Neonicotinoid Pesticides In Wisconsin Groundwater and Surface Water

WISCONSIN DEPARTMENT OF AGRICULTURE, TRADE AND CONSUMER PROTECTION

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A summary of groundwater and surface water test results for neonicotinoid insecticides from 2008 through 2016

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Executive Summary

It has been estimated that agriculture generates $88 billion per year for Wisconsin's economy. The Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) manages groundwater and surface water sampling programs designed to assess and protect water resources from chemicals used in agriculture. This report presents a summary of DATCP groundwater and surface water testing programs for neonicotinoid insecticides from 2008 through 2016.

Neonicotinoid insecticides are used widely in agriculture. Their high toxicity to insects, low toxicity to mammals, long lasting systemic activity and wide range of application methods make them the most widely used class of insecticides worldwide. In Wisconsin, more than 500 products containing neonicotinoid active ingredients are registered for use. They are labelled for use on most major crops, including corn, soybeans, forage, small grains, vegetables and cranberries. They have become the subject of extensive research into possible effects on pollinator populations across the country.

DATCP test results show that three commonly used neonicotinoids (clothianidin, imidacloprid and thiamethoxam) were detected in samples collected from private potable wells, field-edge monitoring wells, and irrigation wells. Two neonicotinoid compounds (imidacloprid and thiamethoxam) were detected in stream water samples. In addition to neonicotinoids, DATCP detected numerous other agricultural chemicals, including nitrate in all types of wells sampled as well as in streams.

For the targeted well sampling program, sampling revealed 5.7 percent of potable wells in agricultural areas contained one or more neonicotinoid compounds. The exceedance well sampling program includes potable wells that once contained a pesticide above a drinking water quality standard (chapter NR 140, Wisconsin Admin Code). For this program, the likelihood of neonicotinoid detection increased to 14.3 percent. An evaluation of field-edge monitoring wells revealed that 53.1 percent of sites had samples test positive for neonicotinoids. For irrigation wells, University studies reported up to 69 percent of irrigation wells with one or more detections of the compound thiamethoxam. The majority of neonicotinoid detections occurred where major agricultural crops are grown in areas with coarse, well-drained surface soils and shallow groundwater (less than about 20 feet deep). Many detections coincided with sandy agricultural areas within the Central Sands region and the Wisconsin River Valley.

Neonicotinoids and other pesticides detected in irrigation wells sampled in the Central Sands and Lower Wisconsin River Valley (LWRV), as well as those detected in stream samples in the Central Sands, have implications for target and non-target insects, honeybees, wild bees and other pollinators, as well as aquatic invertebrates. Aside from concerns over direct exposures to these organisms during application and use of these products, there is additional concern over chronic exposures resulting from residual concentrations in soil and plant tissues, and in contaminated groundwater used for irrigation and occurring as base flow discharge to streams.

Based on results presented in this report, additional research is needed in the Central Sands and other areas where neonicotinoid compounds were detected to evaluate measurable effects on organisms from the long term presence of neonicotinoids and other compounds in groundwater and surface water.

Groundwater and Surface Water Use in Wisconsin

The State of Wisconsin, located in the western Great Lakes Region of North America, has abundant fresh water resources that are extremely important to its residents, businesses, agriculture and recreation. The state borders two Great Lakes, Lake Michigan and Lake Superior. Wisconsin has more than 15,000 inland lakes (WDNR, Water Topics, 2017), most of which were formed as the great Laurentide Ice Sheet receded during the Late Pleistocene Epoch about 13,000 years ago (Flint, 1971). Abundant fresh groundwater exists across much of the state in Paleozoic age sedimentary rocks and Pleistocene glacial sediments (Luczaj & Masarik, 2015).

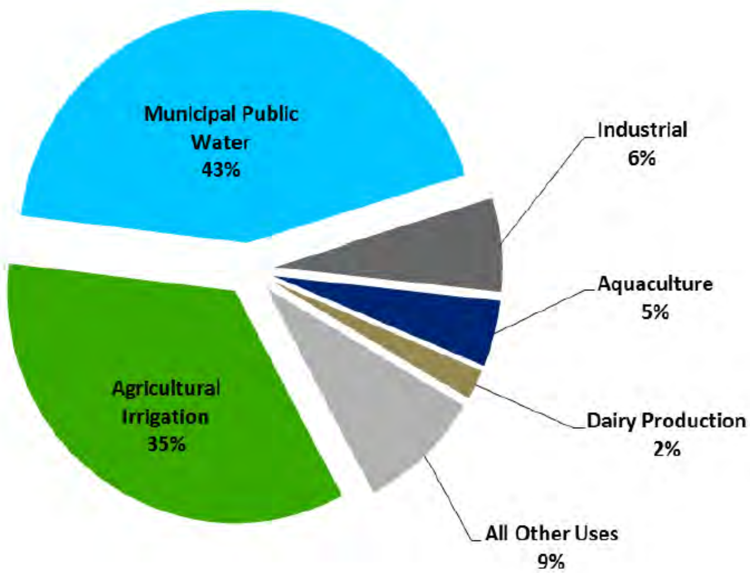
In 2014, just under 2 trillion gallons of water were withdrawn from Wisconsin's surface waters and from groundwater wells. Surface water withdrawals represent about 88 percent of this total, or about 1.73 trillion gallons. Most surface water withdrawals are used for cooling water in power generation (85 percent). Aside from power generation, the largest users of surface water include paper production (5.6 percent), municipal water supplies (4.4 percent), cranberry production (3.6 percent) and mining or other uses (1.8 percent) (WDNR, Wisconsin Water Use Withdrawal Summary 2014, 2016).

As for groundwater uses, it is estimated that two thirds of Wisconsin's population of 5.7 million people (Census, 2010) rely on groundwater as their primary source of drinking water (WDNR, Groundwater Coordinating Council Annual Report to Legislature, 2016). An estimated 800,000 low capacity wells serve private homes, farms and businesses across the state. These wells withdraw approximately 50 to 75 billion gallons of water per year.

In addition to withdrawals from low capacity wells, more than 11,000 registered high capacity wells withdraw groundwater for agricultural irrigation, municipal water supply systems, industrial and other high volume water uses. A high capacity well is defined as one or more wells on a property where the collective withdrawal capacity is 100,000 gallons or more per day. In 2014 (Figure 1), Department of Natural Resources (DNR) reported 224 billion gallons of groundwater withdrawn from high capacity wells for municipal, irrigation and other uses (WDNR, Wisconsin Water Use Withdrawal Summary 2014, 2016).

Agricultural irrigation and municipal water withdrawals represent two of the largest annual groundwater use categories in Wisconsin. Portage, Waushara and Adams Counties have the largest groundwater withdrawals for agricultural irrigation (Figure 2). These counties are centrally located in the state and are home to a large and globally significant potato and vegetable growing area. This area coincides with a central sand plain, or Central Sands region, an area east of the Wisconsin River where glacially derived sand and gravel deposits extend from the surface to depths greater than 50 feet. The area is known for highly permeable sandy soils and abundant shallow groundwater.

FIGURE 1 GROUNDWATER WITHDRAWALS BY WATER USE TYPE, 2014



Left: In 2014, DNR reported 224 billion gallons of groundwater withdrawn from high capacity wells for municipal, agricultural irrigation, industrial and other purposes.

Municipal public water supplies withdrew about 98 billion gallons (43 percent) for residential, commercial, industrial and institutional uses. Agricultural irrigation withdrawals totaled about 78 billion gallons (35 percent), while industrial, aquaculture, dairy and all other uses totaled about 49 billion gallons (22 percent).

Low capacity wells for private homes, farms and businesses withdraw an additional 50 to 75 billion gallons per year.

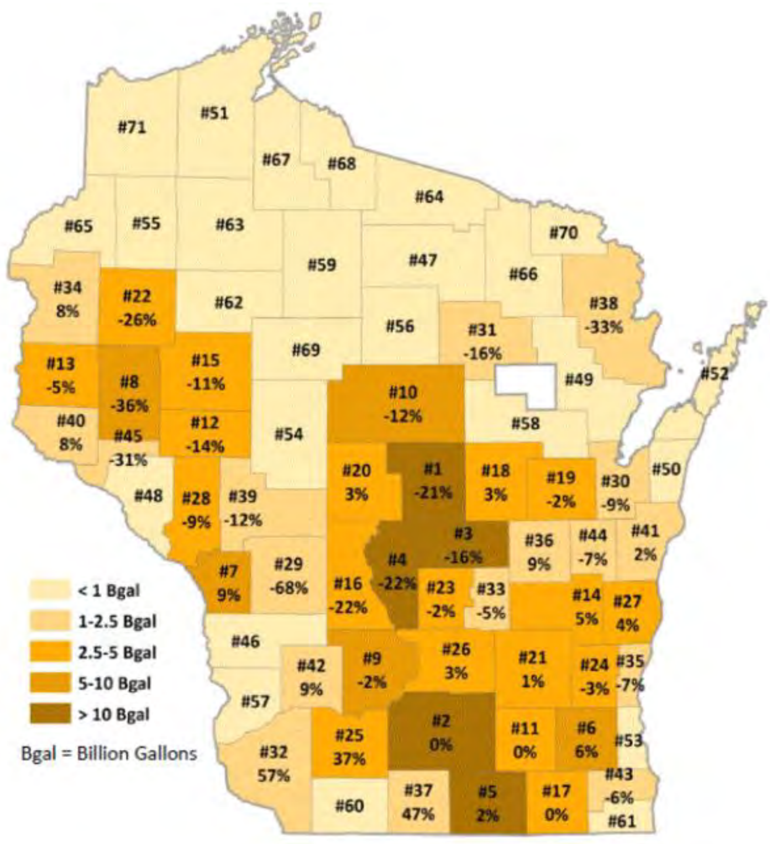
FIGURE 2 GROUNDWATER WITHDRAWALS BY COUNTY, 2014

Right: the top number indicates ranking of total withdrawal by county (#1 = highest, #71 = lowest). For counties having withdrawals exceeding 1 billion gallons, the bottom number shows the percent change from 2013.

In the center of the state, Portage, Waushara and Adams Counties have high agricultural irrigation withdrawals (ranking #1, #3 and #4 respectively). These counties are home to the State's globally significant vegetable and potato producing area. Withdrawals in these counties decreased significantly due to increased precipitation during the 2014 growing season.

Dane and Rock Counties (#2 and #5 respectively) have large urban/suburban populations that rely on groundwater for residential, industrial and commercial needs. Groundwater withdrawals remained similar from 2013 through 2014.

Groundwater withdrawals are lower in the north due to greater forest cover and lower population and agricultural needs.



(WDNR, Wisconsin Water Use Withdrawal Summary 2014, 2016)

Major Crops Grown in Wisconsin

Different crops have different pesticides labeled for various crop protection needs. DATCP uses knowledge about the types of agricultural crops grown across the state to better understand the types of pesticides used on the landscape. This knowledge helps staff design groundwater testing programs to detect pesticides that may contaminate groundwater and surface water resources.

Table 1 shows a summary of the major commodity crops grown in Wisconsin in 2015, as reported by the U.S. Department of Agriculture (USDA) National Agricultural Statistics Service (NASS). Wisconsin often ranks ninth annually among states in the nation for corn grown for grain, with approximately 3 million acres planted in 2015. Corn for silage added about 970,000 acres, for a total of about 4 million acres of corn grown annually. Acres devoted to all forage (alfalfa and hay, dry equivalent) included about 2.6 million acres, and soybeans about 1.9 million acres. Winter wheat, oats and barley combined to represent another 420,000 acres. Potatoes for processing and fresh market were grown on about 62,500 acres, while peas, sweet corn and snap beans combined for another 160,300 acres. Wisconsin routinely ranks as the nation's top producer of cranberries, with production occurring on 20,200 acres in 2015 (USDA-NASS & DATCP, 2016).

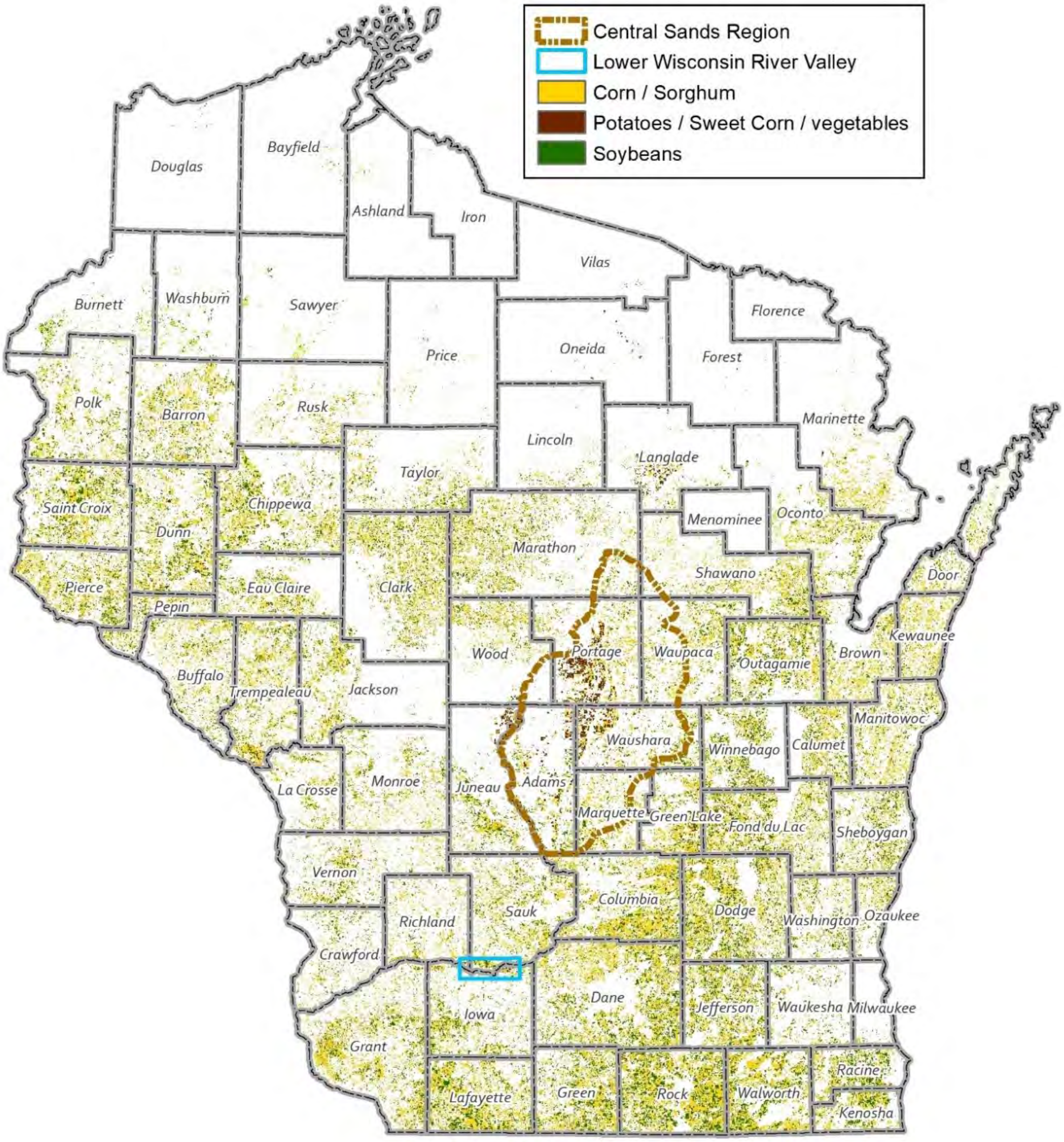
TABLE 1 MAJOR CROPS AND APPROXIMATE ACRES UNDER PRODUCTION IN WISCONSIN IN 2015

Major Crops Grown in 2015	Approximate Acreage
Corn (includes for grain and sileage)	3,970,000
Forage Crops (alfalfa and hay, dry equivalent)	2,600,000
Soybeans	1,900,000
Winter Wheat, Oats and Barley	420,000
Vegetables (peas, sweet corn, snapbeans and potatoes for processing and fresh market)	222,800
Cranberries	20,200

(USDA-NASS & DATCP, 2016)

Figure 3 represents geographic information system (GIS) data from NASS showing the distribution of corn, soybean, potato and other vegetable crops grown in 2015 (USDA-National Agricultural Statistics Service, 2016). This figure helps to illustrate agricultural cropping patterns that typically occur across the state. The image shows corn and soybeans are grown widely across the southern two-thirds of the state. These crops are typically interspersed and often in a rotation with each other, and with forage crops or small grains. Potatoes, sweet corn and other vegetables are specialty crops that are also grown in rotation with corn, soybeans and other crops. The areas that favor vegetable cropping can be seen in clusters across the state, the most notable of which occurs in the center of the state (Central Sands). Smaller areas favorable to vegetable growing can be seen on the figure, including an area within the LWRV. Both the Central Sands Region and the LWRV are shown on the figure.

FIGURE 3 CORN, SOYBEAN, POTATO AND VEGETABLE PRODUCTION IN WISCONSIN, 2015



Above: NASS imagery shows where major crops are typically grown in Wisconsin, including corn, soybeans, potatoes and other vegetables. A sand plain located in the center of the state (brown outline) is known as the Central Sands Region (Luczaj & Masarik, 2015). Marked by deep sandy soils and abundant shallow groundwater, it is where much of the state's vegetable production occurs. Similar conditions exist in the LWRV to the south (blue outline), and in other areas not specifically called out on the figure.

Neonicotinoid Insecticides

Neonicotinoid insecticides are nicotinic acetylcholine receptor agonists. They mimic the action of the neurotransmitter acetylcholine, and bind strongly to nicotinic acetylcholine receptors (nAChRs) in the central nervous system of insects, causing nervous stimulation at low concentrations, and at higher concentrations, receptor blockage, paralysis and death (Tomizawa & Casida, 2005). They bind more strongly to receptors in insects than to those of vertebrates, so they are selectively more toxic to insects (Goulson, 2013). First introduced in 1994 (imidacloprid), they've been widely viewed as safer alternatives to more toxic insecticides in the organochlorine, organophosphate and carbamate classes. They offer advantages of low toxicity to vertebrates, high toxicity to insects, and a broad range of application types and use options over insecticides in other classes. Neonicotinoid insecticides are water soluble and readily absorbed by plant roots or leaves and are readily transported throughout plant tissues to provide long lasting systemic activity to all parts of the plant. These advantages have helped make them the most popular class of insecticides worldwide, with neonicotinoids representing 25 percent of all insecticides used globally (Goulson, 2013).

There are seven compounds classified as neonicotinoids that are commonly used in agriculture. These seven compounds can be further broken out into one of three chemical groups. They include the *N*-nitroguanadines (clothianidin, imidacloprid, thiamethoxam and dinotefuran), the N-cyanoamidines (acetamiprid and thiacloprid), and the nitromethylenes (nitenpyram). Two compounds (nitenpyram and thiacloprid) are not contained in any products registered for use in Wisconsin and they will not be discussed further in this report (one product containing thiacloprid was registered, but the registrant voluntarily canceled the registration in 2016). The five remaining neonicotinoids clothianidin, imidacloprid, thiamethoxam, acetamiprid and dinotefuran, are active ingredients in 600 products registered for use in Wisconsin (Kelly Products Inc., 2017).

There are some important differences in uses of products that contain acetamiprid and dinotefuran that set them apart from clothianidin, imidacloprid and thiamethoxam. Acetamiprid and dinotefuran have products labeled for use on agricultural crops, but they are more widely used in turf, lawn and landscape products, structural pest applications, companion and other animal products, greenhouse and nursery uses, and in bait applications used in homes and other structures. Their crop uses tend to be more limited and do not include use as seed treatments. Their uses are less widespread on the landscape than other neonicotinoid products. Furthermore, DATCP has not detected acetamiprid or dinotefuran in any groundwater or surface water samples collected through 2016. For these reasons, these two compounds are not discussed further in this report.

Major Crop Uses in Wisconsin

Clothianidin, imidacloprid and thiamethoxam are registered in a total of 502 products sold in Wisconsin. Clothianidin is the active ingredient in 29 products registered, imidacloprid in 423 and thiamethoxam in 50 registered products. Out of these total numbers, each active ingredient is found in products labeled for use on major agricultural crops grown in Wisconsin, like corn, soybeans, potatoes, sweet corn, snap beans and other high value vegetables. Clothianidin is in about 15 product formulations, imidacloprid is in about 105, and thiamethoxam is in about 36 product formulations labeled for one or more major agricultural crop uses (Kelly Products, Inc., 2017). Most commonly, these products are used as seed treatments on corn, soybeans and small grains, but they also have formulations that allow their use as soil treatments or as foliar sprays on certain crops. Table 2 lists names of some of the major manufacturers or suppliers, common product names, and common uses and formulations containing clothianidin, imidacloprid and thiamethoxam. The table contains examples and is not intended to be an exhaustive list.

