concentrations in the ZOC groundwater discharge are likely to be correlated.

Summary of key results for nutrient origins based on correlation analysis (from table 9):

- **Phosphorus:** There are moderate correlations between the density of residences in a ZOC with total phosphorus and human indicators (r = 0.69). By contrast, there is no significant correlation between total phosphorus and percent corn (r = –0.15) or percent cropland (r = –0.47). These findings suggest that the phosphorus observed in spring discharge has a residential origin and is not from agriculture. However, this statement deserves the strong caveat that we only sampled spring discharges, not surface-water runoff to wetlands.
- **Nitrate:** Nitrate, measured as NO_3+NO_2–N, is strongly correlated to the percent corn in a ZOC (r = 0.81) and moderately correlated to percent cropland (r = 0.63) and pesticide detects. There is no significant correlation between residences and nitrate (r = –0.33), suggesting that the nitrate observed in spring discharge is likely from agricultural rather than residential sources.

Plots showing the relationship between nitrate and percent corn and between phosphorus and residential density are shown in figures 12 and 13. The r^2 shown on the plots is the correlation coefficient squared. The relationship between percent land in corn in a ZOC and the mean nitrate concentration observed in spring discharge is shown in figure 12. The significance p-value is 0.01 for these two variables, suggesting that it is unlikely that they are uncorrelated. The dashed line on the plot is the best-fit line and equation. Also shown are the 95 percent confidence bands for the data, meaning that any new data have a 95 percent probability of lying between the bands. The wide range of the confidence bands is expected given the variability in the data. It should be noted that the negative nitrate values predicted by the lower range of the 95 percent confidence band are not possible. Those values should instead be interpreted as an increased probability of no-detects of nitrate at lower percent corn values. Using the best-fit relationship, we would expect that if a spring's entire zone of contribution was planted in corn, the nitrate concentration would be (0.52 x 100% corn)–2.60 = 49 mg/L. This value is two to four times what is generally expected for nitrate leaching beneath continuous corn rotation averaged over multiple years (Randall and others, 1997; Masarik and others, 2014). If the linear fit is recalculated without the Dunes Lake West Spring point, which was exceptionally high, the equation for the resulting best-fit line becomes (0.21 x % corn)–0.16. Using this equation with 100% corn gives an estimated concentration of 21 mg/L, a value that is more in agreement with other studies. Since Dunes Lake West Spring nitrate concentrations are much larger than expected for the percentage of corn in its ZOC, it is possible that another source of nitrate, such as feedlot runoff or seepage from septic systems, is present in the Dunes Lake West Spring ZOC or that nitrate was applied to the corn at a rate far in excess of general practice.

We can also use this type of analysis to predict how phosphorus might increase if residential density increases using the linear relationship in figure 13. The best-fit line and equation (y = 0.00021x + 0.01015) are shown in black with the 95% confidence bands shown in gray. The significance p-value is 0.04 for these two variables, suggesting that it is unlikely that they are uncorrelated. If residential density increases to 200 residences/mi^2 (3.2 acres/residence) in the ZOC, then we might expect to see phosphorus concentrations in spring discharge increase to 0.052 mg/L (0.00021 x 200 residences/mi^2 + 0.01015). This value is well above concentrations that are classified in lakes as eutrophic. However, the 95% confidence bands include a wide range of phosphorus concentrations (0.006–0.031 mg/L at 40 residences/mi^2). So, while phosphorus levels will likely increase with higher housing density, there is a wide range of phosphorus concentrations that could occur.

These analyses need to be understood in the context of the statistical variation. The variability seen in the data in figures 12 and 13 and underlying the correlations in table 9 is due to many factors. These factors include variation in the both residential and agricultural source concentrations, attenuation in the soil column and along the groundwater flow path, low sample size, and uncertainty in the area and extent of the ZOCs. While the analyses above are reasonable and based on data, they should be used with caution and validated whenever possible.

Figure 12. Plot of percent land in corn within zones of contribution against nitrate concentration in spring discharge.

