2015 Reconnaissance Study of Pesticide Compounds in Community Public Water Supply Wells

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Minnesota Department of Health

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MDA Laboratory Water Analysis Unit

MDH Public Health Laboratory

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Executive Summary

The Minnesota Department of Health (MDH), in cooperation with the Minnesota Department of Agriculture (MDA), conducted a reconnaissance study of 135 pesticides and pesticide degradates at 108 Minnesota community public water system (CPWS) wells during February and March 2015. This study built upon the results of a 2010 reconnaissance study (MDA, 2010) through the use of improved analytical capabilities at the MDA Laboratory Services Division (MDA Laboratory) and MDH Public Health Laboratory (PHL). Community public water system participation was voluntary, and all MDA and MDH employee resources were funded through existing budgets.

Samples were collected from 108 wells and analyzed for source water quality prior to any applicable treatment and distribution to customers. Analyses for pesticides were performed by the MDA Laboratory using a gas chromatography with tandem mass spectrometry (GC-MS/MS) method along with a liquid chromatography with tandem mass spectrometry (LC-MS/MS) method. Analytical capabilities in 2015 differed from those in 2010 resulting in analysis for additional chemicals and slightly different method reporting limits (MRLs) for certain compounds.

A small set of water chemistry indicators was also monitored concurrent with the pesticide reconnaissance study. These indicators included inorganic compounds nitrate-N, chloride, and bromide. They were analyzed by either the MDA Laboratory or the MDH PHL, depending on the indicator.

Pesticides were detected at low levels in 72 out of 108 samples resulting in an overall pesticide detection frequency of approximately 67 percent. A total of 19 different pesticides and/or pesticide degradates were detected throughout the 2015 study. All detections were well below MDH/EPA established screening level health reference values. Metolachlor ESA was the most frequently detected compound and was found in 68 wells or 63 percent of the wells sampled. Other compounds that were detected in more than 10 wells were alachlor ESA (49 wells, 45 percent), metolachlor OXA (36 wells, 33 percent), acetochlor ESA (21 wells, 19 percent) and alachlor OXA (12 wells, 11 percent). The study results showed no known public health risks from pesticides in Minnesota CPWS wells sampled. In addition to allowing temporal comparisons of several pesticides and their degradates, results provided an initial reconnaissance for the presence of neonicotinoid pesticides in CPWS wells. No neonicotinoid pesticides were detected in the wells sampled. Overall, detection frequency was similar to the 2010 study. Some pesticides were measured at higher levels than found in 2010. MDH conducted a cumulative assessment of the chemicals detected in the CPWS samples and found that the concentrations do not pose a health risk of concern when combining chemicals that have a common health endpoint and common duration period.

Introduction

This report presents the results of a cooperative project between the Minnesota Department of Agriculture (MDA) and the Minnesota Department of Health (MDH) to conduct a reconnaissance study of community public water system (CPWS) wells for pesticide and pesticide break-down (degradate) compounds, as well as select inorganic compounds. The inorganic compounds included nitrate as nitrogen (nitrate-N), chloride and bromide. The purpose of this work was to determine:

- The presence and relative magnitude of pesticides and associated degradates in groundwater collected from CPWS wells;
- If monitoring should be expanded to assess pesticides in other CPWS wells that may be at risk;
- If there were any changes in pesticide concentrations or detections at specific wells between a previous study conducted in 2010 and this study conducted in 2015;
- If neonicotinoid pesticides were present in groundwater collected from CPWS wells;
- The presence and relative magnitude of select inorganics in groundwater collected from the CPWS wells.

This study was designed as a reconnaissance survey. Sample site selection was not random. Therefore, results are not necessarily representative of the larger population of CPWS wells and cannot be directly extrapolated to other wells or regions. In general, wells considered to be at higher risk of pesticide contamination were targeted. All participating CPWS wells drew their drinking water from groundwater sources.

Background

Pesticides are chemicals that include herbicides (to manage undesirable plants), insecticides (to manage insects) and fungicides (to manage molds and fungi). Pesticide contamination of groundwater may result when there is infiltration of precipitation or surface water into aquifers in areas where pesticides are used.

In 1987, the Minnesota Legislature amended the Minnesota Pesticide Control Law (Chapter 18B of Minnesota State Statutes). Minnesota Statute 18B.04 requires: *"The commissioner shall:*

> *(1) determine the impact of pesticides on the environment, including the impacts on surface water and groundwater in this state;*
> *(2) develop best management practices involving pesticide distribution, storage, handling, use, and disposal; and*
> *(3) cooperate with and assist other state agencies and local governments to protect public health and the environment from harmful exposure to pesticides."*

In response to this charge, MDA initiated a groundwater monitoring program in 1987 and began monitoring surface water in 1991. MDA is responsible for the management of pesticides and one of the ways it does that is by operating a groundwater monitoring network that evaluates the impact of pesticides on groundwater. Much of this monitoring is focused on shallow monitoring wells. Only

limited pesticide data has been collected from deeper aquifer systems and pumping wells of the type presented here.