Table 2 Some Common Examples of Manufacturers, Products and Formulations Containing Clothianidin, Imidacloprid and Thiamethoxam

Neonicotinoid Active Ingredient	Manufacturers and Suppliers	Registrations and Some Product Names	Common Formulations and Applications
Clothianidin	Bayer CropScience Sumitomo Chemical Co Takeda Chemicals	A total of 29 products registered in Wisconsin, about 15 for major agricultural crop uses. Some product names include Deter, Modesto, and Poncho.	Commonly supplied as a flowable concentrate prepared for uses as a seed treatment.
Imidacloprid	Bayer CropScience Makhteshim-Agan Scotts	A total of 423 products registered in Wisconsin, about 105 for major agricultural crop uses. Some products include Admire, Gaucho, Raxil, and Chinook Blue.	Often supplied as granules that are mixed with water and applied as a spray, used as a seed treatment or applied directly to compost. For animal use it is usually supplied as a spot-on solution.
Thiamethoxam	Syngenta AgroCare Kingtai Chemicals	A total of 50 products registered in Wisconsin, about 36 for major agricultural crop uses. Some products include Actara, Cruiser SB, Optigard and Platinum.	Formulations include flowable concentrates for seed treatments, water dispersible granules and suspension concentrates.

(Lewis, 2016) (Kelly Products, Inc., 2017)

With 502 products registered in Wisconsin, it is clear that neonicotinoid products are widely available for sale and use in the state. But actual amounts of neonicotinoids used in agriculture is difficult to determine. NASS conducts grower surveys and publishes data on pesticides used in Wisconsin and other states. A 2014 NASS survey of pesticides and insecticides used on corn and potatoes in Wisconsin and several other states reported that about 8 percent of Wisconsin corn acres had an insecticide applied, for a total of about 22,000 pounds of insecticides. Eight percent of Wisconsin's annual 4 million corn acres amounts to 320,000 acres treated. But the same survey further reports that 10 percent of corn growing operations in Wisconsin treat their own seed *after* purchase for insect or disease control (USDA-NASS, 2014). It is unknown if the NASS estimates counted seed that had been treated prior to purchase.

Meanwhile, a 2015 study that evaluated pesticides applied to treated seed reported that national estimates of neonicotinoid uses on corn and soybean were likely much higher. Douglas and Tooker estimated the use of neonicotinoids and other pesticides on treated seed may be as high as 79-100 percent of corn seed and 34-44 percent of soybean seed planted nationally (Douglas, 2015).

For potatoes grown in Wisconsin, the 2014 NASS survey provides some detail on neonicotinoids used. Growers used insecticides on 99 percent of acres planted, with 56 percent of operations treating their own seed *after* purchase. Acres treated broke down as follows: clothianidin was used on 36 percent, imidacloprid on 15 percent, and thiamethoxam on 56 percent of potato acres. A total of 16,000 pounds of insecticides were reported used on potatoes, with 2,000 pounds used for each of the three neonicotinoids clothianidin, imidacloprid and thiamethoxam.

In summary, it is difficult to accurately estimate the actual amount of neonicotinoids used year to year in Wisconsin agriculture. A large number of products are registered and available for use. Combined with NASS grower-surveys and reports by others, the available data suggest that neonicotinoid use is common on high value vegetable crops like potatoes, as well as other major crop types grown in the state. It may be that the NASS grower surveys provide a conservative estimate of overall use when one considers the use of these products on seed that is treated prior to the grower's purchase. Other estimates suggest that as high as 79-100 percent of corn seed and 34-44 percent of soybean seed planted annually may receive neonicotinoid treatments.

Physiochemical Properties of Neonicotinoids

In plants, clothianidin, imidacloprid and thiamethoxam are all taken up via the roots or across plant stems and leaves. All three are considered xylem mobile, with dominant uptake routes following the transpiration stream (*i.e.*, no downward transport from leaves to roots). Numerous field studies have demonstrated that clothianidin, imidacloprid and thiamethoxam applied via foliar, soil or seed treatment methods can result in residues in pollen and nectar of blooming plants (U.S. EPA, January 4, 2016). Available data also suggests that thiamethoxam is metabolized within plants to form clothianidin (U.S. EPA, January 5, 2017).

Clothianidin, imidacloprid and thiamethoxam also have similar physical and chemical properties. They are all highly soluble in water, have low vapor pressures, low Henry's Law Constants and low octanol-water partition (Kow) coefficients. Compounds with these properties are readily soluble in water, mobile in groundwater, and not likely to volatilize. In addition, their organic carbon partition coefficient (Koc) values are consistent with compounds that are highly leachable. A list of physical and chemical properties of these three compounds is included in Appendix 1.

The dominant transformation process for all three of these compounds is photolysis, or chemical breakdown that occurs under direct exposure to the sun's rays. Photolysis may occur on soil surfaces following soil application and on wet foliage in the case of foliar application. Photolysis on foliage tends to occur more rapidly than on soil. Photolysis can occur in days to weeks in water and months on the soil. Aerobic transformation processes within the soil biome for each of these compounds is very slow, with half- life values on the order of months to more than a year. Imidacloprid persists very long in soil, with an aerobic soil half-life as long as 1600 days or more (U.S. EPA, January 4, 2016).

DATCP Groundwater and Surface Water Testing Programs

DATCP collects groundwater and surface water samples and tests for agricultural chemicals under a number of routine sampling programs housed within the Agricultural Resource Management Division (ARM). ARM sampling programs are designed to meet groundwater protection obligations required under Ch. 160, Wisconsin Statutes. The statute requires state regulatory agencies to determine whether activities, facilities or practices under their regulation impact groundwater, and to evaluate contamination of groundwater relative to established numeric groundwater quality standards (i.e. Preventive Action Limits (PALs) and Enforcement Standards (ESs) per Wisconsin Admin Code). To meet these statutory obligations, ARM conducts sampling programs that test private potable wells and non-potable wells for agricultural chemical contaminants resulting from routine agricultural use. Table 3 includes a listing of routine ARM groundwater monitoring programs.

TABLE 3 ARM SAMPLING PROGRAMS, WELLS SAMPLED AND PROGRAM FREQUENCY

Sampling Program	Wells Sampled	Purpose	Frequency / Number
Statewide Survey	Private potable	Randomly distributed	Occasional / ≈400 per event
Targeted	Private potable	At-risk, near agricultural area	Annual / 50-120 per year
Exceedance	Private potable	Trend, environmental fate	Annual / 20-30 per year
Field Edge	Monitoring	Surveillance/early warning	Annual / 30-90 per year
Irrigation	High Capacity	Surveillance/early warning	New & evolving

Sampling of private potable wells generally occurs under three sampling programs: statewide random sampling, targeted sampling, and exceedance-well sampling. Potable wells can also be sampled outside of routine sampling programs. Sampling of non-potable wells occurs via field edge monitoring wells and irrigation wells. ARM also performs some annual surface water testing on a small percentage of stream samples DNR collects annually under their surface water monitoring programs. A description of sampling programs is provided below.

Private Potable Well Sampling

Statewide Survey

The statewide survey is a random sampling of private wells for pesticides and nitrate. It is performed on about 400 private wells on an occasional basis, typically once every 5 to 10 years. The purpose of this sampling program is to obtain "snapshots" of statewide water quality over time. Survey wells are selected using a statistically random approach. Half of the wells in each survey are selected using a stratified random sampling procedure. The other half of wells included in the survey are repeats of the randomly selected wells from the prior survey. Benefits of this approach are that statistical comparisons can be made showing the distribution of agricultural chemicals in groundwater statewide as a function of agricultural intensity, and to show water quality changes with time. The three most recent statewide surveys were conducted in 2016, 2007, and 2000. Those completed prior to 2016 did not analyze for neonicotinoid compounds.

Targeted Sampling

Targeted sampling occurs annually with 50 to 120 wells sampled per year. Unlike the statewide random survey, targeted sampling intentionally uses a biased well selection approach. Under targeted sampling, areas are selected for sampling based on factors that reflect an increased likelihood of pesticides and nitrate leaching to groundwater. Factors like the amounts and types of pesticides used, crop density, lack of crop rotations year after year, depth to groundwater, depth to bedrock and soil texture are all considerations that can go into targeted sample planning. Targeted sampling focuses on sampling wells that are “at-risk” of being contaminated by pesticides through agricultural use.

Exceedance Sampling

State administrative rules require that DATCP take action to prevent further degradation of groundwater quality. For potable wells with a pesticide ES exceedance, this response typically involves restrictions or full prohibitions placed on local uses of the offending pesticide through special orders or administrative rules that apply to growers and landowners near the impacted well. Owners of any impacted wells are issued drinking water advisories to inform them of known health risks associated with exposures so they can take action to limit ongoing exposures. Impacted well owners may purchase and install a water treatment device, or install a replacement well. The state cannot require owners of contaminated private water wells to treat or replace their water supply, but many owners elect to do so. Exceedance sampling involves re-testing potable wells that have exceeded an ES for a pesticide, but which remain in service after contaminant discovery. For wells with an ES exceedance that remain in service, ARM selects 20 to 30 each year for repeat testing to evaluate trends over time. Exceedance sampling allows ARM to determine if pesticide use restrictions are effective at reducing groundwater contamination. Monitoring also helps document the time needed for an agricultural contaminant to attenuate following implementation of pesticide use restrictions for each area.

Potable Wells Sampled for Other Purposes

Aside from the potable well sampling programs identified above, potable wells can be sampled for other regulatory purposes. An example of this is when a groundwater contaminant investigation is performed around a private well that has been found to contain a pesticide above an ES or nitrate significantly above the ES. When this occurs, the impacted well and possibly others in the area of the impacted well are sampled so that appropriate management strategies can be considered. Between April 2011 and September 2016, about 87 potable wells were sampled for purposes not related to another specified sampling program.

Non-Potable Well Sampling

Field-Edge Monitoring

ARM also tests non-potable wells for agricultural chemicals at select field edge monitoring sites as part of the field edge monitoring program. Between October 2006 and December 2016, the agency collected groundwater samples from monitoring wells located on approximately 32 field-edge monitoring sites across the state, representing a total of about 65 wells. The number of sites and wells has varied over time as sites and wells are added or removed and as growers enter and leave the program.

Field-edge monitoring sites are typically installed under agreements with growers who allow ARM to install monitoring wells to test shallow groundwater for agricultural chemicals applied to fields. Over time, monitoring well sites have been installed in a variety of geologic settings, often within areas susceptible to groundwater contamination (i.e. areas with sandy soil and shallow bedrock or shallow groundwater). Typically one to three groundwater monitoring wells are installed at each field edge site. Sites typically have a shallow well intersecting the water table, and one or more adjacent wells screened at deeper intervals. ARM collects 30 to 90 samples from these wells annually. Testing of these wells is used to identify contaminants that may be present in shallow groundwater at fields where agricultural chemicals are used as intended. Testing of these well networks provides an early warning about pesticides that leach to groundwater and are more likely to impact streams or down gradient potable water wells.

Irrigation Well Monitoring

Non-potable well sampling also performed by ARM includes irrigation wells. In 2015 and 2016, ARM collected samples from 22 high-capacity irrigation wells that extract groundwater from underlying aquifers in the Central Sands growing area. Irrigation wells are typically large diameter deep wells with well screens that intersect a large section of aquifer strata to meet high-capacity pumping needs. While field edge monitoring wells provide information on water quality within the upper portion of an aquifer, irrigation wells provide information on groundwater quality from larger and deeper sections of the aquifer. This is a relatively new type of site sampling that ARM intends to expand in future years.

Surface Water Sampling

In addition to groundwater sampling programs, ARM collaborates with DNR to collect surface water samples for pesticide testing. DNR performs annual surface water sampling on hundreds of streams and rivers statewide to monitor a variety of stream water quality parameters. ARM works with DNR to obtain samples from a small subset of the streams that DNR samples to help evaluate surface water quality impacts from agricultural land use. Under this program, the two agencies identify streams of interest for pesticide testing. DNR sets a sampling schedule and collects the samples. ARM staff coordinates pesticide testing at the agency's Bureau of Laboratory Services (BLS), and communicates results with DNR to supplement DNR surface water quality programs. The number and type of streams sampled, as well as the frequency of sampling varies annually. BLS analyzes approximately 80 stream samples per year under this program.

Laboratory Analyses

Laboratory testing for ARM sampling programs is provided by BLS. BLS is ISO 17025 accredited and performs gas chromatography, high-pressure liquid chromatography and mass spectrometric analytical services consistent with their accreditation. A full listing of BLS groundwater analytes and laboratory reporting limits is listed in Appendix 2 and includes 101 pesticides and nitrate.

Changes to BLS equipment and testing capabilities have occurred over time. BLS first began testing for thiamethoxam in 2008. In 2010, clothianidin and imidacloprid were added to the groundwater analyte list, and the three remaining neonicotinoids (acetamiprid, dinotefuran and thiacloprid) were added in 2011. Since 2011, all six compounds have been included in all ARM surface water and groundwater analyses. ARM sampling programs have detected clothianidin, imidacloprid and thiamethoxam numerous times, but acetamiprid, dinotefuran and thiacloprid have not been detected in any samples collected through 2016.

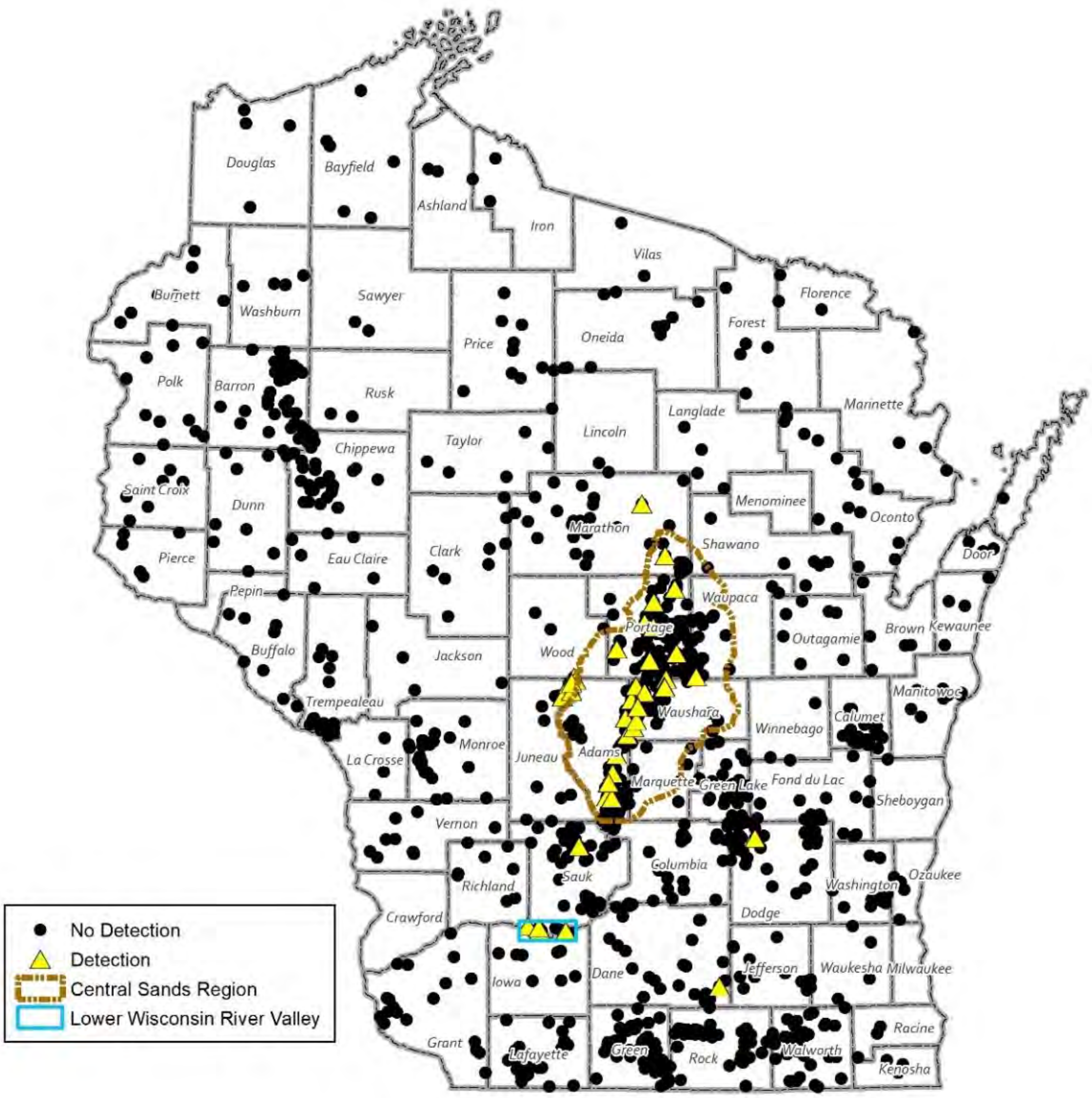
Monitoring Results and Discussion

Results of All Private Potable Wells

<u>Summary of All Potable Well Results</u>

In total, ARM programs sampled 1,048 potable wells over 9 years, from 2008 through 2016. Locations of all potable wells sampled, including those having detectable concentrations of neonicotinoids are shown in Figure 4.

FIGURE 4 LOCATIONS OF NEONICOTINOID DETECTIONS IN ALL POTABLE WELLS SAMPLED - 2008 THROUGH 2016



Out of 1,048 private potable wells sampled, 41 had a detection of one or more neonicotinoid compounds yielding an overall neonicotinoid detection frequency of 3.9 percent of potable wells sampled.[1] Imidacloprid was the most frequent neonicotinoid compound detected in potable wells. It was detected in samples from 35 wells (3.3-percent detection frequency) at concentrations ranging from 0.052 to 1.59 micrograms per liter (µg/L). The average imidacloprid concentration was 0.500 µg/L. Clothianidin was detected 28 times (2.7-percent detection frequency) and included the highest concentrations of the neonicotinoids. Clothianidin concentrations ranged from 0.069 to 3.88 µg/L, with an average of 0.608 µg/L. Thiamethoxam was detected 25 times (2.4-percent detection frequency) at concentrations ranging from 0.141 to 1.61 µg/L with an average of 0.699 µg/L.

All potable well results included testing related to programmatic sampling in the following areas: a statewide sampling survey performed in 2016; targeted and exceedance program sampling performed annually, and some sampling for other purposes, like groundwater investigations. Most wells were sampled just one time, but a few were sampled more than once, such as when samples revealed a pesticide detect above a standard, triggering confirmation testing or additional investigation. A more detailed breakdown of test results by program type is provided below.

The majority of potable wells having detectable concentrations of neonicotinoids are located near agricultural areas with coarse grained soils and shallow groundwater. Other commonalities included crop rotations of corn and/or soybeans intermixed with vegetable crops like potatoes, peas and sweet corn, and areas under irrigation.

Breakdown of All Private Potable Well Results by Program Areas

Statewide Survey Results

ARM conducted random sampling survey of 401 potable wells in 2016 for the Statewide Survey. All wells were tested for 101 pesticide compounds and nitrate. Although nitrate and numerous pesticide compounds were detected statewide, just one sample collected from a well in Marathon County had a detection of the compound imidacloprid (0.0798 µg/L). The detection frequency for neonicotinoids was 0.25 percent of samples collected on a statewide, random basis. The two most commonly detected pesticide compounds were the ethane sulfonic acid breakdown products of the herbicides metolachlor and alachlor. Metolachlor ESA and alachlor ESA were present in 32.2 and 21.5 percent of samples, respectively. Figure 5 shows 2016 Statewide Survey well locations.

Because the 2016 Statewide Survey was the first survey to include analyses for neonicotinoid compounds, comparisons to previous surveys is not possible. However, the 2016 sampling report does make comparisons with prior surveys for nitrate and other pesticides detected (Wisconsin Department of Agriculture, Trade and Consumer Protection, April 2017).