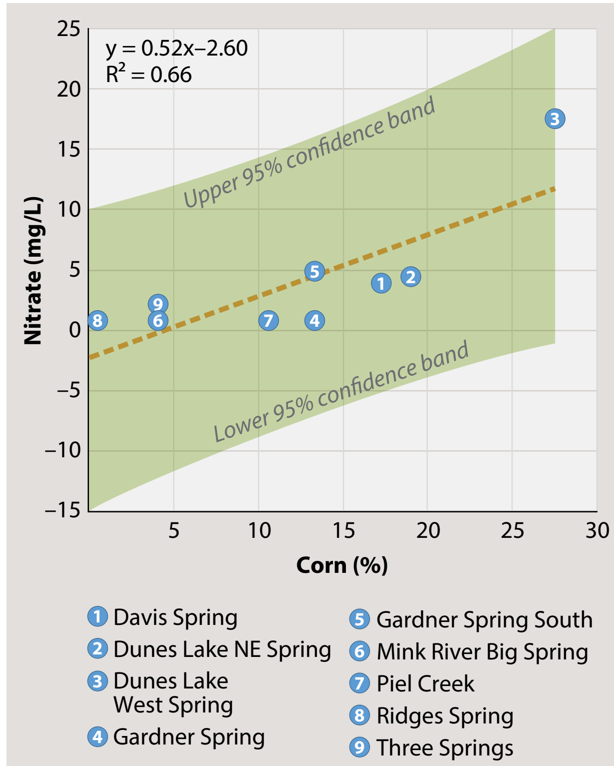
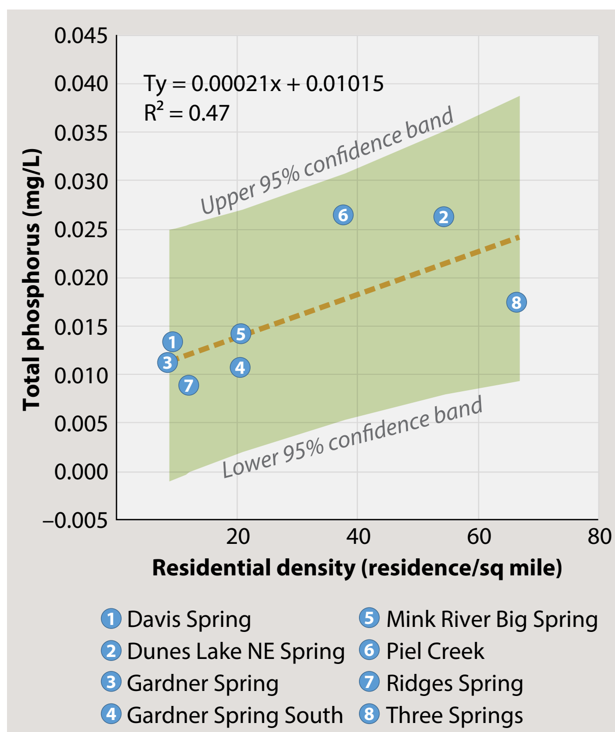


Figure 13. Plot of total phosphorus related to residential density.



Conclusions and recommendations

We sampled spring discharge to wetlands in the early fall, midwinter, spring snowmelt, and early summer between September 2017 and June 2018. The samples were analyzed for major ions, nutrients such as nitrate and phosphorus, PPCPs such as artificial sweeteners, and pesticides. Both PPCPs and pesticides were detected in some spring discharge samples. Neonicotinoids, a group of insecticides of particular concern for wetland ecology, were detected in only one sample and at a low concentration.

We found correlations between both agricultural and residential land use in the zones of contribution to springs in the wetlands we studied and contaminants in spring discharge. Most significantly, we found that:

- Agricultural land use (averaged over three years) in a zone of contribution is correlated to higher nitrate concentrations and a higher probability of pesticide detects in spring discharge.
- Housing density is correlated to a greater number of detects of PPCPs and higher phosphorus concentrations in spring discharge
- Increased housing density is not correlated to nitrate concentration in spring discharge.
- Agricultural land use is not correlated to phosphorus concentration in spring discharge. However, phosphorus carried in surface-water runoff was not considered in this groundwater study.