MDH was granted authority through the Safe Drinking Water Act (SDWA) of 1977 (Minnesota Statutes 144.381) to "ensure safe drinking water in all public water supplies." (Minnesota Statutes 144.383) In so doing, part 141 and part 142 sections 142.40 to 142.64 of the SDWA were adopted by reference in Minnesota Rule 4720.0350. The resulting responsibilities for protecting public health from regulated pesticide compounds are exercised through the authorities of the MDH Commissioner:

(a) To approve the site, design, and construction and alteration of all public water supplies and, for community and nontransient, noncommunity water systems as defined in Code of Federal Regulations, title 40, section 141.2, to approve documentation that demonstrates the technical, managerial, and financial capacity of those systems to comply with rules adopted under this section;

(b) To enter the premises of a public water supply, or part thereof, to inspect the facilities and records kept pursuant to rules promulgated by the commissioner, to conduct sanitary surveys and investigate the standard of operation and service delivered by public water supplies;

(c) To contract with community health boards as defined in section 145A.02, subdivision 5, for routine surveys, inspections, and testing of public water supply quality;

(d) To develop an emergency plan to protect the public when a decline in water quality or quantity creates a serious health risk, and to issue emergency orders if a health risk is imminent;

(e) To promulgate rules, pursuant to chapter 14 but no less stringent than federal regulation, which may include the granting of variances and exemptions.

MDH tests the drinking water that enters CPWS distribution systems for 24 pesticide compounds as part of its routine SDWA compliance monitoring program. MDA and MDH agreed that a continued evaluation of pesticide presence in the source water of CPWS systems was warranted, and assumed the following roles for the 2015 reconnaissance survey. MDA provided the bottles and associated supplies needed for sample collection, laboratory staff, lab equipment used to analyze water samples and analytical results. MDH identified wells to sample, solicited cooperation from well owners, coordinated collection of samples and sample submission to the MDA Laboratory Services Division (MDA Laboratory), and provided a report of the results to the cooperating well owners. Both agencies cooperated to ensure that water samples were collected, delivered and analyzed according to schedule, as well as collaborated on this summary report.

Well Selection

The CPWS systems that are most likely to be at risk for pesticide contamination are those that pump from shallow aquifers that are quickly recharged by precipitation or surface water and are located in areas where pesticide use is widespread. The presence of pesticides in well water indicates that the well is being impacted by surrounding land uses and that testing for other types of human-caused contaminants, such as nitrate, may be warranted. The possible public health impacts of drinking water that contains pesticides and pesticide degradates needs to be assessed when they are detected. Because of the limited number of samples to be collected, CPWS wells that would most likely be

impacted by pesticides were targeted. In addition, approximately 10 percent of the wells were selected to reflect aquifer settings that would be unlikely to be impacted. The latter set of wells has the potential to be used to evaluate the well vulnerability assessment protocol used by MDH, and to provide a comparison group for the reconnaissance study. This may be investigated as part of future analysis of the data from 2010 and 2015.

MDH selected CPWS wells that were already scheduled for inspection during the first quarter of 2015 to maximize the efficiency of staff time required for sample collection. MDH Source Water Protection Unit staff selected wells for sampling from these CPWS systems based upon 1) well vulnerability, 2) an assessment of the capture areas for these wells, and 3) a review of aerial photos to confirm that agricultural land use occurred within the capture areas. Ninety percent of the wells that were selected 1) pumped from geologically sensitive aquifers; and 2) captured groundwater from areas that extended under land that was either cultivated or managed forest. As discussed above, ten percent of the wells were selected for the comparison group that pumped groundwater from geologically protected aquifers where cultivated land use occurs.

Moreover, the well selection process targeted a statewide sample site distribution (Figure 1) in order to include a variety of hydrogeologic settings and well construction practices. In order to verify hydrogeologic setting and well construction information, site selection was limited to wells for which MDH had a well construction record. The final CPWS wells sampled represented geographic coverage of all but the northeastern area of Minnesota.

The 2015 Reconnaissance Study analyzed raw (untreated, source) water from 108 CPWS wells. The wells sampled in 2015 included 80 of the 83 CPWS wells that were sampled during the 2010 Reconnaissance Study. During the 2010 study, wells were selected from a list of those scheduled to be visited by MDH field engineers during the first quarter of 2010. Using the same selection criteria as in 2010, 27 additional wells were selected in 2015.

Sample Collection

The timing of the study was dictated by analytical capacity at the MDA Laboratory and the availability of MDH field engineers to collect the samples from the selected systems. A review of historical monitoring data for pesticides in Minnesota groundwater across seasons indicated no difference in results due to the season in which a well was sampled. When surface water is the source of a community water supply, however, the sampling season (period) may have greater relevance for both detection and concentration because there is much greater seasonality in surface water pesticide concentrations.

MDH Drinking Water Protection field engineers collected water samples in February and March, 2015. Samples were collected from water drawn from untreated groundwater pumped from wells through a sample tap. MDA's quality assurance and quality control (QA/QC) sampling protocol prescribed collection of duplicate and field replicate samples. Duplicate samples were collected from six wells, and field replicate samples were collected from five wells. MDA sampling protocol called for all samples to be placed into an iced cooler immediately following sample collection and submitted to the lab within 48 hours. If this wasn't possible, samples could be kept at 4 degrees Celsius and submitted within seven days of collection.