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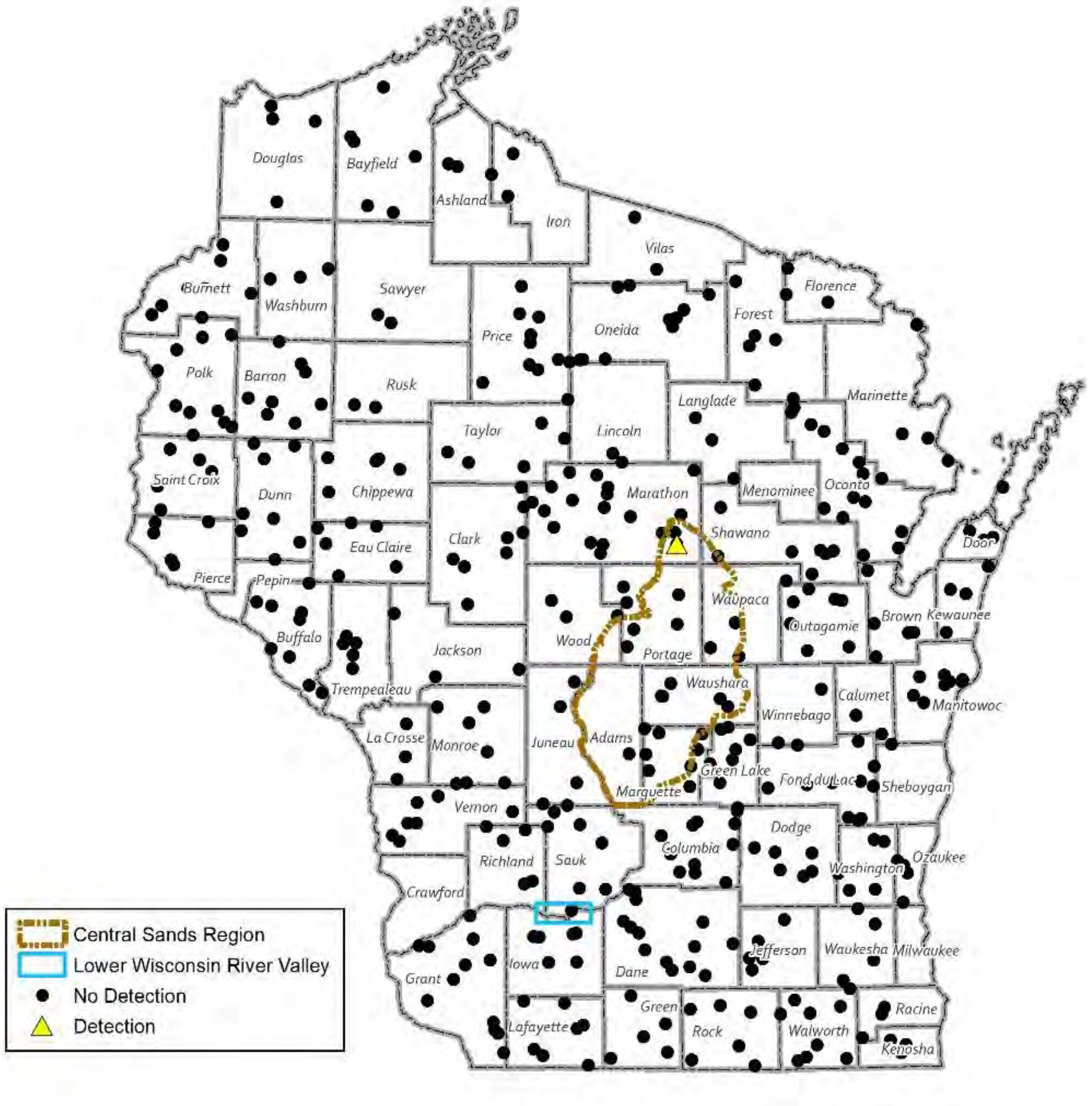
[1] Some potable wells were sampled more than once. Unless specified otherwise in a figure or text, wells sampled more than once that have multiple detects of a neonicotinoid compound are counted once for purposes of reporting detection frequency by well. Where the average or a range of concentrations is reported for a compound, the sample having the highest total neonicotinoid result is used to represent the data from that well.

FIGURE 5 LOCATIONS OF NEONICOTINOID DETECTIONS IN POTABLE WELLS -- 2016 STATEWIDE SURVEY



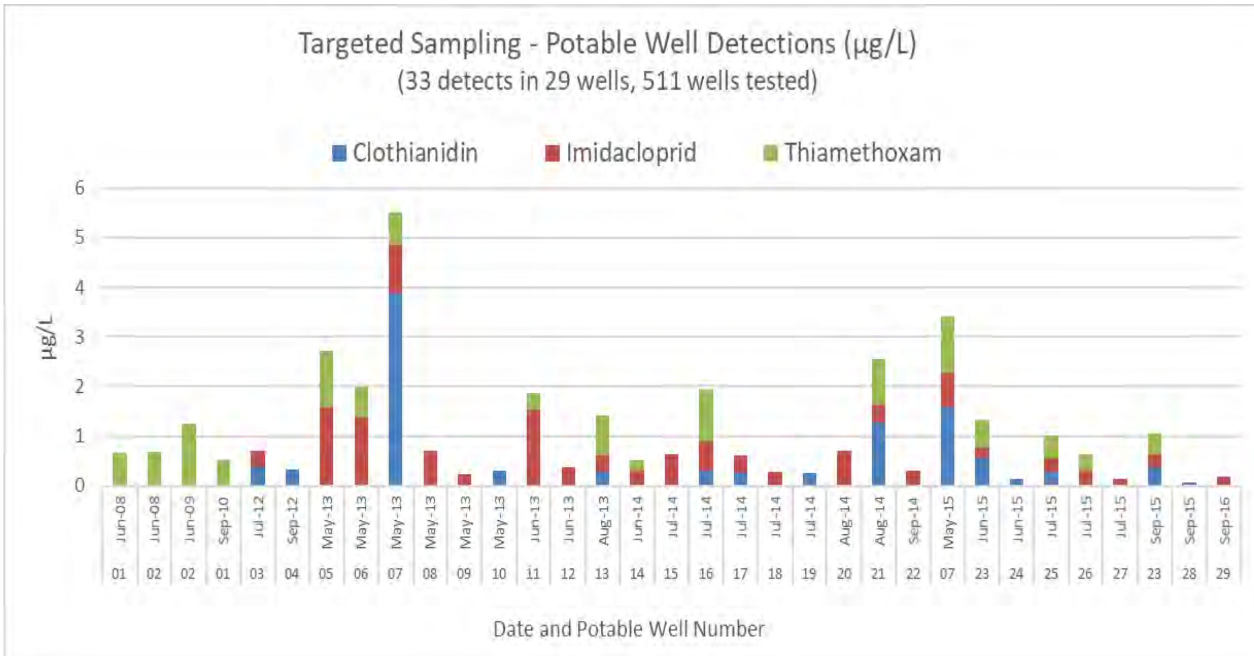
Above: Out of 401 samples collected during random sampling survey in 2016, imidacloprid was detected in one Marathon County well.

Targeted Well Sampling Program Results

Unlike the statewide random sampling survey, the targeted sampling approach focuses on wells in known agricultural areas. Water samples are collected from private wells in areas where major crops like corn, soy beans, potatoes, sweet corn and other vegetables are grown year after year. Targeted sampling areas vary by program year, and wells are typically not resampled unless a test result approaches an ES for a pesticide, triggering verification sampling and a possible investigation.

Between June 2008 and October 2016, 525 samples were collected from 511 private potable wells for the targeted sampling program. All samples were tested for pesticides and nitrate. One or more of the compounds clothianidin, imidacloprid and thiamethoxam were detected in 33 samples collected from 29 wells. The overall neonicotinoid detection frequency for wells tested under the targeted program is 5.7 percent of wells (or 6.2 percent of samples), a sharp contrast to the 0.25 percent of wells sampled on a statewide random basis. The detections are shown below in Figure 6.

FIGURE 6 RESULTS FROM TARGETED SAMPLING (525 SAMPLES FROM 511 WELLS)



Because these compounds are in the same chemical class and share similar physiochemical characteristics and toxicity to insects, the neonicotinoid data is presented in a stacked format to allow total combined concentrations to be easily visualized. Three neonicotinoid compounds were detected in eight samples, and two compounds were detected in seven samples. One compound was detected in the remaining samples. Imidacloprid was the most frequently detected compound, detected in 24 samples at concentrations ranging from 0.147 to 1.59 µg/L. Thiamethoxam was detected in 17 samples at concentrations ranging from 0.206 to 1.26 µg/L, and clothianidin was detected in 15 samples at concentrations ranging from 0.0686 to 3.88 µg/L.

The highest cumulative concentration of neonicotinoids detected was 5.525 µg/L in the May 2013 Well 07 sample. Well 07 had all three compounds present, and contained clothianidin at a concentration greater than the combined concentrations detected in any of the remaining 28 wells with detections. A second sample collected from this well two years later (May 2015) exhibited a cumulative concentration of 3.41 µg/L. Other wells with multiple detections included Well 01 (June 2008 and September 2010), Well 02 (June 2008 and June 2009), and Well 23 (June 2015 and September 2015). No State or Federal drinking water standards have been established for any of these detected neonicotinoids.

The black dots on Figure 7 show the locations of wells where targeted sampling occurred from 2008 through 2016. Yellow triangles represent locations where one or more neonicotinoids were detected.

FIGURE 7 LOCATIONS OF NEONICOTINOID DETECTIONS IN POTABLE WELLS -- TARGETED SAMPLING PROGRAM

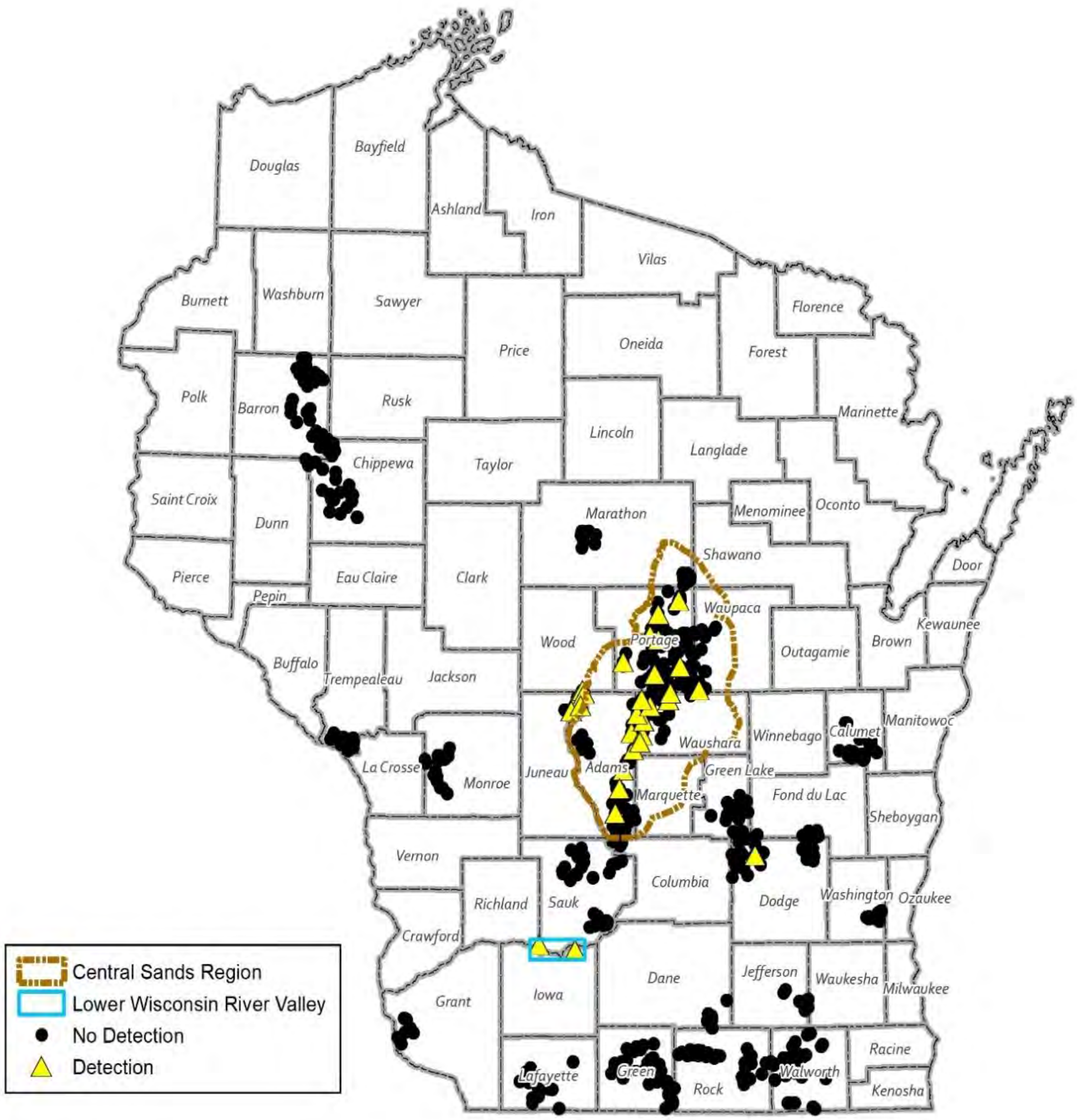


Figure 7 shows a higher incidence of detects in potable well samples collected from the Central Sands region (Portage, Waushara, and Adams Counties). Detections were also observed at wells along the Wisconsin River in northern Adams and Juneau Counties and further south in the Lower Wisconsin River Valley in Sauk, Iowa and Richland counties. The hydrogeologic setting for these areas consists of sandy soil with shallow groundwater. Irrigation is also widely used in these areas. Crops grown in the Central Sands and LWRV include potato and vegetable crops in rotation with corn and soybeans. It is likely that routine labelled use of products containing neonicotinoid active ingredients on crops grown in this hydrogeologic setting combined with large areas under irrigation contributes to the contaminants detected in potable wells.

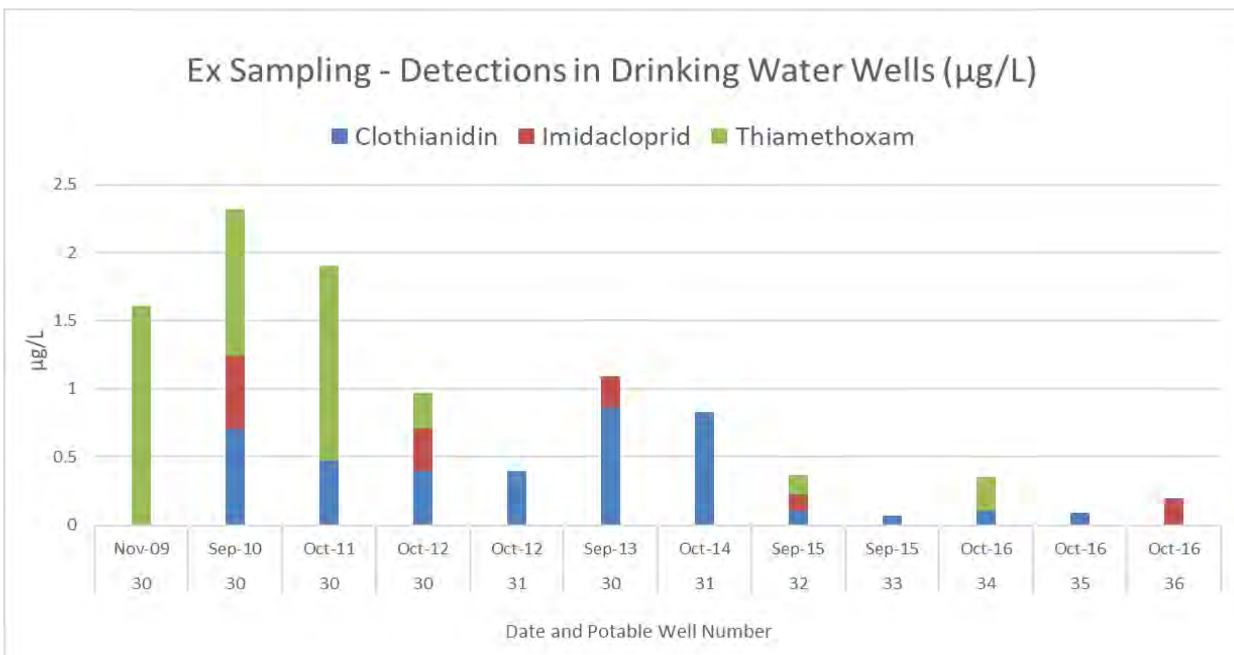
One neonicotinoid detection occurred outside the Central Sands and LWRV areas. Clothianidin was detected at 0.131 µg/L in a sample collected from a potable well in Dodge County. The sample was collected from Well 24 in June 2015. Crops grown on fields near this well are predominantly rotations of corn, soy and forage crops, with soil types within ½-mile consisting of predominantly silt loam (Plano and Markesan) on 0-6-percent slopes (USDA-NRCS, October 2017).

Exceedance Well (Ex) Sampling Program Results

Exceedance wells are private potable wells that have had two or more samples with pesticide contaminants present in excess of an ES during past sampling events. Most wells in the exceedance program are in the program as a result of elevated detections of the compounds atrazine or alachlor, two herbicides that have been used extensively on corn crops statewide. Neonicotinoids are commonly used on corn seed, but no wells are in the exceedance sampling program as a result of past neonicotinoid detects. Through prior testing, this set of wells is known to be susceptible to leaching of contaminants used in agriculture.

Between November 2009 and October 2016, 140 samples were collected from 49 different exceedance wells. Neonicotinoid compounds were detected in 12 samples collected from seven wells, a 14.3 percent detection frequency for wells in this dataset (8.6 percent of samples). Figure 8 shows detected neonicotinoid compounds by well.

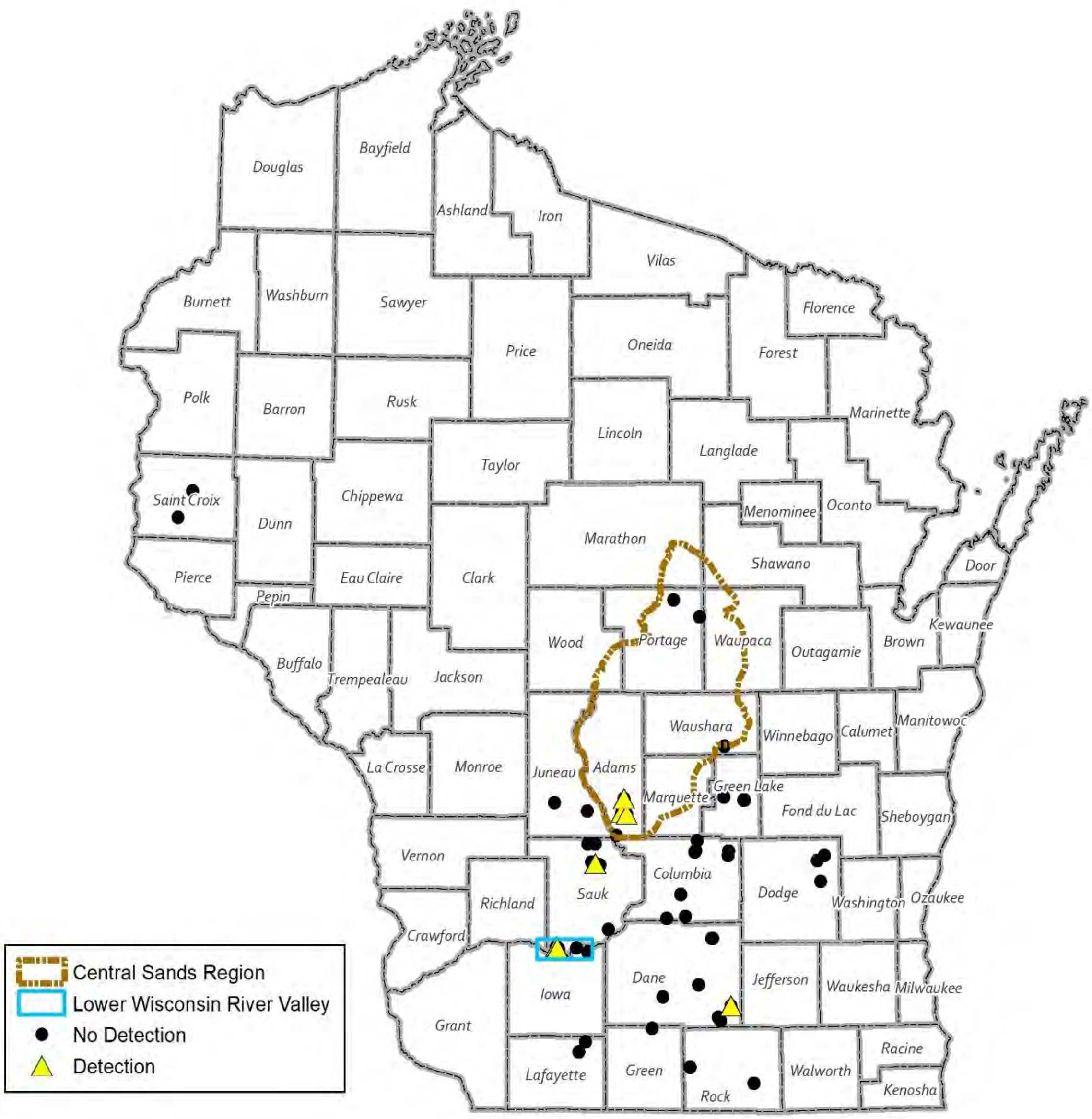
FIGURE 8 DETECTIONS OF NEONICOTINOIDS IN POTABLE WELLS--EXCEEDANCE SAMPLING PROGRAM



Concentrations detected were generally less than 1.0 µg/L with the exception of thiamethoxam. Thiamethoxam was present in three samples collected from Well 30 at 1.61 µg/L in November 2009, 1.08 µg/L in September 2010, and at 1.43 µg/L in October 2011. Clothianidin was detected most frequently (six wells, 10 samples) at concentrations ranging from 0.0698 to 0.859 µg/L. Imidacloprid was detected in three wells (five samples) at concentrations ranging from 0.118 to 0.537 µg/L. Thiamethoxam was detected in five wells (six samples) at concentrations ranging from 0.141 to 1.61 µg/L. All three compounds were detected in three samples (Well 30 in September 2010 and October 2012 and Well 32 in September 2015). The highest total combined concentration for all three compounds was 2.3 µg/L at Well 30 in September 2010.