Correlations between local land use and the water quality of spring discharges in groundwater-fed wetlands indicate a need for careful land-use planning to avoid negative impacts to the coastal wetlands of Door County.

Results of this study could be used as a benchmark for future groundwater conditions. Any changes in land use should be coupled with water-quality sampling to continue to monitor and avoid groundwater quality impacts.

Local watershed and wetland managers can use these findings to guide the determination of nutrient, pesticide, and PPCP concentrations that will limit or reduce impacts to wetlands and other groundwater resources. These findings can also be used as a tool to inform land-use management and to better protect groundwater quality for humans and the natural environment.

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The Ridges | Winter water sample collection

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Shivering Sands Steel Bridge | Spring meltwater sample, same location used for all samples

Appendix A: Water sampling results

Field and laboratory water sampling results and stream-flow measurements are available in the following Microsoft Excel spreadsheets (files available for download, https://wgnhs.wisc.edu/pubs/000974/).

- **Appendix A1: Field water chemistry data**
- **Appendix A2: Laboratory water chemistry data**
- **Appendix A3: Stream-flow measurements**

The water chemistry results were also submitted to the Wisconsin Department of Natural Resources Surface Water Integrated Monitoring System database (https://dnr.wisconsin.gov/topic/SurfaceWater/SWIMS). If you have difficulty accessing the database, please contact a report author. Any interpretation of the data outside of the conclusions found in this report is the responsibility of the user and does not reflect the opinions of the report authors.

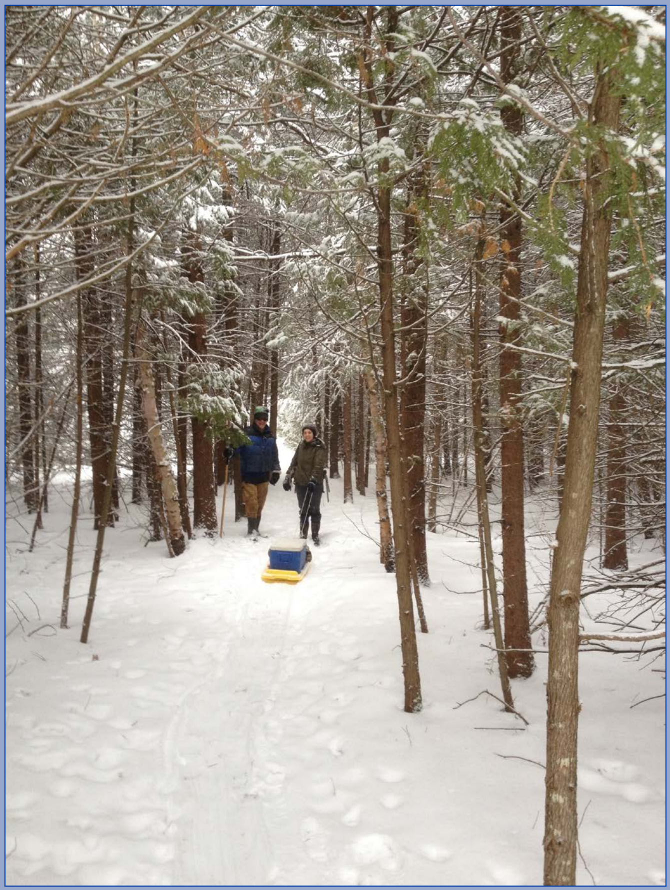
Gardner Marsh South Spring | Using PVC pole to place tubing in center of spring pool

Gardner Marsh Spring | Arrow shows location of sampled spring discharge area

Appendix B: Project data

Appendix B contains all project data produced for this report—sampling locations, land-use layers, septic density, base maps, zones of contribution, and associated shapefiles. The appendix is available for download at https://wgnhs.wisc.edu/pubs/000974/. Any interpretation of the data outside of the conclusions found in this report is the responsibility of the user and does not reflect the opinions of the report authors.

Dunes Lake West Spring | Winter water sample collection



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This report is an interpretation of the data available at the time of preparation. Every reasonable effort has been made to ensure that this interpretation conforms to sound scientific principles; however, the report should not be used to guide site-specific decisions without verification. Proper use of the report is the sole responsibility of the user.

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