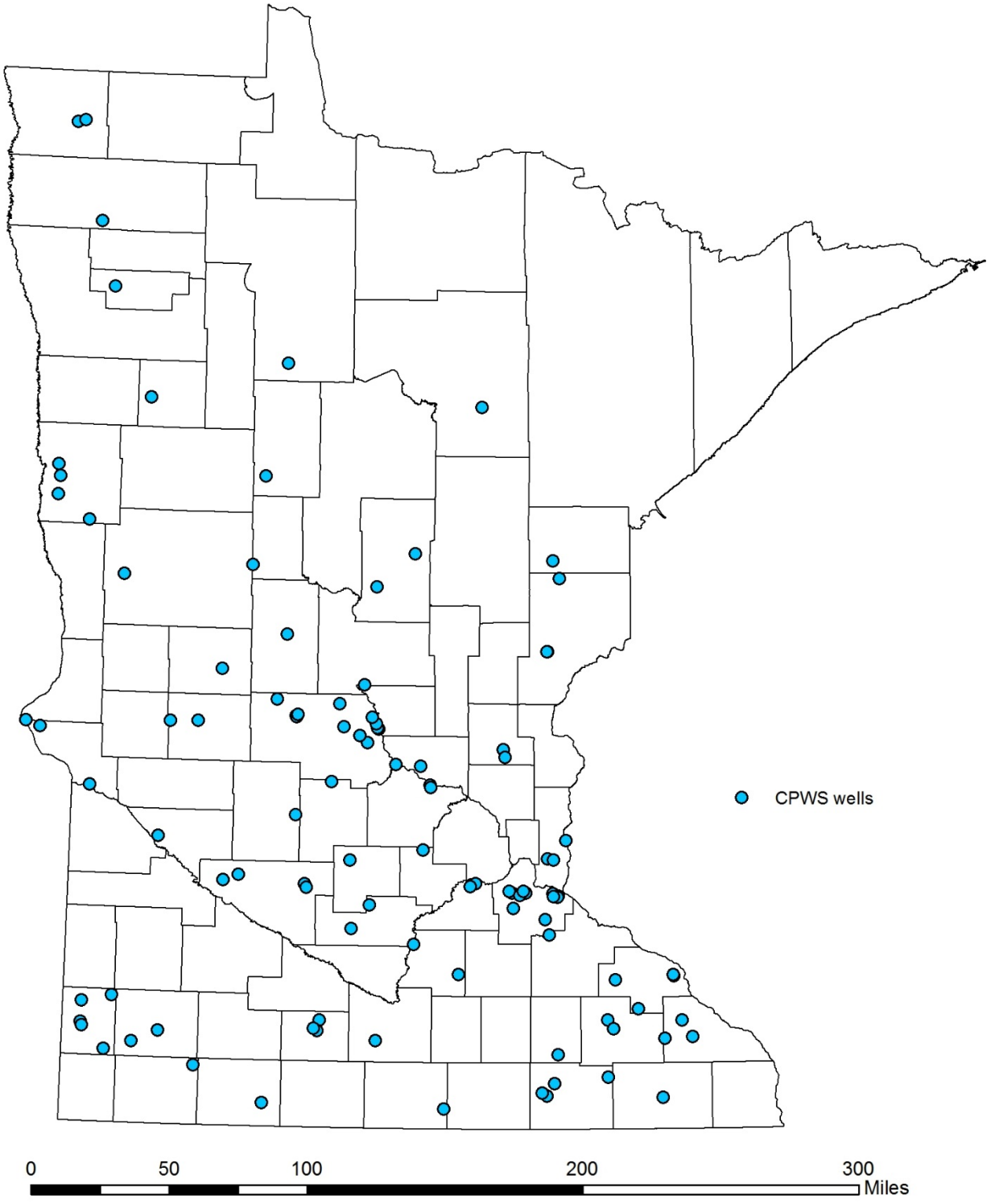

Figure 1. 2015 locations of CPWS wells selected for the pesticide reconnaissance survey.

Sample Analysis

Water samples were analyzed by the MDA Laboratory for pesticides and inorganic compounds (nitrate – N, bromide and chloride). The gas chromatography with tandem mass spectrometry (GC-MS/MS) method, along with the liquid chromatography with tandem mass spectrometry (LC-MS/MS) method, were used to analyze the samples for 135 different pesticides and degradates. All pesticide analyses were quantified at levels of parts per trillion (ppt) or nanograms per liter (ng/L). Inorganic water quality was described as milligrams per liter (mg/L). More detailed descriptions of acronyms and definitions (Appendix 1) as well as pesticide analytes and reporting limits (Appendix 2) have been included in this report.

During the course of the project, detection limits for bromide and chloride were determined to be lower at the MDH Public Health Laboratory (PHL) than at the MDA Laboratory. Therefore, sample analyses for bromide and chloride were shifted to the MDH PHL. Sufficient water volume was present in all water quality samples to allow for MDH PHL bromide analyses. However, chloride analyses were distributed between the MDA Laboratory (42 samples) and the MDH PHL (65 samples). A summary of inorganic analyses and corresponding method reporting limits (MRLs) at the MDA Laboratory and MDH PHL can be found in Appendices 3, 4 and 5, respectively.

Groundwater Reference Values and Standards

Pesticide concentrations were evaluated for potential health risks through comparison with existing reference values and standards. MDA and MDH used a variety of water quality reference values and standards to compare against the monitoring results. Federal Safe Drinking Water Act (SDWA) maximum contaminant levels (MCLs), as established by the U.S. Environmental Protection Agency (EPA), are used by MDH for CPWS regulatory compliance. In addition to MCLs, MDH evaluated results against Minnesota Health Risk Limits (HRLs), Health Based Values (HBVs), and Risk Assessment Advice (RAAs). MDH develops these health-based standards to evaluate potential health risks from drinking water contaminants. Their values represent concentrations of chemicals in drinking water which were likely to pose little or no health risks to humans over a lifetime of consumption. MCLs and health-based standards were used to evaluate study results for compliance with the SDWA and potential drinking water consumption health risks.

For some pesticides, no federal or state standards or reference values are available. In these cases, results from this study were compared to Rapid Assessment values (RAs) developed by MDH. RAs have not undergone a formal MDH review process and are not designed or intended as definitive estimates of risk. However, rapid assessment methodology generally produces more protective results than the reference values MDH would produce in a formal chemical review. Therefore, MDH is confident that pesticides in water below the RA values can be used for human consumption without harming health.