Figure 9 shows the locations of exceedance wells sampled. Similar to wells sampled under the targeted program, four of the six wells sampled that have detections (yellow triangles) are located in the Central Sands and LWRV. The two remaining wells are located in southeastern Dane County (Well 30) and in north central Sauk County (Well 32).

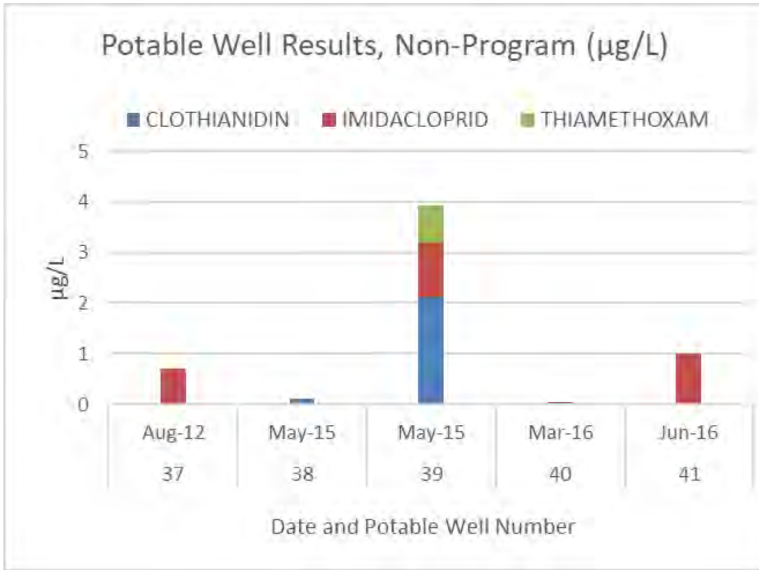
FIGURE 9 LOCATIONS OF NEONICOTINOID DETECTIONS IN POTABLE WELLS -- EXCEEDANCE SAMPLING PROGRAM



Non-Program Potable Well Sample Results

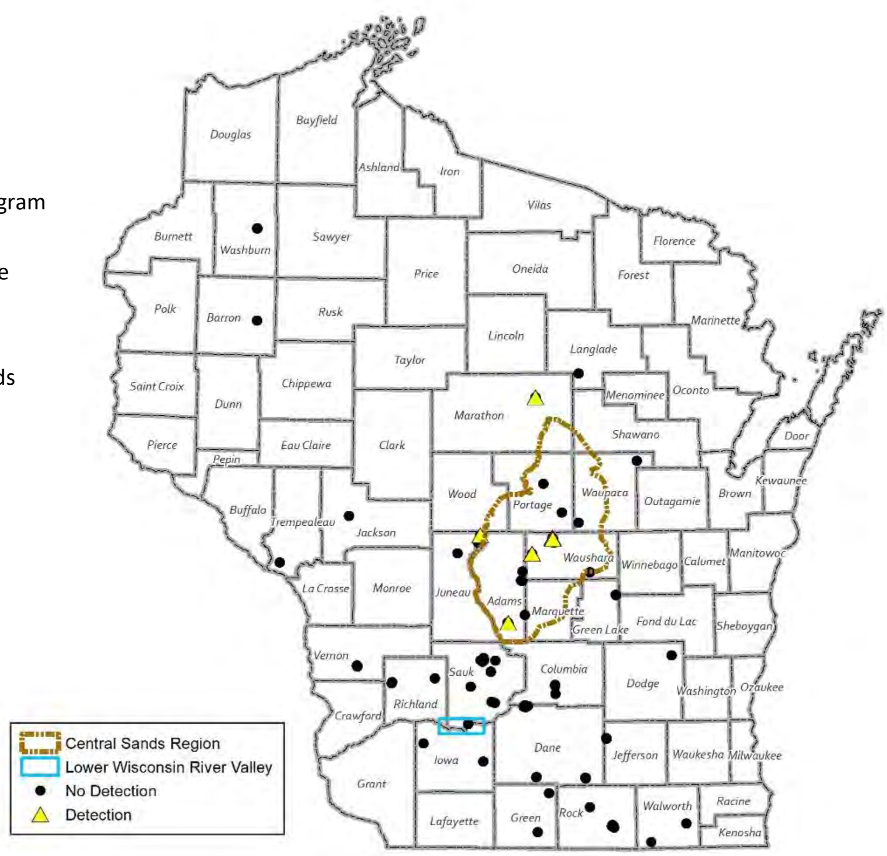
In addition to samples collected for ARM programs shown in Table 3, between April 2011 and September 2016, 107 samples were also collected from 87 potable wells.   One or more neonicotinoid compounds were detected in 5 of the 87 non-program wells. Figure 10 includes a graphical presentation of the concentrations of these compounds as well as locations where sampling occurred.

FIGURE 10 DETECTIONS OF NEONICOTINOIDS AND LOCATIONS OF NON-PROGRAM POTABLE WELLS SAMPLED



Left: Out of 87 non-program potable wells sampled over a 10-year period, one or more neonicotinoid compounds were detected in five samples (well numbers 37 through 41).

Right: Locations of 87 non-program potable wells. One or more neonicotinoid compounds were detected at five wells (yellow triangles). Four of the five are located within the Central Sands Region, while one is located in northern Marathon County.



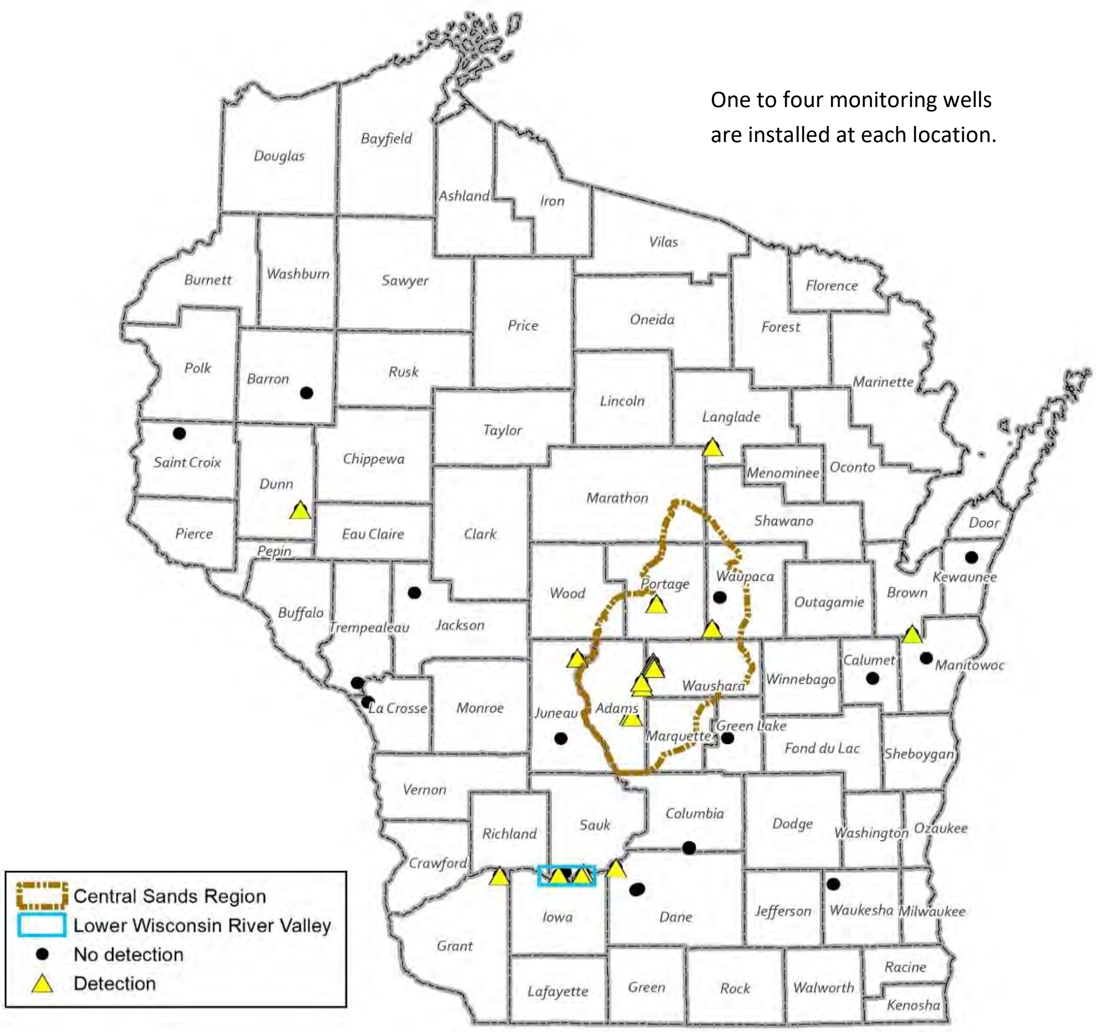
Four out of five of the non-program wells with neonicotinoid detections are located within the Central Sands. Concentrations of individual neonicotinoid compounds detected in these non-program wells was generally less than 1 µg/L. Imidacloprid was detected most frequently in this group of wells (four times) at concentrations ranging from 0.052 to 1.06 µg/L. Clothianidin was detected at two wells at concentrations ranging from 0.112 to 2.13 µg/L, and thiamethoxam was detected at one well at 0.743 µg/L. All three neonicotinoid compounds were detected at a combined concentration of 3.93 µg/L at Well 39 (a well in Waushara County). A well in Marathon County (Well 40) had a very low detection of imidacloprid (0.112 µg/L).

Non-Potable Wells

Field-Edge Monitoring Program

The locations of field edge monitoring sites are shown on Figure 11. Between November 2006 and October 2016, 479 samples were collected from monitoring wells at 32 different field sites around the state.

FIGURE 11 FIELD-EDGE MONITORING WELL LOCATIONS WITH NEONICOTINOID DETECTIONS



Neonicotinoid compounds were detected in samples collected at 17 of the 32 sites. One or more neonicotinoid compounds were detected in 198 samples.

The compound clothianidin was detected in 120 samples collected from 32 monitoring wells at 17 sites. Clothianidin concentrations ranged from 0.0762 to 3.43 µg/L, and the average was 0.540 µg/L. Imidacloprid was detected in 109 samples from 28 monitoring wells at 12 sites. Concentrations of imidacloprid ranged from 0.0594 to 4.54 µg/L, and the average was 0.764 µg/L. Thiamethoxam was detected 129 times from 23 monitoring wells at 15 sites. Thiamethoxam concentrations ranged from 0.0864 to 8.93 µg/L, and the average concentration was 1.28 µg/L. Thiamethoxam was detected at the highest concentration and had the highest average concentration relative to the other compounds.

The field monitoring sites with neonicotinoid detections generally coincided with locations of potable wells that had neonicotinoid detects (Figure 4). These monitoring sites generally include sites located in the Central Sands counties of Adams, Portage and Waushara, and in locations near the Wisconsin River (Juneau, Sauk, Iowa, Dane and Grant Counties). All monitoring well sites having neonicotinoid detections also have coarse grained soils and shallow groundwater. The highest concentration of any neonicotinoid compound detected was thiamethoxam at a concentration of 8.93 µg/L in a sample collected from a monitoring well located at Adams Site 2.

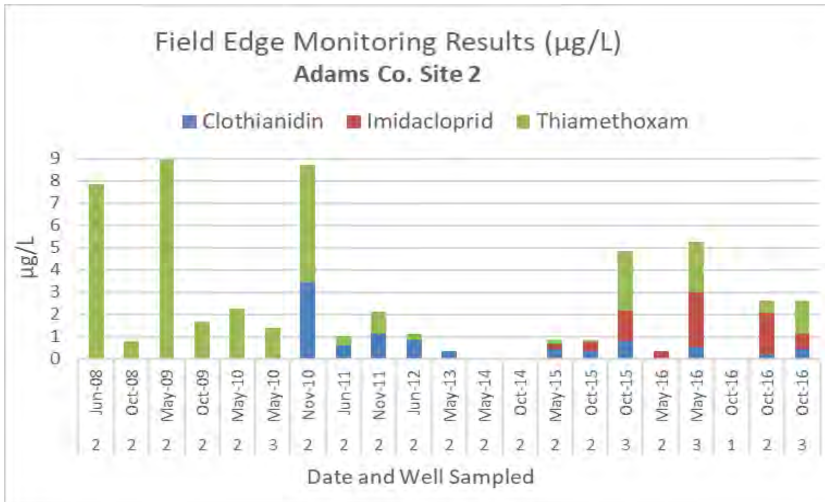
The data from Adams Site 2 and Adams Site 5, are shown in Figure 12. These locations generally had some of the highest concentrations of thiamethoxam detected. Also presented in the figure is Waushara County Site 6, another Central Sands site that had the highest concentration of imidacloprid detected in ARM samples. Crops grown at Adams Sites 2 and 5, and Waushara Site 6 typically includes rotations of high value vegetable crops like sweet corn, snap beans and potatoes. The crop rotation at Waushara Site 6 includes carrots and peas with the other high value vegetable crops.

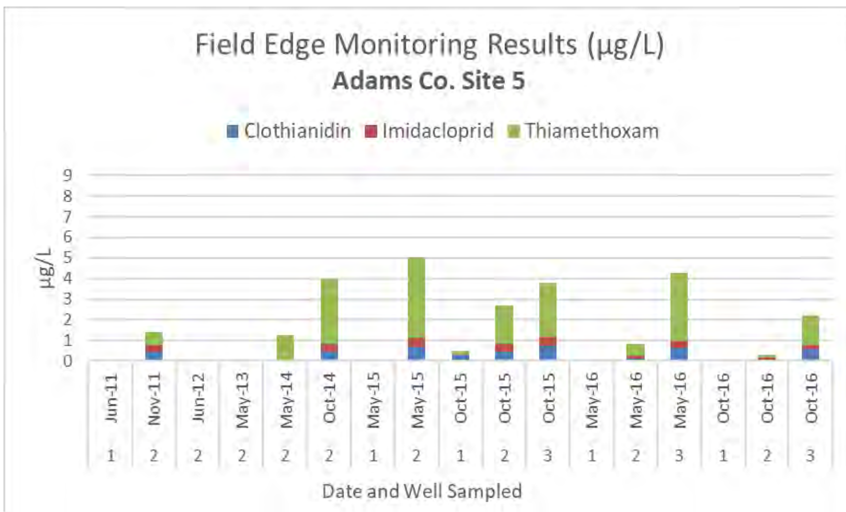
For comparison to the Central Sands sites, the results of monitoring at three sites located within the LWRV are shown in Figure 13 (Dane, Iowa and Sauk Counties). Sites located outside of the Central Sands and Wisconsin River Valley that had neonicotinoid detects included sites in Langlade and Dunn Counties. These sites also have coarse grained soils and shallow groundwater. At the Langlade site, the neonicotinoids clothianidin and thiamethoxam were detected in three of eight samples collected from one well: clothianidin concentrations ranged from 0.431 to 0.57 µg/L while thiamethoxam ranged from 0.479 to 1.33 µg/L. In Dunn County, two sites had detections. One Dunn County site had detects in four out of eight samples with clothianidin only ranging from 0.076 to 0.12 µg/L. The second Dunn County site had detects of clothianidin and imidacloprid ranging from 0.128 to 0.263 µg/L and 0.069 to 0.297 µg/L respectively.

The Brown County site with detections of neonicotinoids is located in a different geologic setting than the other field monitoring sites with detections. This site has gravelly silt soil overlying dolomite bedrock at about 12 feet. Groundwater is encountered in the bedrock approximately 28 feet below grade, and the monitoring well is 40 feet deep. At this site, thiamethoxam was detected at concentrations of 0.524 µg/L and 0.123 µg/L in two out of eight samples collected. Neither clothianidin nor imidacloprid were detected in any samples here. This site was initially used for a separate study that evaluated the influence of fracture flow infiltration following precipitation events. Researchers reported that fracture flow was evident at the site, with significant changes in water chemistry and temperature occurring in the well about two days following a precipitation event. The main crop grown at this location is corn. It is possible that thiamethoxam

FIGURE 12 RESULTS FROM THREE CENTRAL SANDS MONITORING WELL SITES

Right: Adams County Site 2, 21 samples were collected from wells 1, 2, and 3 at this site. Samples are typically collected from the shallowest well with groundwater present, but in October 2016, samples were collected from all three wells at this site. Well 2 had the greatest detect of thiamethoxam at 8.93 µg/L in May 2009. Clothianidin and imidacloprid were not analyzed until November 2010. Imidacloprid was first detected in 2015. Crops grown include a rotation of sweet corn, snap beans and potatoes.





Left: Adams County Site 5, 17 samples were collected from wells 1, 2 and 3 between June 2011 and October 2016 at this site. Samples are typically collected from the shallowest well with groundwater present. Note that samples were collected from all three wells in 2016. Similar to Adams Site 2, thiamethoxam is present at significantly greater concentrations than clothianidin or imidacloprid. Crops grown include a rotation of sweet corn, snap beans and potatoes.

Right: Waushara County Site 6, showing results of 20 samples collected from two wells between May 2011 and October 2016. Well 2 had just one detect of imidacloprid in October 2015, while well 1 had detects of imidacloprid in every sample collected, including the highest concentration of imidacloprid detected at any monitoring well site, 4.54 µg/L in October 2014. Crops grown are similar to the rotation of vegetables at the Adams sites, but also includes regular rotations of carrots and peas.