When a groundwater reference value (i.e. MCL, HRL or HBV) was available for a pesticide degradate, then the degradate concentration was compared to that value. However, in instances where compound specific toxicological information for pesticide degradates did not exist, MDH assumes the degradate has the same toxicological potential as the pesticide parent compound. In these cases, the groundwater reference value for the parent pesticide was used to make the comparison. Groundwater reference values were included in results summary tables (Tables 1 and 2) under the column heading “Reference

Value." The displayed reference values in the results tables represent the lowest health-based reference value for each individual chemical. Further information on all of these reference values and their derivation were included in Appendix 2.

Findings

Pesticides

2015 Pesticide Results

The 2015 Reconnaissance Study pesticide results were summarized and described by detection frequency, median, 75th percentile, 90th percentile and maximum values (Table 1). Only compounds that were detected are listed on Table 1. Each detection of a pesticide and/or pesticide degradate was compared to its lowest reference value (i.e. available MCL, HRL, HBV, RAA and/or RA). There was no pesticide concentration above its applicable reference value in this study.

Of the 135 different pesticide compounds analyzed for, 19 were detected. Metolachlor ESA was the most frequently detected compound and was found in 63 percent of the wells sampled. Other compounds that were detected in more than 10 wells were alachlor ESA (45%), metolachlor OXA (33%), acetochlor ESA (19%) and alachlor OXA (11%).

Figure 2 presents the number of detections by chemical and chemical type. Herbicide degradates were the most commonly detected pesticide class, with 12 different herbicide degradates detected. Six different herbicide parent compounds were detected. All herbicide parent detections frequencies were below 10 percent. One fungicide (metalaxyl) was detected in a single well at 9.57 ng/L. No neonicotinoids or other insecticides were detected in the CPWS wells. There were three herbicides and one herbicide degradate that were detected once, including clopyralid, metalaxyl, metolachlor and metribuzin DADK (Table 1).

With one exception, all pesticide and pesticide degradates were measured at concentrations lower than 10 percent of their individual applicable reference values. However, one well exceeded 10 percent of the atrazine Health Risk Limit of 3,000 ng/L when accounting for additivity of atrazine plus desethylatrazine and DEDI atrazine (354.7 ng/L). This well was located in southwest Minnesota. Only five of the 18 detected compounds had maximum concentrations above one percent of their reference values: DEDI atrazine (6%), metribuzin DADK (6%), alachlor ESA (4%), atrazine (3%), and desethylatrazine (3%).

When multiple chemicals are present in drinking water, MDH risk assessment methods require evaluation of the potential risk from the combined exposure. For each exposure duration, the concentrations of all chemicals with the same health endpoint are aggregated using the equations specified in Minnesota Rule Sections 4717.7880 and 4717.7890. MDH conducted a cumulative assessment of the chemicals detected in the CPWS samples and found that the concentrations do not pose a health risk of concern when combining chemicals that have a common health endpoint and common duration period.

Table 1. 2015 Summary of CPWS pesticide and pesticide degradate detections.

Pesticide Analyte	2015 Detection and Frequency (n=108)	2015 Median (ng/L)	2015 75th percentile (ng/L)	2015 90th percentile (ng/L)	2015 Maximum (ng/L)	Reference Value (ng/L)	Value Type†
Acetochlor ESA	**21 (19%)**	nd	nd	**83.3**	**1,460**	300,000	HRL_{11}
Acetochlor OXA	**7 (6%)**	nd	nd	nd	**94.0**	100,000	HRL_{11}
Alachlor ESA	**49 (45%)**	nd	**176**	**1,318**	**3,130**	50,000	RAA_{16}
Alachlor OXA	**12 (11%)**	nd	nd	**34.7**	**111**	50,000	RAA_{16}
Atrazine	**7 (6%)**	nd	nd	nd	**92.9**	3,000	HRL_{MCL}
DEDI Atrazine	**6 (6%)**	nd	nd	nd	**182**	3,000*	Parent HRL_{MCL}
Desethylatrazine	**7 (6%)**	nd	nd	nd	**88.2**	3,000*	Parent HRL_{MCL}
Hydroxyatrazine	**3 (3%)**	nd	nd	nd	**44.7**	20,000	HBV_{05}
Bentazon	**9 (8%)**	nd	nd	nd	**56.2**	30,000	HBV_{15}
Bromacil	**2 (2%)**	nd	nd	nd	**76.2**	30,000	RA_{14}
Clopyralid	**1 (1%)**	nd	nd	nd	**928**	200,000	RA_{14}
Dimethenamid ESA	**2 (2%)**	nd	nd	nd	**34.3**	300,000	RAA_{13}
Dimethenamid OXA	**1 (1%)**	nd	nd	nd	**12.7**	300,000	RAA_{13}
Imazapyr	**3 (3%)**	nd	nd	nd	**57.0**	900,000	RA_{14}
Metalaxyl	**1 (1%)**	nd	nd	nd	**9.57**	20,000	RA_{14}
Metolachlor	**1 (1%)**	nd	nd	nd	**56.0**	300,000	HRL_{11}
Metolachlor ESA	**68 (63%)**	**27.3**	**176**	**546**	**3,690**	800,000	HRL_{11}
Metolachlor OXA	**36 (33%)**	nd	**23.5**	**128**	**996**	800,000	HRL_{11}
Metribuzin DADK	**1 (1%)**	nd	nd	nd	**607**	10,000	RAA_{12}

Notes: nd = not detected

* – In the absence of compound-specific toxicological information for pesticide degradates, MDH assumes by default that a pesticide degradate had the same toxicological effect and potency as the pesticide parent compound.

†Reference value type information can be found in Appendix 2.

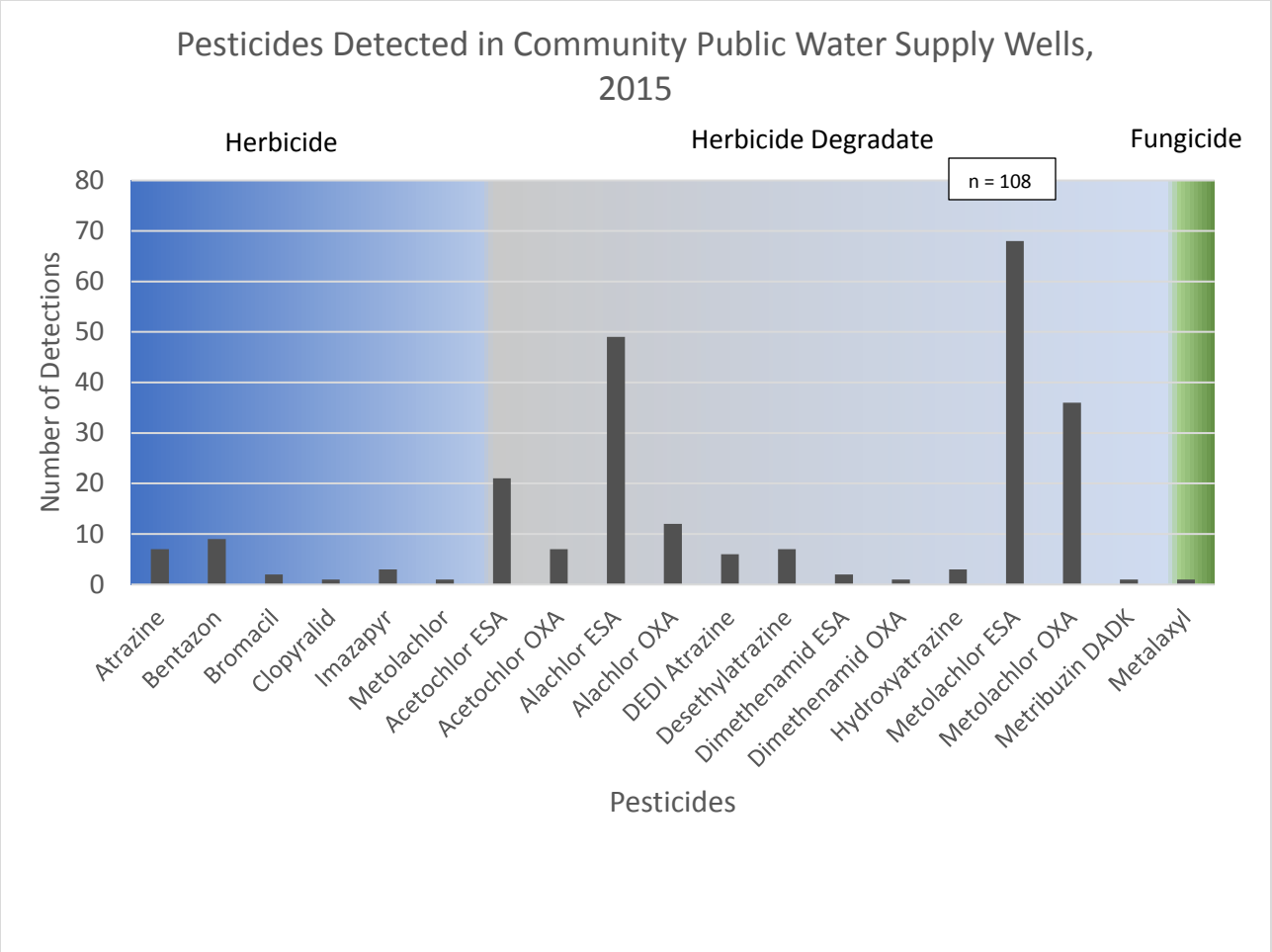

Figure 2. Pesticides detected in the CPWS wells by chemical and chemical type.

Figure 3 presents the number of total pesticide compound detections found per location. Of the 108 wells sampled, 36 wells (33%) had no pesticide detections. While wells without pesticide detections were distributed randomly across the reconnaissance study geographic range, the 72 wells (67%) with detections were more prevalent in the central, southeastern, and southwestern areas of the state. Numbers of detections ranged from one to nine per sampled well, with the detection of nine pesticides and degradates compounds occurring in two wells, in Renville and Wright Counties. Seventy-five percent of the wells had three or fewer pesticide compounds detected.