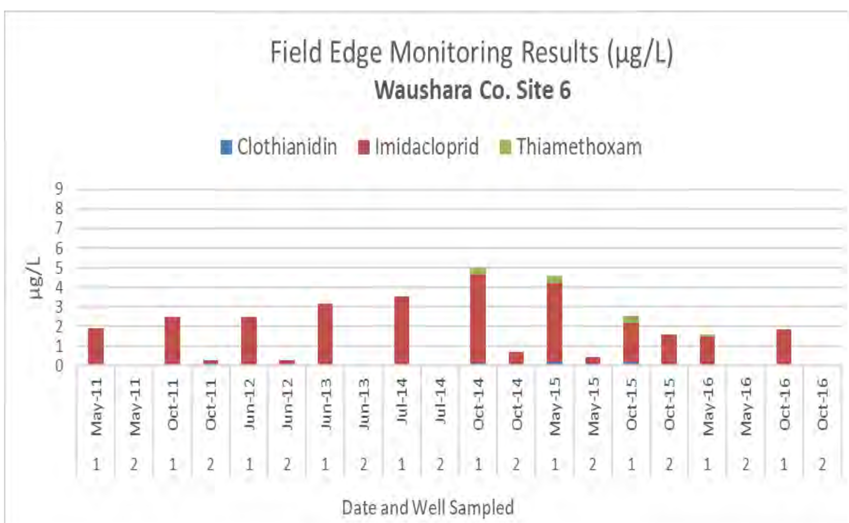
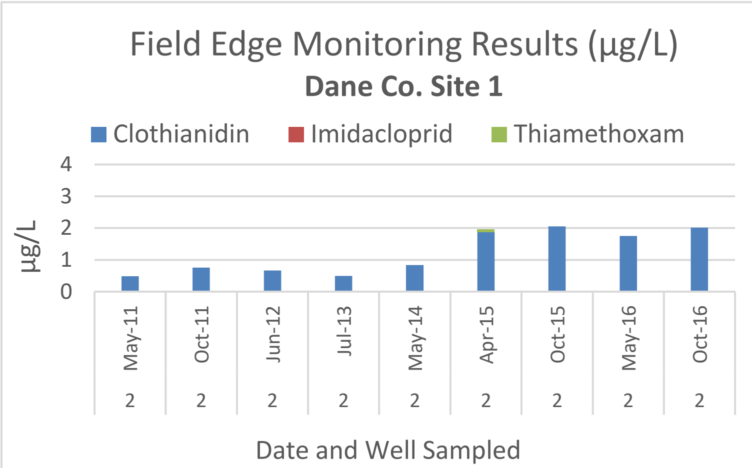
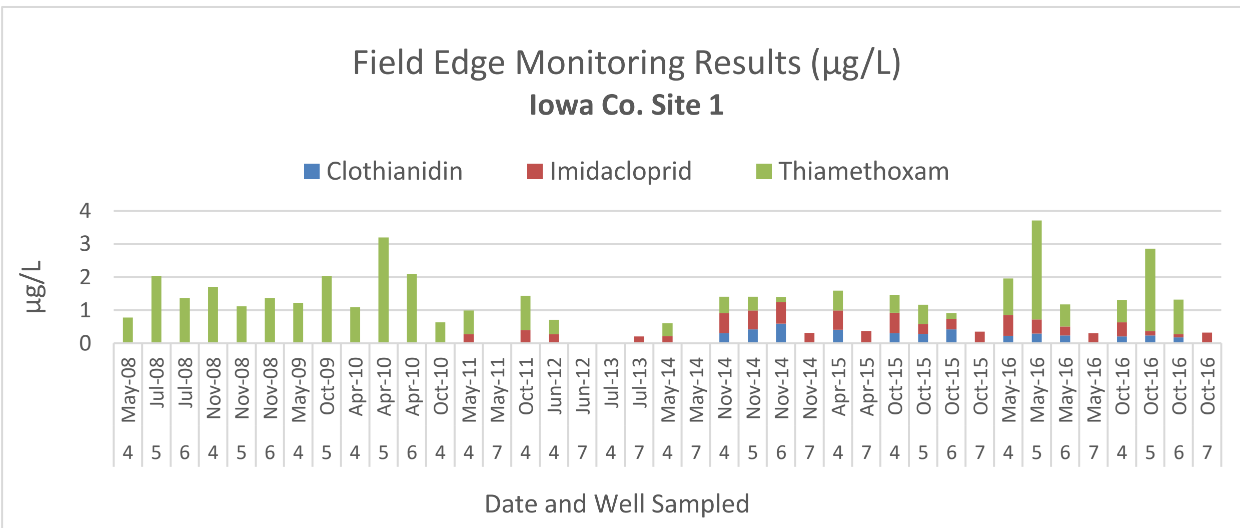


FIGURE 13 RESULTS FROM SELECT DANE, IOWA AND SAUK COUNTY FIELD EDGE SITES (LWRV)

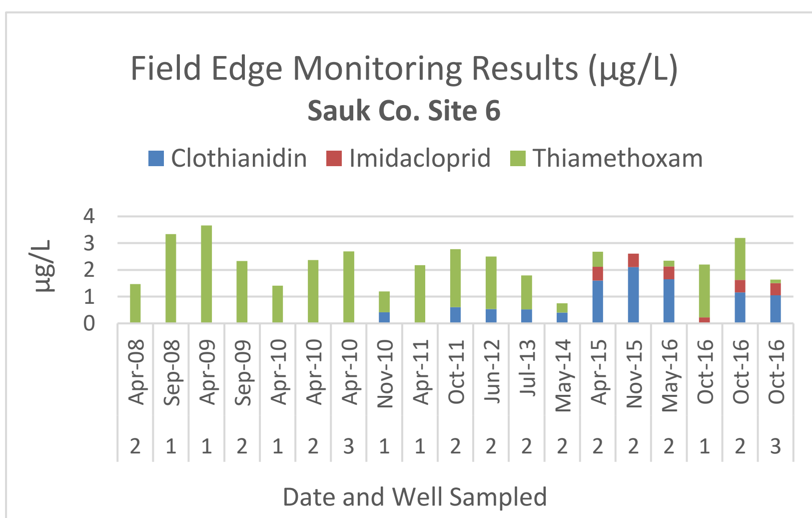


Left: Dane County Site 1, showing results for 9 samples collected from one monitoring well between May 2011 and October 2016. All samples contained clothianidin. The highest concentration was 2.05 µg/L (October 2015) and just one sample (April 2015) had a trace of thiamethoxam detected. This site has coarse soils with shallow groundwater and is equipped with irrigation. The grower reports only corn grown at this site year after year.



Above: Iowa County Site 1 results for 22 samples collected from four wells. Note that this site has four wells, all of which were tested on four separate events. Field is coarse grained, shallow to groundwater, and irrigated. Crops include rotations of potatoes and other vegetables with corn and cover crops.

Right: Sauk County Site 6, showing results for 12 samples collected from three wells. Field is coarse grained, shallow to water, and irrigated. Crops include rotations of potatoes and other vegetables with corn and cover crops.



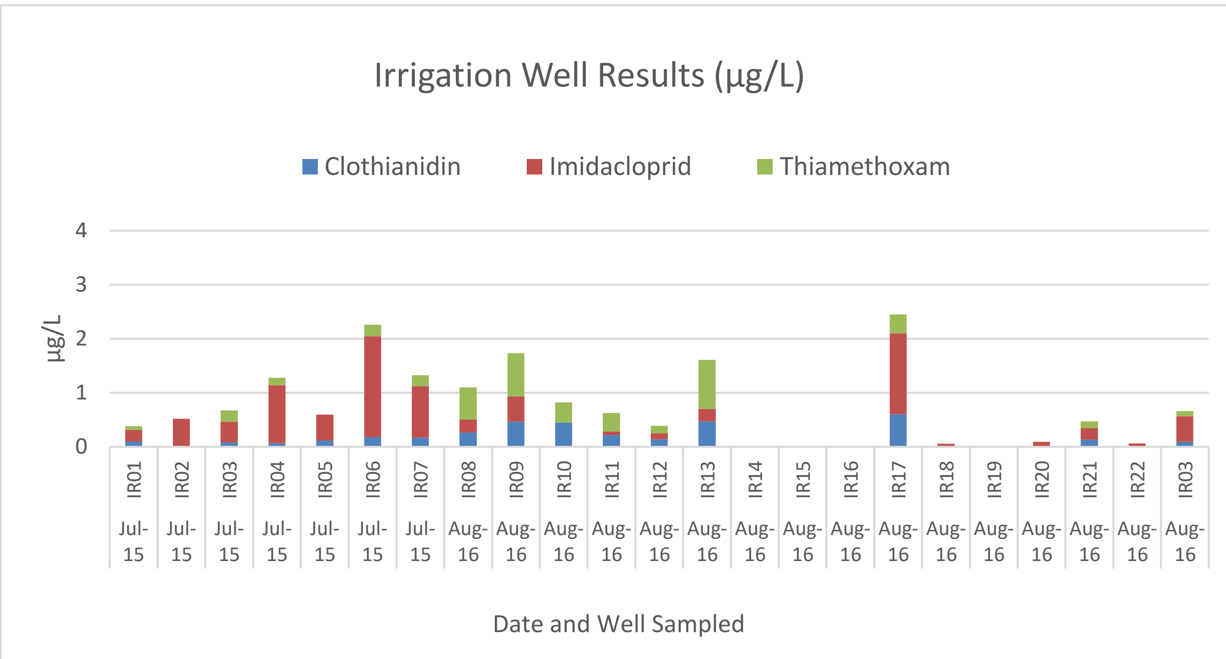
treated corn seed had been planted at the site, but this was not confirmed with the grower.

The monitoring sites in Kewaunee, Manitowoc and Calumet Counties are in geologic settings similar to the Brown County site, but neonicotinoids were not detected in seven samples collected at each of these sites.

Irrigation Well Sample Results

Between 2015 and 2016, ARM collected 23 samples from 22 irrigation wells owned by three cooperating growers within the Central Sands growing area. One or more neonicotinoid compounds were detected in 18 irrigation well samples. The results of testing for neonicotinoids in irrigation wells is shown in Figure 14.

Figure 14 Neonicotinoid Detections in Irrigation Well Samples



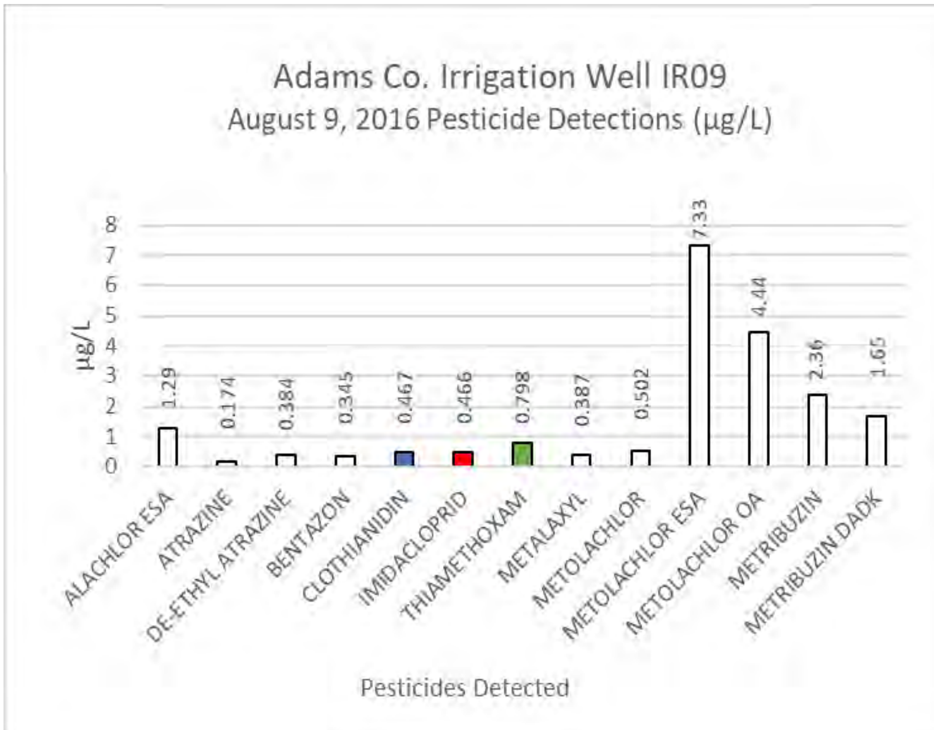
Clothianidin was detected in 15 samples ranging in concentration from 0.0815 to 0.602 µg/L. The average detection for clothianidin was 0.254 µg/L. Imidacloprid was detected in 18 samples ranging in concentration from 0.0592 to 1.87 µg/L. The average detection for imidacloprid was 0.500 µg/L. Thiamethoxam was detected in 14 samples ranging in concentration from 0.0746 to 0.904 µg/L. The average concentration of thiamethoxam detected was 0.325 µg/L. Generally, the sum of neonicotinoids detected in samples was less than 2 µg/L: only two samples exceeded 2 µg/L.

ARM only recently began sampling irrigation wells, so these results are from a small number of wells, all of which are located within the Central Sands. For comparison, University of Wisconsin-Madison (UW) researchers have published results of testing for neonicotinoids in a much larger set of irrigation wells that included both Central Sands and LWRV wells. Between 2013 and 2015, UW researchers analyzed 289 samples from 92 high capacity irrigation wells for the presence of thiamethoxam. Wells tested were widely located across the Central Sands and the LWRV vegetable growing areas. Each well was tested one to six times over three years. The results showed detections of thiamethoxam over the limit of quantitation (0.5

µg/L) in 69 percent of the 92 wells sampled. Six samples exceeded 1.0 µg/L. The concentration of thiamethoxam ranged from non-detect to 1.69 µg/L. The mean concentration detected was 0.291 µg/L thiamethoxam (Groves, Prince, & Bradford, 2017).

Neonicotinoids were not the only pesticide compounds detected in irrigation well samples collected by ARM. Numerous other pesticides were also detected. Figure 15 shows concentrations for thirteen pesticide compounds detected in the August 2016 sample collected from irrigation well IR09. Nitrate was also detected at a concentration of 29.1 milligrams per liter (mg/L) in this sample, but is not shown on the chart.

Figure 15 Pesticides Detected in a Sample from Well IR09, Adams County



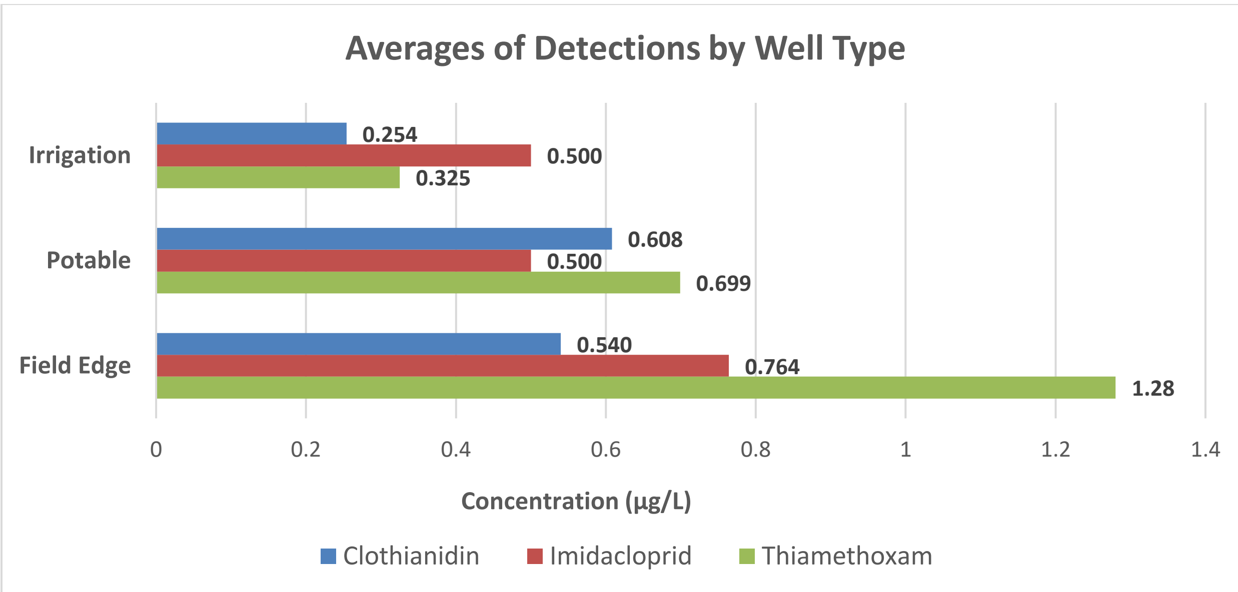
Left: Irrigation wells sampled by ARM typically detected multiple pesticides in addition to clothianidin, imidacloprid and thiamethoxam. The example to the left shows one sample from irrigation well IR09 collected in August 2016. A total of 13 pesticides and pesticide metabolites were detected at concentrations ranging from 0.174 (atrazine) to 7.33 µg/L (metolachlor ESA).

Like the neonicotinoids, many of the compounds detected have no established drinking water standard. For compounds with drinking water standards, the concentrations detected did not exceed their corresponding ES. The herbicidal metabolite metolachlor-ESA (7.33 µg/L) was present at a concentration nearly 10 times greater than the highest neonicotinoid concentration (thiamethoxam, 0.798 µg/L). In addition to pesticide concentrations, the number of pesticides detected in irrigation well samples is also a concern. The presence of numerous pesticide compounds in irrigation well samples indicates that agricultural contaminants are migrating to significant depths within the sand and gravel aquifer, increasing the likelihood that they can also enter nearby private drinking water wells.

Comparison of Groundwater Results across Well Types

Because most detections of neonicotinoids occurred at wells located in similar geologic conditions at areas with similar agricultural practices, the averaged concentrations of neonicotinoid detections for all well types was evaluated. Figure 16 shows a comparison of the average concentrations of neonicotinoid compounds detected at field edge monitoring wells compared to irrigation wells and potable wells sampled. As shown in the figure, the average concentrations of thiamethoxam were significantly higher in field-edge monitoring well samples, intermediate in potable well samples, and lowest in irrigation well samples. Average imidacloprid concentrations were highest in field edge monitoring well samples, and about the same in potable and irrigation well samples. Average clothianidin concentrations were the greatest in potable well samples, followed by field edge monitoring well samples, and lowest in irrigation well samples.

FIGURE 16 AVERAGES OF NEONICOTINOID DETECTIONS BY WELL TYPE



Well location and design likely explains why monitoring wells have the highest average concentrations observed. Field edge monitoring wells are located within or immediately adjacent to fields where pesticides are applied. These test wells are designed to allow samples to be collected from the uppermost few feet of the aquifer. This is not the case with potable wells. Potable wells may be located near a cropped field, but they are not within a field of application. Potable wells may be shallow or deep, but are typically designed to draw water from deeper reaches of an aquifer. With consideration to these differences, it is reasonable to conclude that if a pesticide is present, it would likely be observed and at higher concentrations at a shallow field edge monitoring well, and at lower concentrations at deeper potable wells. Irrigation wells, like monitoring wells, are also often located within or adjacent to fields of application. To achieve sustained high volume water withdrawals, irrigation wells are constructed with large diameter casing and installed deeper with well screens open to longer intervals of an aquifer. Considering this design, pumping an irrigation well is likely to induce significant dilution in the well as clean water is drawn from depth and mixes with contaminants that are more likely to enter the well from shallower depths of the aquifer. This helps explain why irrigation wells had the lowest average concentrations observed.

It is unknown why a higher average clothianidin concentration was observed for deeper potable wells rather than at shallow field edge monitoring wells. Migration of pesticides to deeper portions of the aquifer is concerning, and deserves some discussion. Additional research and monitoring is likely needed to explain why. Based in limited data, two possible explanations are discussed below.

First, the average clothianidin concentration detected in potable wells (0.608 µg/L) is only slightly higher than the average detected in field edge monitoring wells (0.54 µg/L). This could be the result of an outlier. If one sample has a concentration that greatly exceeded others in the dataset, the result could be questioned. One potable well (Well 07, 3.88 µg/L, Figure 5) did, in fact, have an observed detection of clothianidin that was significantly higher than other detects observed at the remaining potable wells. By removing this single high detection of clothianidin from the potable well dataset, the average clothianidin concentration drops to 0.486 µg/L, a concentration much closer to other detected concentrations. However, there is no valid reason for discarding this data point, as a second sample collected from the same well (two years later) revealed yet another high detection of clothianidin along with similar ratios of the other neonicotinoids previously observed. Furthermore, irrigation wells *and* monitoring wells in the area near potable Well 07 identified similar detections of all three neonicotinoids.