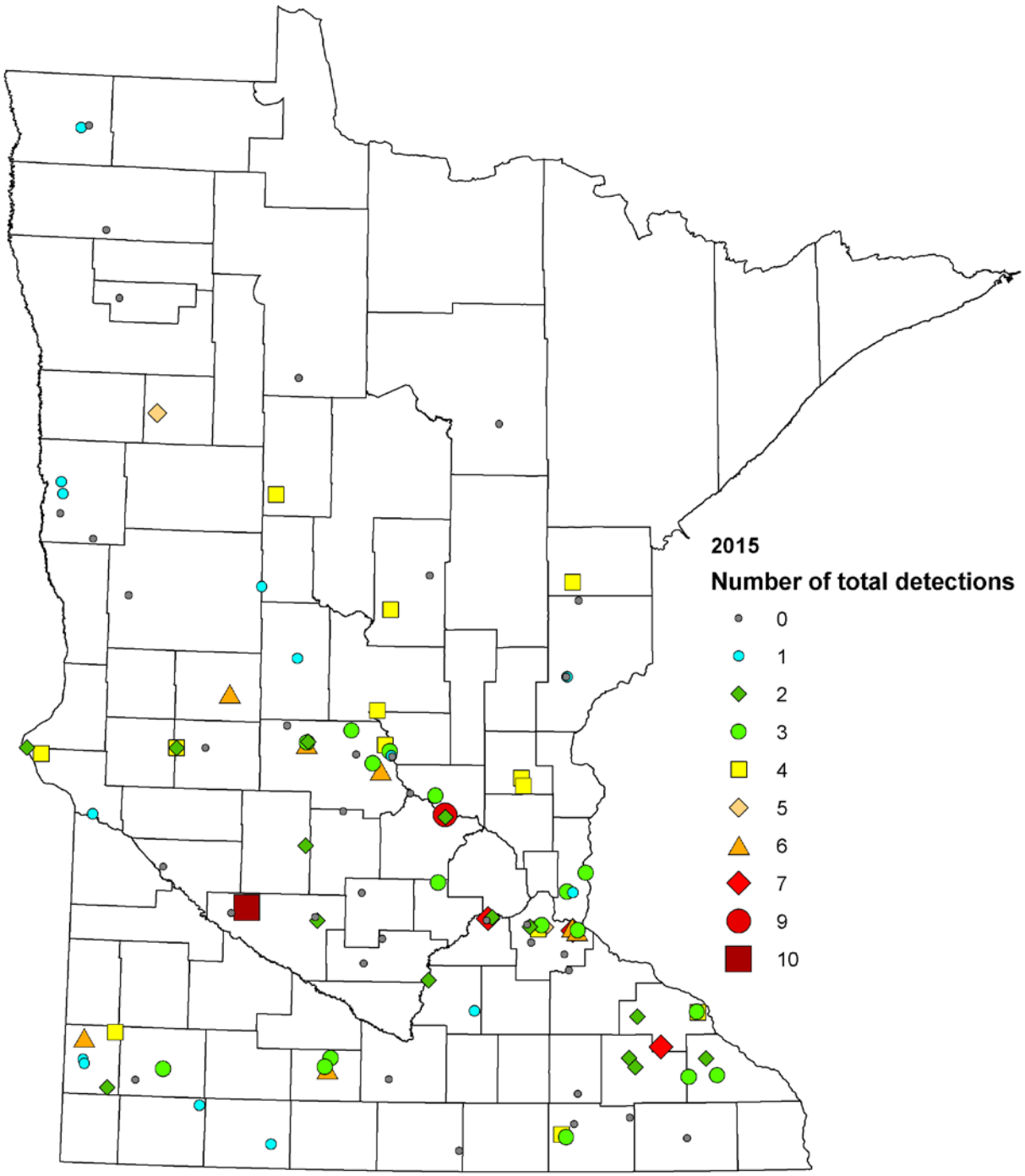

Figure 3. Total number of pesticide compound detected in each sampled CPWS well.

Neonicotinoid Results

In the past few years, there has been growing interest in the class of insecticides called neonicotinoids. MDA recently completed a "Scoping a Review of Neonicotinoid Use, Registration, and Insect Pollinator Impacts in Minnesota" (MDA, 2014). There are seven neonicotinoids registered for use in crop or animal agriculture, urban landscapes or domestic settings in Minnesota. Six of these are included in the MDA Laboratory LC-MS/MS method including acetamiprid, clothianidin, dinotefuran, imidacloprid, thiacloprid and thiamethoxam. The insecticide nithiazine is not analyzed for by the MDA Laboratory because of its limited use (fly abatement strips) and the possibility of occurrence in water is considered remote. In 2010, the MDA Laboratory was not capable of analyzing samples for these chemicals but new capabilities for testing became available and were utilized for the 2015 sampling. All samples were non-detect for neonicotinoid pesticides.

Detection Maps

Common detection is an official designation made by MDA Commissioner when a pesticide is detected in groundwater frequently and/or at levels of concern as a result of normal use (Minn. Stat 103H.005, subd 5). The process of designating a common detection pesticide is described in the Minnesota Pesticide Management Plan (www.mda.state.mn.us/pesticides). As a result of their common detection status, these pesticides and their degradates received heightened scrutiny from MDA during reporting of monitoring results. Acetochlor, alachlor, atrazine, metolachlor, and metribuzin have been designated as common detection pesticides in Minnesota by MDA.

As mentioned earlier in the results summary provided for Table 1, the common detection compounds of acetochlor, alachlor, and metolachlor were found the most frequently in this study. Table 1 also shows that 12 out of the 19 compounds detected (63%) were common detection pesticides and degradates.

Figures 4 through 6 depict statewide graphics for the five common detection compounds that were detected in the CPWS reconnaissance study. Each map indicates the locations where detections occurred for the common detection chemicals and their degradates, and were useful for evaluating spatial patterns that may suggest detections were regionally specific. The figures indicate if concentrations were increasing or decreasing and the relative magnitude of the change. Maps for the other chemicals detected in the CPWS reconnaissance can be found in Appendix 6.

There were no parent pesticide compound detections found for acetochlor or alachlor. Detections for their degradates were generally found in the southern two thirds of the state (Figure 4). Atrazine was the parent pesticide compound detected the most frequently. Four out of the seven detections were found in southeast Minnesota (Figure 5). Metolachlor degradates were detected the most out of any chemical tested (Table 1). Metolachlor degradates were detected mainly in the southern two thirds of the state (Figure 5). Metribuzin was not detected in any samples, however there was one detection of metribuzin DADK which occurred in the central part of the state (Figure 6).

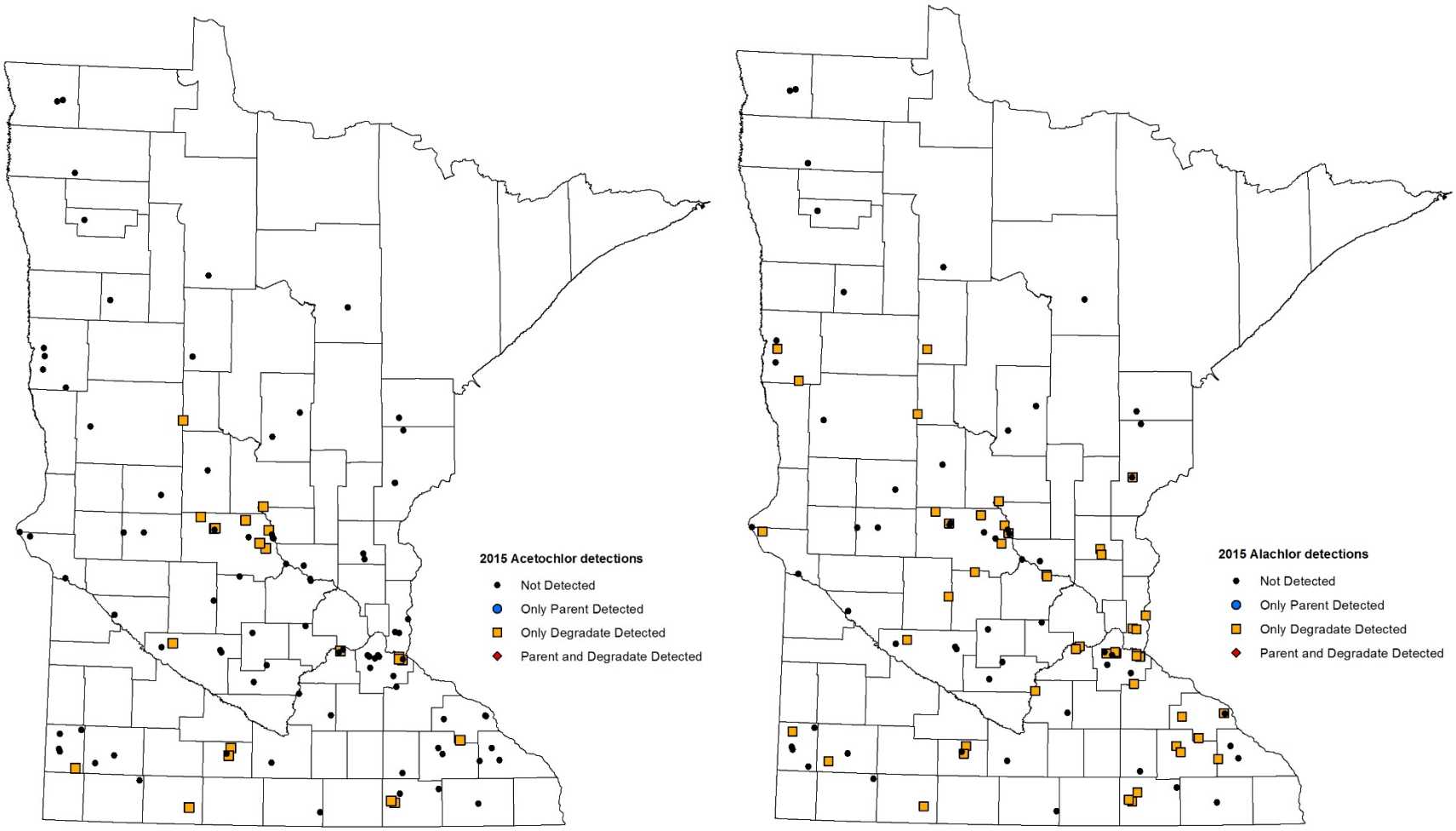

Figure 4. Statewide detections of acetochlor compounds (left) and alachlor compounds (right).