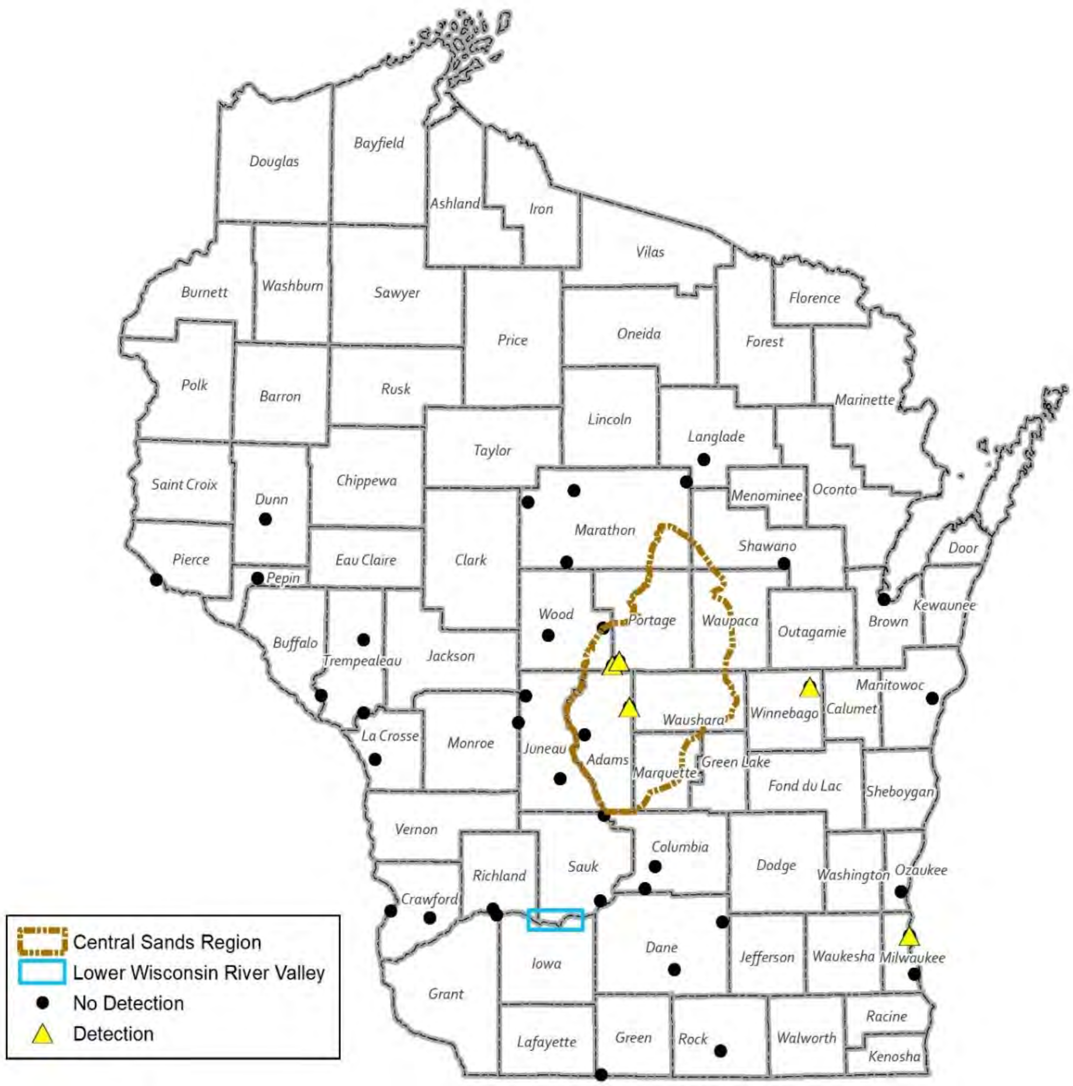
A second explanation for higher average clothianidin concentrations at potable wells rather than at shallow monitoring wells may involve chemical degradation. The physiochemical characteristics of these compounds suggests that, once in groundwater, these compounds degrade more slowly and can migrate significant distances in highly permeable sand and gravel aquifers, especially with repeated field use. The Environmental Protection Agency (EPA) reports that clothianidin was observed as a significant component of thiamethoxam degradation. From fate studies, they suggest that thiamethoxam degradation could result in as much as 13 percent of clothianidin observed in the subsurface (U.S. EPA, January 5, 2017). Therefore, it is possible that degradation of thiamethoxam that occurs along the groundwater flow path may result in elevated clothianidin concentrations at wells away from fields of application. This explanation seems reasonable because both clothianidin and thiamethoxam were detected in many shallow monitoring wells near fields of application. The average concentration of thiamethoxam in field edge monitoring wells was significantly higher than the clothianidin average, and the physiochemical characteristics of both compounds suggests they both migrate and persist in subsurface soils and groundwater. Additionally, thiamethoxam degradation has (in part) been shown to result in clothianidin formation; and thiamethoxam degradation is likely to occur with greater time and migration distance from the application site. The most likely explanation for the higher average clothianidin at potable wells is likely more complicated and would require a more detailed study to verify conditions observed.

Surface Water Monitoring Results

Between March 2011 and December 2016, ARM collaborated with DNR to obtain surface water samples from 34 streams that were being sampled under other DNR sampling programs. A total of 430 surface water samples were collected and analyzed for pesticides. Streams were generally sampled six or more times, with samples collected monthly from spring through fall. Some streams were sampled two or more years.

Figure 17 shows 34 streams sample locations as well as locations of neonicotinoids detections. The neonicotinoid compound imidacloprid was detected in samples from two streams, while thiamethoxam was detected in samples from four streams. Most detections occurred in samples collected from just two streams, Tenmile Creek in Portage County (two sampling stations) and Carter Creek in Adams County. Both of these streams are located within the Central Sands Region. A third stream located in the Central Sands, Little-Roche-Cri Creek was sampled eight times in 2011, but had no neonicotinoid detections.

FIGURE 17 STREAM SAMPLING LOCATIONS WITH NEONICOTINOID DETECTIONS



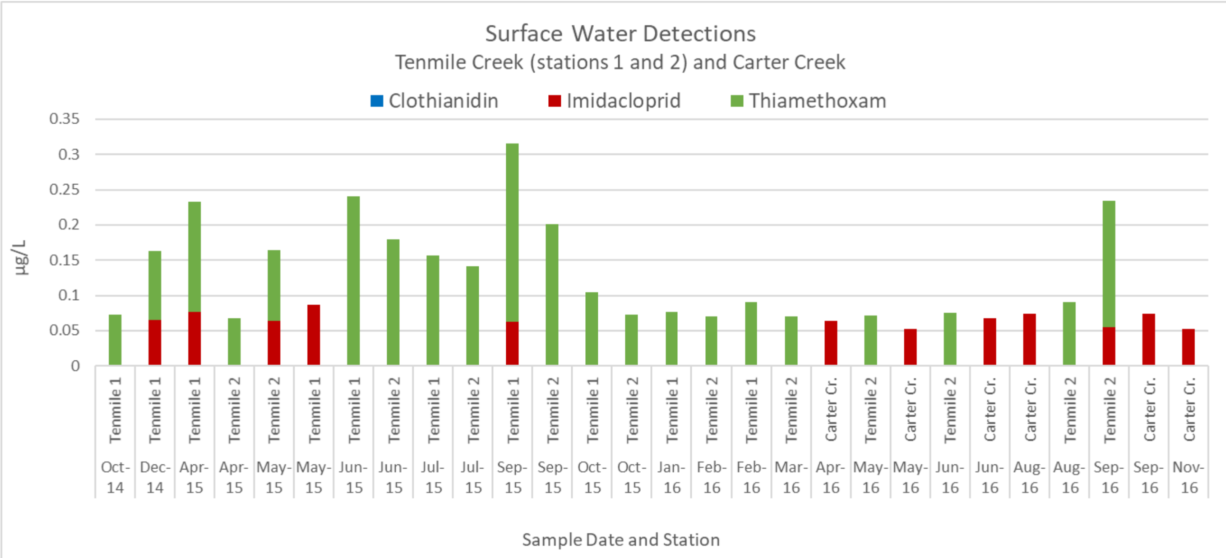
Above: Between March 2011 and December 2016, DATCP analyzed a total of 430 surface water samples from 34 streams for pesticides. Each stream was sampled six or more times, and some streams were sampled at more than one location.

Two streams not located within the Central Sands, the Milwaukee River (33 samples) and the Neenah Slough (eight samples), each had one detection of the compound thiamethoxam. Figure 18 shows the dates and concentrations of neonicotinoid compounds detected in samples from Tenmile and Carter Creeks. The compound clothianidin was not detected in any stream samples.

Implications for Important Receptors

There are a number of important receptors that could receive inadvertent exposures to the neonicotinoids detected during DATCP groundwater and surface water sampling efforts. Below is a discussion of potential

FIGURE 18 NEONICOTINOID DETECTIONS IN TWO STREAMS IN WISCONSIN'S CENTRAL SANDS REGION



exposure pathways for humans through drinking water, potential exposure pathways for target and non-target insects and pollinators through contaminated groundwater, and potential surface water exposure pathways for aquatic invertebrates and other organisms.

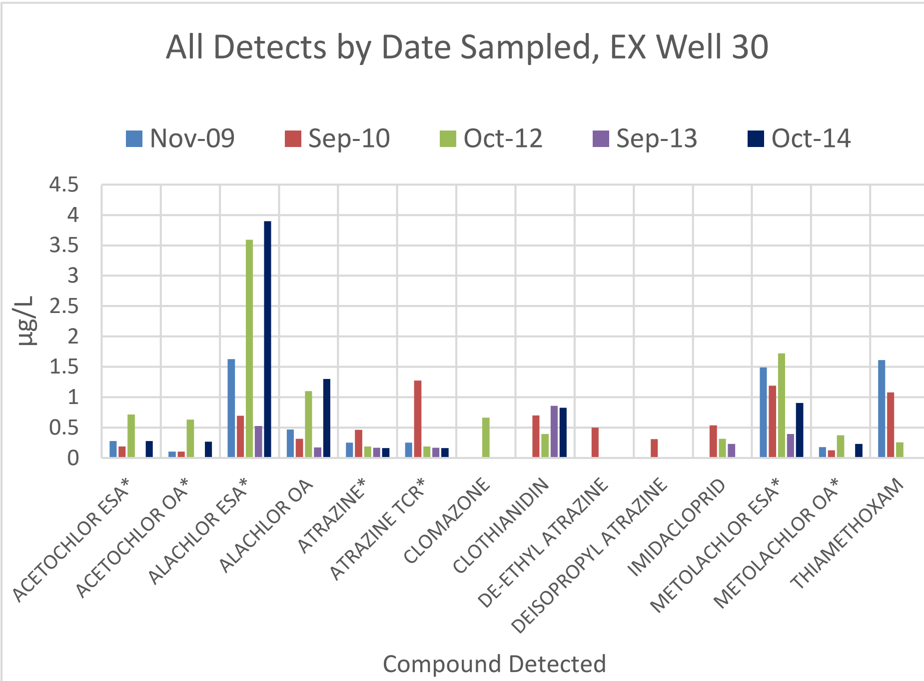
Risks for Human Consumption of Drinking Water

National Primary Drinking Water Standards (e.g., maximum contaminant levels-MCLs) or state drinking water standards have not been established for clothianidin, imidacloprid or thiamethoxam. Considering the number of detections observed by ARM in private potable water wells and the extensive use of neonicotinoids in agriculture, DATCP has requested the Department of Health Services (DHS) and DNR review these compounds for new standards development under chapter 160, Wis. Stats. In the event these agencies determine standards are warranted, DNR will draft administrative rules to promulgate new standards. Once the decision is made to set standards by administrative rule, it will take two to three years to develop and finalize the standards through Wisconsin's administrative rulemaking process.

In the absence of specific state drinking water standards or federal MCLs, EPA publishes a list of Human Health Benchmarks for Pesticides (HHBPs). HHBPs are not in themselves enforceable as numeric standards. They are developed based on an assumed lifetime exposure scenario to assist in considering whether the detection of a pesticide in drinking water may pose a significant human health risk (U.S. EPA, January 2017). Detected concentrations of neonicotinoids in potable water samples are below the chronic HHBP values derived by EPA for clothianidin (630 µg/L), imidacloprid (360 µg/L), and thiamethoxam (77 µg/L).

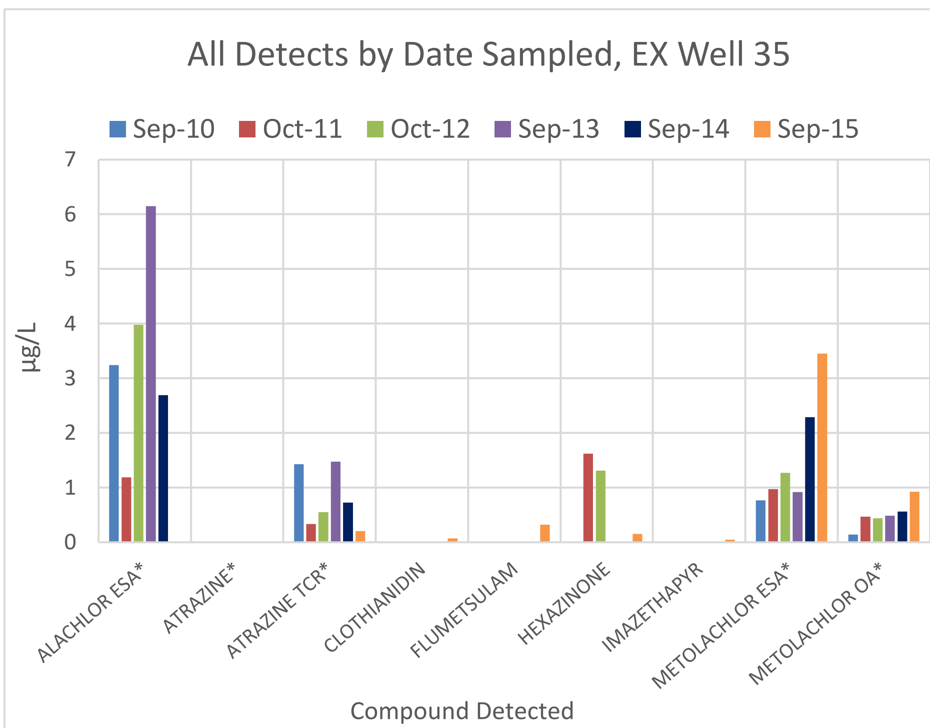
With regard to consumptive exposures to neonicotinoids and other pesticides in drinking water, there is added uncertainty related to possible combined effects that may result from exposures to multiple pesticide contaminants and elevated nitrate in drinking water. The DATCP data show that, in agricultural areas, wells often contain detectable concentrations of several pesticides and high nitrate. Figure 19 shows all pesticides detected in samples collected from two potable wells during ARM exceedance well sampling efforts.

FIGURE 19 ALL PESTICIDE COMPOUNDS DETECTED ON MULTIPLE SAMPLE DATES -- POTABLE WELLS 30 AND 35



Left: Range of pesticide concentrations detected at Exceedance (EX) Well 30 (southern Dane County) between November 2009 and October 2014. Between 7 and 12 pesticides were detected in each sampling event. There were no ES exceedances for any pesticides detected. Only those compounds with an asterisk (*) have a published ES. In addition to pesticides detected, all samples exceeded the NR 140 ES of 10 mg/L for nitrate. Nitrate ranged from 15.4 mg/L to 38.2 mg/L, with an average concentration of 22.6 mg/L.

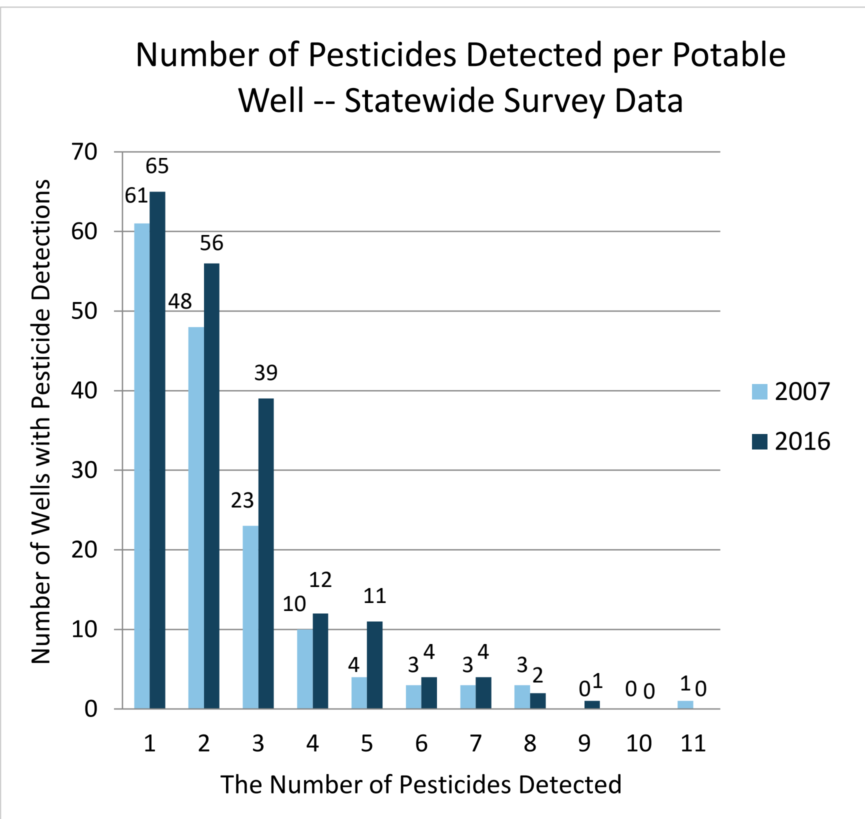
Right: Concentrations of eight pesticide compounds detected at EX Well 35 (Sauk County, LWRV) between September 2010 and September 2015. Four to seven pesticides were detected during each sampling event, plus nitrate. There were no ES exceedances for any pesticides detected. Only those compounds with an asterisk (*) have a published ES. Nitrate concentrations ranged from 6.76 to 16.1 mg/L, with an average concentration of 12.4 mg/L.



At a southern Dane County well, five samples revealed high nitrate and between seven to 12 pesticide compounds in each sample. At a Sauk County well that was sampled six times, high nitrate and between four to seven pesticides were detected in each sample. The concentrations of individual pesticides detected at these private wells is low, but these results suggest that multiple pesticides and nitrate are often present in a mixture or “cocktail”. Standards and benchmarks may exist for individual compounds, but there is currently a lack of research on additive or synergistic effects when these conditions exist in drinking water.

The presence of multiple pesticides in groundwater detected at both potable private wells and irrigation wells is a significant concern. Unfortunately, random sampling surveys of private wells conducted by ARM suggests that the number of pesticides detected in potable wells is increasing. To help illustrate this, Figure 20 shows a comparison of the numbers of wells having multiple pesticide detections in the 2007 and 2016 Statewide Surveys. After adjusting for differences in laboratory detection limits and reporting limits, this figure shows that the number of wells with more than two, three, four, five, six and seven different pesticides increased between 2007 and 2016.

FIGURE 20 PESTICIDE DETECTIONS PER WELL IN STATEWIDE SURVEYS



Left: The number of pesticides detected per well generally increased between the 2007 and 2016 surveys.

DATCP identified all wells in the 2007 and 2016 surveys with a single pesticide detection. Next the number of wells with two pesticides were identified, then three, then four, *etc.*, until all wells with multiple detected pesticides are included. To eliminate bias in comparison, only pesticides that were included on the analytical list for both the 2007 and 2016 surveys were included for this evaluation. The data were also adjusted for differences in detection and reporting limits between the two surveys.

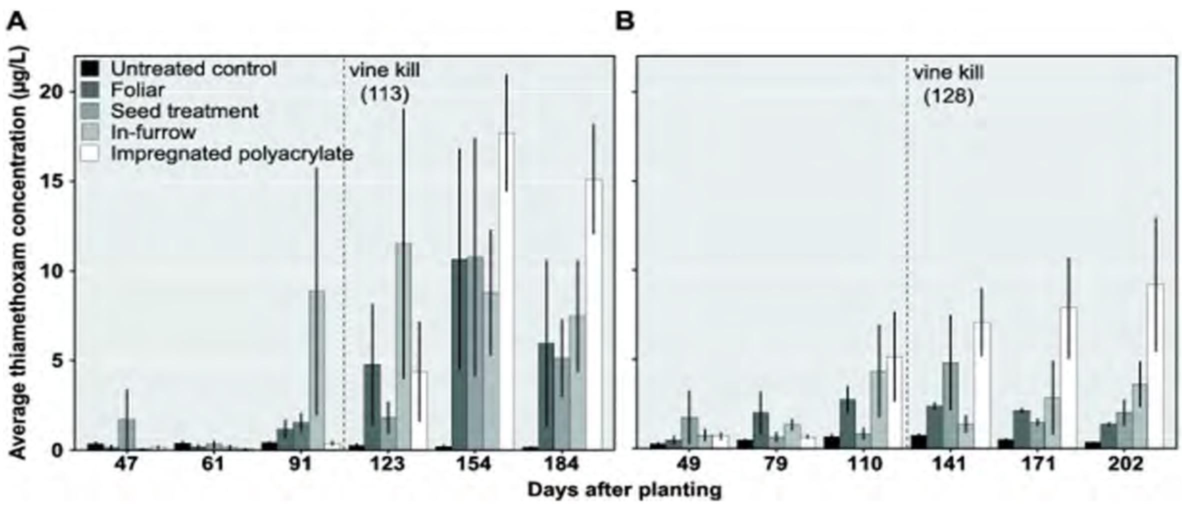
Risks for Target and Non-target Insects and Pollinators

Direct exposures to bees and other non-target insects can occur when neonicotinoids are applied as foliar sprays when bees are foraging. Significant bee kills resulting from exposures to pesticide dust abraded from treated seed during bulk transfers in the field have been documented (Pistorius J, Bischoff G, Heimback U, and Stahler M, 2009). In recent years, the number of studies that look at the effects of low-dose exposures to bees and non-target organisms has increased tremendously. It is estimated that more than half of all research published on neonicotinoids since 1995 has occurred from 2013 to 2016 (Wood & Goulson, 2017). The following paragraphs highlight recent research and data collected specifically within the Central Sands region. These studies help illustrate concerns over the presence of low level concentrations of neonicotinoids like those detected in samples collected during ARM groundwater and surface water sampling efforts.

A study performed by UW researchers in the Central Sands (Huseth, Lindholm, Groves, & Groves, 2014) determined that applications of low concentrations of neonicotinoids may be a significant concern for target insects that are repeatedly exposed to low concentrations. The study focused on insecticide resistance development in Colorado potato beetle (*Leptinotarsa decemlineata*) populations resulting from different types of soil-applied applications of imidacloprid and thiamethoxam on potatoes. Researchers measured insecticide concentrations in plant tissues over time and monitored beetle populations for two-years following applications. They found that regardless of soil application method or neonicotinoid used, the insecticides lost efficacy over time, but were still detectible in plant tissues at sub-lethal concentrations long after being applied. An important conclusion from the study was that chronic exposure to soil-applied systemic insecticides resulting from in-furrow, treated seed, and side dress application methods may accelerate selection for resistance in insect pests in potatoes.

Another study by UW researchers (Huseth & Groves, 2014) looked closely at leaching of soil-applied thiamethoxam on irrigated Central Sands potato plots over two years. Researchers used pan lysimeters to collect leachate beneath a control plot, three plots that received different soil-applied treatments, and one plot that received a foliar treatment of thiamethoxam. Samples were collected from lysimeters throughout the growing season each year, including after vine-kill and harvest. Samples were analyzed and leaching of thiamethoxam was documented at all plots ranging from trace concentrations within the control plots to samples containing as high as 20 µg/L (Figure 21). Interestingly, concentrations in lysimeter samples were highest in samples collected late in the season after the potato vines were killed to prepare the crop for harvest. To evaluate why there were low concentrations of thiamethoxam detected in the control plots, the researchers collected water samples directly from the operating irrigation systems. Testing revealed low concentrations of thiamethoxam being unintentionally applied to the crop through irrigation water. This study points to the need for additional research to help determine the effects related to exposures of non-target species of arthropods to low concentrations of thiamethoxam via contaminated groundwater used as irrigation water. It suggests that area-wide applications of low concentrations in irrigation water may have unanticipated effects on non-target organisms through repeated low-dose exposures to insecticides (Huseth & Groves, 2014). The study further highlights the potential for leaching of thiamethoxam residues from treated and decaying plant tissues and suggests the need for studies over the final disposition and use of residues of crops treated with thiamethoxam and other neonicotinoids.

FIGURE 21 THIAMETHOXAM CONCENTRATIONS IN LYSIMETER SAMPLES BENEATH POTATO (HUSETH & GROVES, 2014)



Above: Huseth and Groves studied thiamethoxam concentrations in leachate from potato. Average thiamethoxam recovered from in-furrow and foliar treatments in (A) 2011 and (B) 2012 (error bars show range in +/- standard deviations). Dotted lines indicate the date that the producer applied vine desiccant prior to harvest. Lysimeter studies continued in undisturbed soil following vine kill. doi:10.1371/journal.pone.0097081.g002

Another study by UW researchers in the Central Sands region examined whether flowering vegetable crops in the Central Sands represented a significant foraging source for honeybees and wild bees, and looked to quantify thiamethoxam concentrations in tissues and floral structures of treated plants for comparison to a proposed EPA threshold of 5 parts per billion (ppb) for floral structures (Prince & Groves, 2016). Researchers identified captures of both honeybees (Apis mellifera) and wild bee species in fields planted to sweet corn, snap beans and green peas throughout the growing season. A total of 53 fields and 13 field edges were included during the peak bee foraging months of June through August, representing about 6,000 acres. Within cropped fields, 60 percent of bees captured were honeybees and 40 percent were wild bees. In field edges, 15 percent of captures were honeybees and 85 percent were wild bees, representing 39 different species. Lasioglossum was the most prevalent wild genus, comprising mostly solitary and soil-nesting species. The diversity of bee species was comparable between fields and field edges across all three crop types, though bee abundance was consistently higher in field edges. Thiamethoxam concentrations were measured in plant foliage and flowers over time, as a result of applications made via treated seed at time of planting. Thiamethoxam was detected in crop leaves at concentrations that effectively control and repel pest insects, but were not detected in floral structures above the 30 ppb detection limit. Preliminary conclusions from the study indicate that vegetable processing crops in Central Wisconsin may provide foraging habitat for both honey and wild bees, and that average concentrations of thiamethoxam in tested floral structures of treated crops were not detected at or above 30 ppb, the study detection limit. Unfortunately, due to the elevated detection level, researchers were unable to evaluate whether the 5 ppb proposed EPA threshold for floral structures might be exceeded (Prince & Groves, 2016). Regardless, the study showed that honeybees and wild bee species do forage on significant areas of vegetable crops and on adjacent field-edge areas in the Central Sands where neonicotinoids are used.

Other than honeybees and wild bees, studies have identified endangered and threatened species of pollinators in Central Sands and/or LWRV areas where neonicotinoids are used and where irrigation water has been documented to have concentrations of neonicotinoids present. The application of irrigation water contaminated with neonicotinoids increases the potential for unintended exposures of these pollinators to these compounds. A list of pollinators whose populations are low enough to be classified as endangered, threatened or of special concern in Wisconsin is provided in Table 4. The list includes the likelihood that these pollinators could frequent agricultural areas based on their foraging habits and proximity of known habitat areas to agricultural fields (WDNR, January 5, 2017).

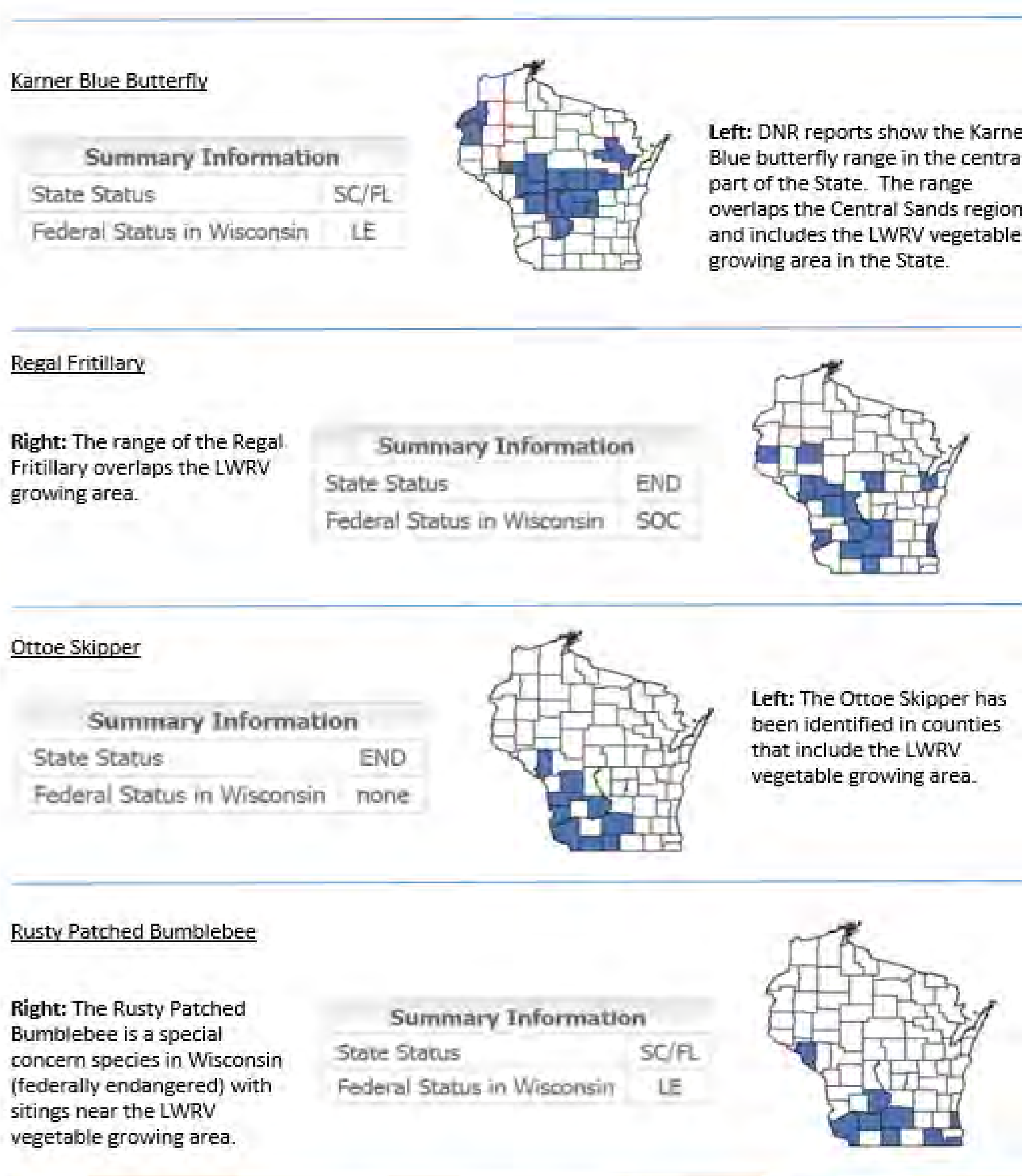
Table 4: Endangered, Threatened and Special Concern Pollinators in Wisconsin

Scientific Name	Common Name	Species Group	Federal Status*	WI Status**	Could be found Adjacent to Agriculture
Bombus affinis	Rusty-patched Bumble Bee	Bee	LE	SC/FL	Yes (historically statewide)
Bombus terricola	Yellowbanded Bumble Bee	Bee	SOC	SC/N	Yes (historically central through north)
Calephelis muticum	Swamp Metalmark	Butterfly	SOC	END	No
Danaus plexippus	Monarch	Butterfly	SOC		Yes statewide
Hesperia ottoe	Ottoe Skipper	Butterfly		END	Probably not
Lycaeides idas	Northern Blue	Butterfly		END	No
Lycaeides melissa samuelis	Karner Blue	Butterfly	LE	SC/FL	Possibly
Oarisma poweshiek	Poweshiek Skipperling	Butterfly	LE	END	No
Speyeria idalia	Regal Fritillary	Butterfly	SOC	END	Possibly
Papaipema silphii	Silphium Borer Moth	Moth		END	Probably not
Schinia indiana	Phlox Moth	Moth		END	Probably not

* LE=Federal listed endangered. SOC=Federal listed species of concern.
**SC/FL=Federally protected as endangered or threatened, but not so designated by DNR. SC/N=Species of special concern, no laws regulating use, possession, or harvesting. END=State listed endangered.

Figure 22 shows four species from Table 4 whose known habitat areas overlap or are adjacent to the Central Sands and LWRV growing areas. Maps for the Monarch butterfly and Yellow Banded Bumblebee are not

FIGURE 22 DOCUMENTED HABITAT AREAS OF FOUR ENDANGERED/SPECIAL CONCERN POLLINATOR SPECIES



Source: (WDNR, January 5, 2017) http://dnr.wi.gov/topic/EndangeredResources/ETList.html

LE-federal listed endangered. SOC-federally listed species of concern. SC/FL-federally protected as endangered or threatened, but not so designated by DNR. SC/N-species of special concern, no laws regulating use, possession, or harvesting. END-state listed endangered.

included in Figure 20, but their historic ranges include central sands counties and other areas having significant cropland. The habitat areas for these species increases the likelihood for possible interactions with crops treated with neonicotinoids. Research is needed to document any such interaction, as well as the potential for exposures and any resulting effects. Neonicotinoids found in groundwater sprayed by irrigation wells creates an added potential for chronic exposures to pollinators foraging in areas where neonicotinoids are unintentionally applied through irrigation water.

Risks for Aquatic Invertebrates

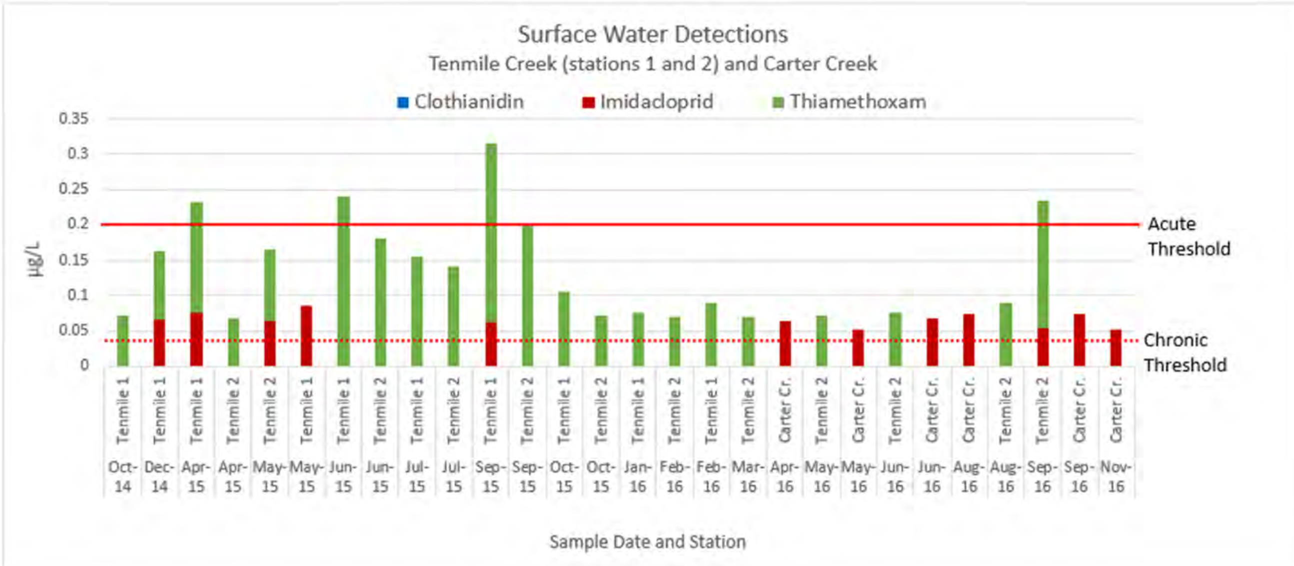
The Central Sands region is a unique geologic area of the state. With nearly level topography and unconsolidated sandy deposits often greater than 30 meters thick, infiltration rates are high and there is very little runoff (Stites & Kraft, 2000). Most areas are extremely well drained and groundwater recharge is high (USDA-Soil Conservation Service, 1980). Groundwater is intimately connected to surface waters, with base flow representing upwards of 90 percent of annual streamflow of headwater streams (Weeks, Ericson, & Holt, 1965). Contaminants that persist and leach to groundwater and potable wells in the region are likely to also be detected in streams and other surface water bodies.

Out of 33 streams sampled by DNR and ARM, two streams, Tenmile Creek and Carter Creek are located within the Central Sands vegetable growing area. Samples from each stream had multiple detects of the neonicotinoid compounds imidacloprid and thiamethoxam. The highest detections occurred during the months of June through September, but detections were also noted during the winter months from November through March, when concentrations detected are more likely a result of contaminated groundwater that is discharging into the streams as base flow. Clothianidin was not detected in samples from either stream.

For imidacloprid, EPA lists the aquatic life benchmarks for invertebrates in freshwater at 0.385 µg/L (acute) and 0.01 µg/L (chronic). For thiamethoxam, EPA lists only an acute benchmark for invertebrates at 17.5 µg/L (U.S. EPA OPP, November 2017). With specific regard to total neonicotinoids present in surface water environments, a recent and growing body of research is forming on the acute and chronic effects of neonicotinoids on aquatic invertebrates. Several researchers recently reviewed some of the most recent aquatic toxicity studies performed in surface waters from 29 studies in nine countries worldwide along with published data on their acute and chronic toxicities to 49 species of aquatic insects and crustaceans, including 12 invertebrate orders (Morrissey, et al., 2015). These reviewers recommended that in order to avoid lasting effects on aquatic invertebrate communities, ecological thresholds for cumulative concentrations of neonicotinoids needs to remain below 0.2 µg/L for short-term acute, or 0.035 µg/L for long-term chronic exposures. Figure 23 shows these recommended cumulative thresholds relative to the results of samples from Tenmile and Carter Creeks.

The figure shows that the recommended acute threshold was reached or exceeded in five samples collected from Tenmile Creek. The recommended chronic threshold was exceeded in all samples for which there were detections, in both streams. It is important to note that the 0.035 µg/L recommended chronic threshold for cumulative neonicotinoids is less than the BLS reporting limits of 0.05 µg/L for imidacloprid and 0.067 µg/L for both clothianidin and thiamethoxam.

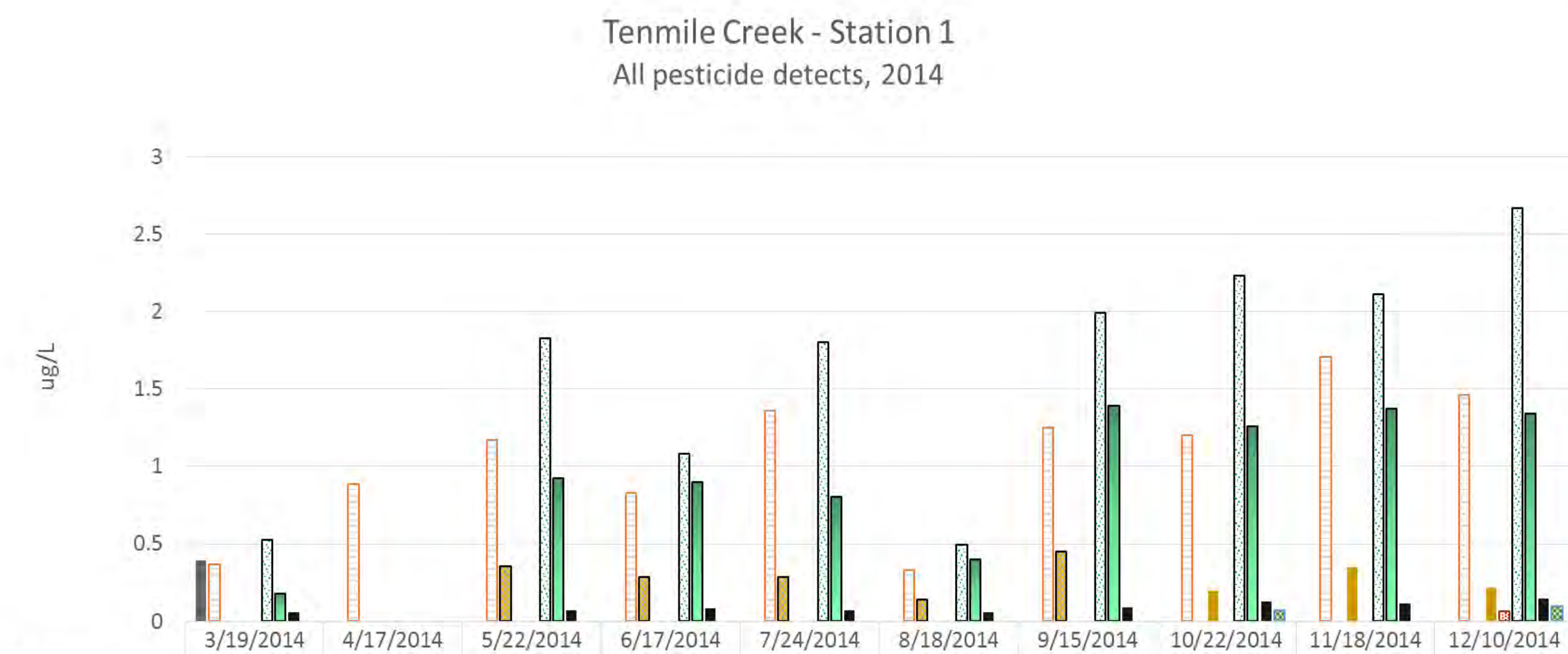
FIGURE 23 SURFACE WATER RESULTS WITH RECOMMENDED ACUTE AND CHRONIC THRESHOLDS, AFTER MORRISSEY ET AL.



As with the groundwater samples collected, the surface water samples collected from Tenmile and Carter Creeks also had multiple pesticides detected. Figures 24 and 25 illustrate the total number of pesticide compounds and frequency of detections of these compounds in these streams. Figure 24 shows concentrations of all pesticides detected in 10 samples collected during consecutive months in 2014 from Tenmile Creek. Figure 25 shows concentrations of all pesticides detected in 10 samples collected during consecutive months in 2016 from Carter Creek. Samples from Tenmile Creek had one to seven pesticides detected, with an average of about five pesticides per sample. Samples from Carter Creek had six to 15 compounds detected with an average of 13 pesticides detected per sample. Similar to the groundwater samples collected from wells in the Central Sands, most detects of individual compounds were less than 3 µg/L, and none of the pesticides detected in stream samples exceeded state ESs.

Although there is a growing body of research worldwide on the effects of neonicotinoids in aquatic communities, additional research is needed locally on these and other streams in the Central Sands where neonicotinoids are being detected in shallow groundwater that makes up a large percentage of stream base flow. ARM and DNR sampling to date has been primarily opportunistic and exploratory in nature, limited to monthly grab sampling, which tends to miss acute episodic concentrations of chemicals associated with timing of pesticide applications and flushes of agricultural chemicals via precipitation and runoff. ARM plans to continue providing DNR with analytical services for surface water bodies that they sample, but more comprehensive studies are needed, and on more streams in the Central Sands and in other areas of the state. Studies need to not only look at the presence of neonicotinoids, but also at the effects they have on aquatic life in these and other streams in the Central Sands area, including possible combined effects that may result from the numerous pesticide compounds present.

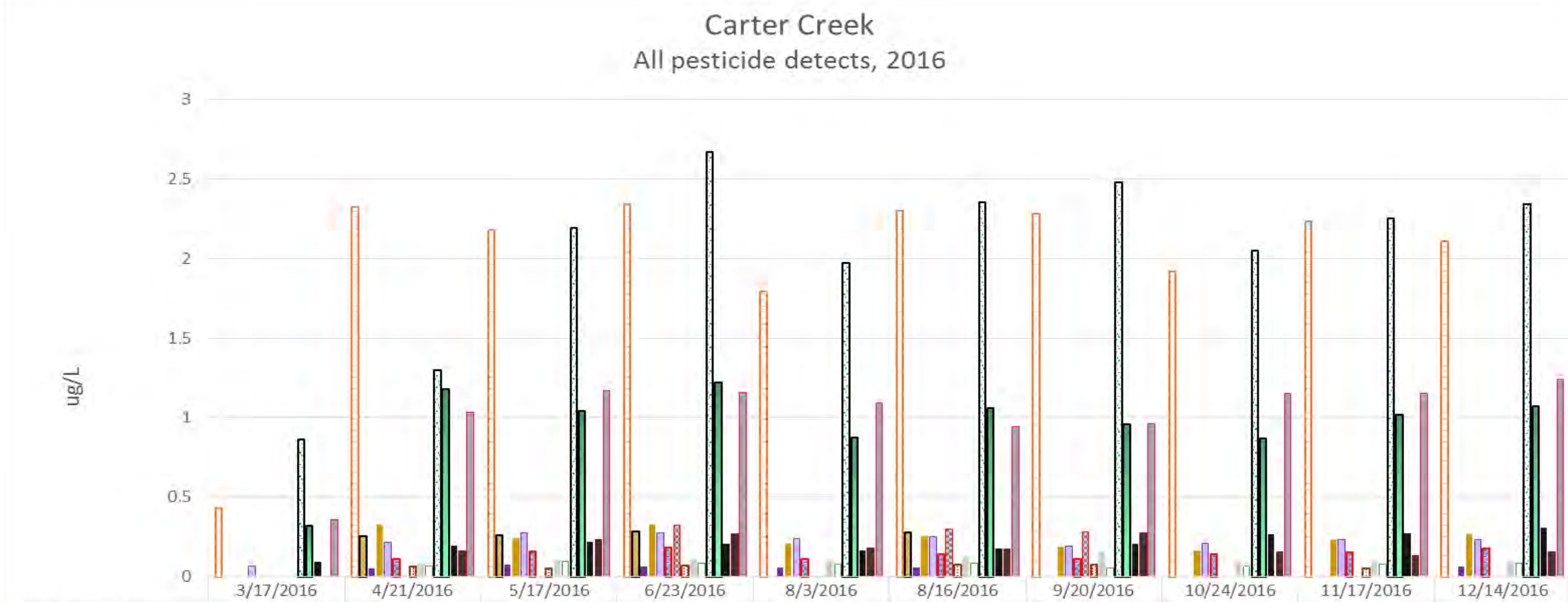
FIGURE 24 ALL PESTICIDE DETECTIONS IN TENMILE CREEK AT STATION 1 IN 2014



	3/19/2014	4/17/2014	5/22/2014	6/17/2014	7/24/2014	8/18/2014	9/15/2014	10/22/2014	11/18/2014	12/10/2014
Acetochlor ESA	0.396									
Alachlor ESA	0.367	0.885	1.17	0.829	1.36	0.331	1.25	1.2	1.71	1.46
Alachlor OA			0.354	0.283	0.284	0.141	0.452			
Bentazon								0.195	0.347	0.214
Imidacloprid										0.0656
Metolachlor ESA	0.525		1.83	1.08	1.8	0.494	1.99	2.23	2.11	2.67
Metolachlor OA	0.177		0.924	0.897	0.803	0.4	1.39	1.26	1.37	1.34
Metribuzin	0.0615		0.0706	0.0841	0.0698	0.0559	0.0924	0.127	0.116	0.148
Thiamethoxam								0.0726		0.0969

Combined sum of neonicotinoids exceeds 0.035 µg/L chronic threshold recommended by Morrissey, et al.

FIGURE 25 ALL PESTICIDE DETECTIONS IN CARTER CREEK, 2016



	3/17/2016	4/21/2016	5/17/2016	6/23/2016	8/3/2016	8/16/2016	9/20/2016	10/24/2016	11/17/2016	12/14/2016
Alachlor ESA	0.434	2.32	2.18	2.34	1.79	2.3	2.28	1.92	2.23	2.11
Alachlor OA		0.255	0.26	0.284		0.28				
Atrazine		0.0508	0.0737	0.0648	0.0581	0.0575				0.0622
Bentazon		0.328	0.243	0.326	0.209	0.256	0.187	0.165	0.233	0.264
De-ethyl Atrazine	0.0644	0.213	0.278	0.274	0.242	0.249	0.192	0.207	0.232	0.236
Deisopropyl Atrazine		0.111	0.158	0.183	0.114	0.139	0.11	0.14	0.152	0.176
Diamino Atrazine				0.326		0.298	0.281			
Imidacloprid		0.0644	0.0529	0.0679		0.0745	0.0746		0.0528	
Metalaxyl		0.0872	0.102	0.106	0.102	0.124	0.162	0.0964	0.101	0.0941
Metolachlor		0.0678	0.0949	0.0835	0.0774	0.0846	0.0556	0.0695	0.0775	0.0861
Metolachlor ESA	0.865	1.3	2.19	2.67	1.97	2.35	2.48	2.05	2.25	2.34
Metolachlor OA	0.323	1.18	1.04	1.22	0.875	1.06	0.96	0.871	1.02	1.07
Metribuzin	0.092	0.193	0.22	0.205	0.165	0.176	0.209	0.269	0.27	0.311
Metribuzin DA		0.16	0.231	0.271	0.18	0.174	0.278	0.155	0.132	0.156
Metribuzin DADK	0.359	1.03	1.17	1.16	1.09	0.943	0.962	1.15	1.15	1.24

Combined sum of neonicotinoids exceeds 0.035 µg/L chronic threshold recommended by Morrissey, et al.

Conclusions

An evaluation of DATCP groundwater and surface water sample results for neonicotinoids in Wisconsin between 2008 and 2016 has revealed the following:

- Statewide randomized sampling of 401 private potable wells in 2016 revealed one detection of the neonicotinoid imidacloprid (0.25 percent of wells). Targeted sampling of 511 private potable wells in agricultural areas from June 2008 to October 2016 revealed 29 wells with detections of one or more of the neonicotinoid compounds clothianidin, imidacloprid and thiamethoxam (5.7 percent of wells).

- No drinking water standards have been established for neonicotinoid compounds. However, the concentrations detected in drinking water samples are below advisory human health benchmarks for these pesticides established by EPA (HHBPs).

- Testing of water table monitoring wells installed near agricultural fields identified detectable concentrations of one or more neonicotinoid compounds at 53 percent of sites tested (17 of 32 field locations).

- Irrigation well sampling was limited, but neonicotinoid compounds were detected in 18 of 22 high-capacity irrigation wells sampled (82 percent).

- Most detections in groundwater occurred in the Central Sands Region (Portage, Waushara and Adams counties) and other agricultural areas with sandy soils and a shallow water table. Other commonalities included crop rotations of corn or soybeans with vegetable crops like potatoes or sweet corn, and irrigation.

- Between 2011 and 2016, a total of 430 samples were collected from 34 streams. Neonicotinoids detected in stream samples included imidacloprid and thiamethoxam. Imidacloprid was detected in two streams, and thiamethoxam was detected in four streams.

- The majority of surface water detections occurred in samples collected from just two streams, Tenmile and Carter Creeks, whose drainage basins both lie within the Central Sands growing area.

- Imidacloprid and thiamethoxam detections in Tenmile and Carter Creeks exceeded newly recommended chronic toxicity values of 0.035 µg/L for total neonicotinoids (Morrissey, et. al) in every sample where a detection occurred (28 samples).

- Imidacloprid and thiamethoxam detections in Tenmile Creek exceeded newly recommended acute toxicity value of 0.2 µg/L for total neonicotinoids (Morrissey, et. al) in five samples.

- Neonicotinoid detections at field edge monitoring wells suggest leaching of these compounds to shallow groundwater occurs in sandy settings following routine pesticide applications.

- Neonicotinoid detections in high capacity irrigation wells and private potable wells shows that these compounds can migrate significant distances vertically and horizontally away from application sites.

- Numerous pesticides and nitrate detected over time in two streams within the Central Sands indicates that surface water quality can be influenced by contaminated groundwater that discharges to streams draining the Central Sands grower region.

- In addition to clothianidin, imidacloprid and thiamethoxam, numerous herbicide compounds and nitrate were also detected in groundwater samples collected from potable, water table monitoring and irrigation wells, and in stream samples collected.

Recommendations

Considering recent reductions in EPA acute and chronic thresholds for aquatic invertebrates, DATCP BLS should work to achieve lower laboratory reporting limits for clothianidin, imidacloprid and thiamethoxam. In addition, DATCP suggests numerous areas for further study, including:

- Studies of Tenmile and Carter Creeks are needed to better understand the chronic effects of neonicotinoids on aquatic invertebrates and other organisms in both creeks. Studies should employ the use of auto samplers to more fully characterize temporal changes in neonicotinoid concentrations and to allow for better evaluations of acute and chronic effects on aquatic organisms.

- Pesticide sampling studies are warranted for streams within the Central Sands region and within other agricultural areas where similar pesticide use patterns occur and where contaminated groundwater discharge is likely to contribute to a significant percentage of total stream flow.

- Studies are needed to help determine the effects that repetitive low-dose exposures have on pollinators and non-target insects through recurring applications of contaminated irrigation water.

- Studies are needed to better understand whether accelerated resistance development occurs in target pest species through unintended recurring exposures to neonicotinoid insecticides at less than acute concentrations through contaminated irrigation water.

- Studies are needed to better define the risks posed by the observed complex mixtures of pesticides and high nitrate to humans through contaminated drinking water; to pollinators and non-target insects exposed to contaminated irrigation water; and to aquatic invertebrates and other aquatic life exposed to contaminated surface water.

DATCP shares the data it collects with the public, University of WI-Extension, local government officials, and other agencies like the Department of Natural Resources (DNR), the Department of Health Services (DHS) and the U.S. Environmental Protection Agency (EPA). It is hoped that this report and accompanying data will aide EPA's current efforts to evaluate neonicotinoid compounds for effects on pollinators and non-target organisms. DATCP remains dedicated to helping the citizens of Wisconsin grow quality food and healthy plants and animals through the sound use of land and water resources.

Appendix 1 **Physical, Chemical and Fate Properties of Clothianidin, Imidacloprid and Thiamethoxam**

Parameter (units)	Clothianidin*	Imidacloprid**	Thiamethoxam*
Formula	C6H8ClN5O2S	C9H10ClN5O2	C8H10ClN5O3S
Molecular weight (g/mol)	249.7	255.7	291.7
Water solubility (mg/L)	327 (@20oC)	580 (@ 20oC)	4100 (@25oC)
Vapor pressure (mm Hg)	2.9x10-13 (@20oC)	1.5 x 10-9 torr (@ 20 oC)	4.95 x10-11(@25oC)
Henry's law constant (atm m3/mol)	2.9x10-16 (calculated)	9.9 x 10-13	4.62x10-15 (calculated)
Octanol-water partition coefficient (Kow)	13	3.7	0.74
Soil partition coefficient (Koc; L/kgoc)	84 (sandy loam) 119 (sand) 123 (clay loam) 129 (loamy sand) 345 (sandy loam)	Average= 318 (n=5) with a range from 277 to 411 L Kg-1 in soils differing in texture (sand, loamy sand, silt loam "replicated" and loam), cation exchange capacity (4-16 meq/100 g), organic carbon content (0.4-2.6%) and pH (4.5-6.5); Found no relation with O.C., clay or pH	33.1 (silty clay loam) 38.3 (loam) 43.0 (sand) 53.1 (loam) 77.2 (sandy clay loam) 176.7 (sandy loam)
Hydrolysis half-life (t½) (days)	Stable (at pH 5,7,9)	Stable (at pH 5 and 7) Hydrolyzed slowly (extrapolated t ½= 355 d) in sterile alkaline solution pH 9	Stable (at pH 5 and 7) 4.2, 8.4 (at pH 9)
Aqueous Photolysis t½ (days)	14.4	---	2.3, 3.1
Soil Photolysis t½ (days)	34	171	79, 97
Aerobic soil metabolism t½ (days)	148 – 1155	305 -- 1669	101 – 353
Anaerobic aquatic metabolism t½ (days)	27	---	25.3, 28.6
Terrestrial field dissipation t½ (days)	277 – 1386	---	1.1 - 111
GUS leaching potential index (calculated)***	4.91 (high)	3.74 (high)	4.69 (high)

Sources: *Clothianidin and Thiamethoxam (USEPA, January 5, 2017)
**Imidacloprid (USEPA, January 4, 2016)
***Groundwater Ubiquity Score index (Lewis, 2016)

Appendix 2 DATCP BLS Groundwater Sample Analytes and Reporting Limits (RL)

Analyte	RL (µg/L)	Analyte	RL (µg/L)	Analyte	RL (µg/L)
2,4-D	0.050	lambda-Cyhalothrin	0.050	MCPA	0.050
2,4-DB	0.57	Cypermethrin	0.15	MCPB	0.21
2,4-DP	0.058	Cyprosulfamide	0.074	MCPP	0.055
2,4,5-T	0.050	De-ethyl atrazine	0.050	Malathion	0.050
2,4,5-TP	0.050	De-isopropyl atrazine	0.050	Mesotrione	0.18
Acetamiprid	0.050	Dacthal	0.050	Metalaxyl	0.050
Acetochlor	0.050	Di-amino atrazine	0.28	Methyl Parathion	0.078
Acetochlor ESA	0.050	Diazinon	0.050	Metolachlor	0.050
Acetochlor OA	0.30	Diazinon oxon	0.050	Metolachlor ESA	0.050
Acifluorfen	0.056	Dicamba	0.89	Metolachlor OA	0.27
Alachlor	0.050	Dichlobenil	0.050	Metribuzin	0.050
Alachlor ESA	0.050	Dichlorvos	0.076	Metribuzin DA	0.10
Alachlor OA	0.25	Dimethenamid	0.050	Metribuzin DADK	0.12
Aldicarb Sulfone	0.059	Dimethenamid ESA	0.050	Metsulfuron methyl	0.094
Aldicarb Sulfoxide	0.13	Dimethenamid OA	0.054	Nicosulfuron	0.050
Aminopyralid	0.050	Dimethoate	0.050	Norflurazon	0.058
Atrazine	0.050	Dinotefuran	0.050	Oxadiazon	0.050
Azoxystrobin	0.050	Diuron	0.18	Pendimethalin	0.050
Benfluralin	0.050	EPTC	0.050	Picloram	0.050
Bentazon	0.050	Esfenvalerate	0.050	Prometone	0.050
Bicyclopyrone	0.050	Ethalfluralin	0.074	Prometryn	0.050
Bromacil	0.084	Ethofumesate	0.050	Propiconazole	0.055
Carbaryl	0.067	Flumetsulam	0.17	Saflufenacil	0.20
Carbofuran	0.051	Flupyradifurone	0.050	Simazine	0.050
Chloramben	0.57	Fluroxypyr	0.32	Sulfentrazone	0.75
Chlorantraniliprole	0.20	Fomesafen	0.050	Sulfometuron methyl	0.050
Chlorothalonil	0.16	Halosulfuron methyl	0.080	Tebupirimphos	0.050
Chlorpyrifos	0.050	Hexazinone	0.050	Tembotrione	0.21
Chlorpyrifos Oxon	0.050	Imazapyr	0.050	Thiacloprid	0.067
Clomazone	0.050	Imazethapyr	0.050	Thiamethoxam	0.067
Clopyralid	0.078	Imidacloprid	0.050	Thiencarbazone methyl	0.38
Clothianidin	0.067	Isoxaflutole	0.32	Triclopyr	0.10
Cyclaniliprole	2.0	Isoxaflutole DKN	0.47	Trifluralin	0.050
Cyfluthrin	0.10	Linuron	0.087	N-Nitrate/Nitrite	0.50 mg/L

BLS groundwater analyses performed in conformance with ISO 17025 accreditation standards.

Appendix 3 List of Abbreviations

ARM	Agricultural Resource Management Division
Bgal	Billion gallons
BLS	Bureau of Laboratory Services
DATCP	Wisconsin Department of Agriculture, Trade and Consumer Protection
DHS	Wisconsin Department of Health Services
DNR	Wisconsin Department of Natural Resources
END	State listed endangered species
EPA	U.S. Environmental Protection Agency
ESs	Chapter NR 140, Wis. Administrative Code, Enforcement Standards
Ex	Exceedance Well
GIS	Geographic Information Systems
HHBP	Human Health Benchmark for Pesticides
ISO	International Organization for Standardization
Koc	Soil Organic Carbon Partition Coefficient
Kow	Octanol-Water Partition Coefficient
LE	Federally listed endangered species
LWRV	Lower Wisconsin River Valley
MCLs	National Primary Drinking Water Standards Maximum Contaminant Levels
mg/L	Milligrams per Liter
nAChRs	Nicotinic Acetylcholine Receptors
NASS	National Agricultural Statistics Service
PALs	Chapter NR 140, Wis. Administrative Code, Preventive Action Limits
ppb	Parts per Billion
RL	Reporting Limit
SC/F	Species federally protected as endangered or threatened, but not so designated by DNR
SOC	Federally listed species of concern
SC/N	Species of special concern, no laws regulating use, possession or harvest
µg/L	Micrograms per Liter
USDA	U.S. Department of Agriculture
UW	University of Wisconsin-Madison

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