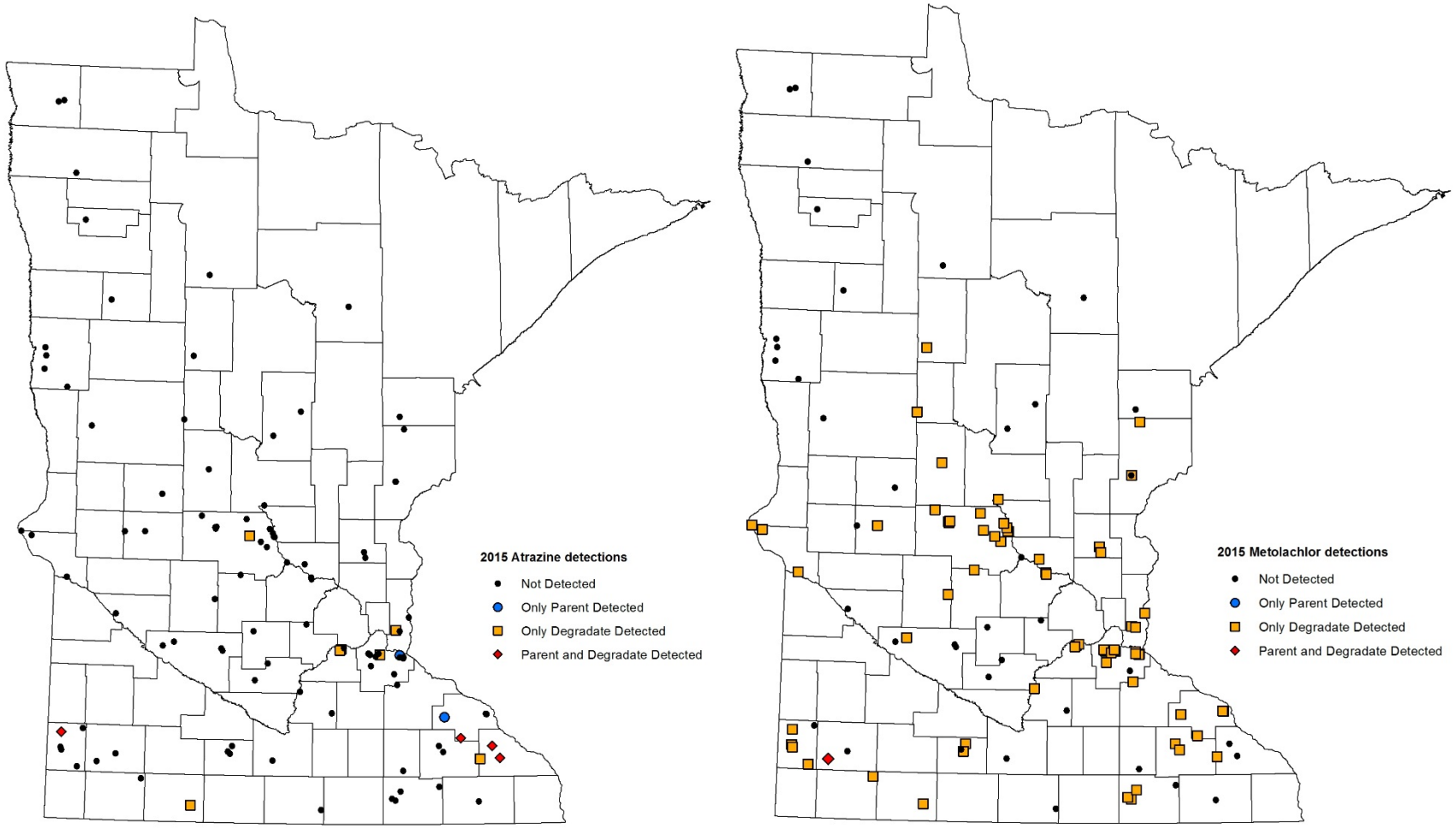

Figure 5. Statewide detections of atrazine compounds (left) and metolachlor compounds (right).

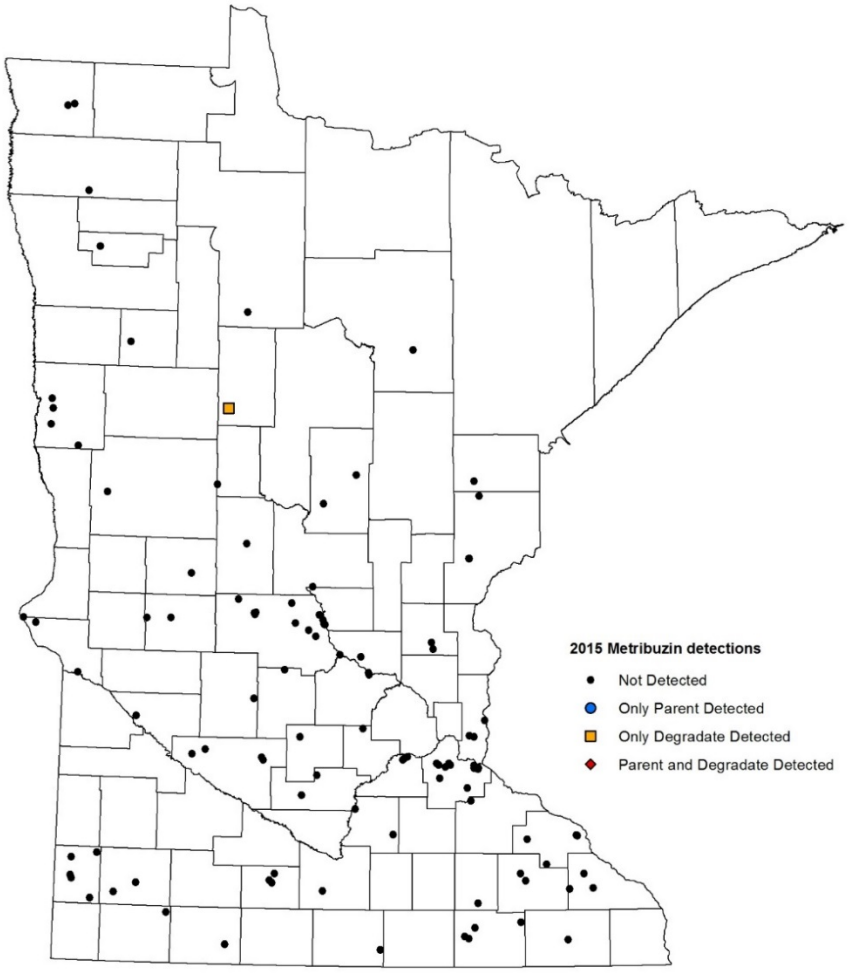

Figure 6. Statewide detections of metribuzin compounds.

A comparison was made between MDA's ambient groundwater monitoring well network results in 2015 and the results in the 2015 reconnaissance study, for metolachlor and degradates. MDA has developed regional water quality monitoring networks, known as Pesticide Monitoring Regions (PMRs) as indicated in Figure 7. The PMRs establish geographical areas for the purposes of collecting, assessing, and reporting monitoring data. Minnesota was divided into ten PMRs on the basis of agricultural practices and hydrologic/geologic characteristics. The PMRs follow county boundaries, but are intended to generally represent different hydrologic regions in Minnesota.

Figure 8 presents the median metolachlor and degradate concentrations for MDA's ambient monitoring well network with the results from the CPWS well sampling by PMR. The majority of PMRs indicate a higher median concentration in MDA monitoring well network (PMRs 1, 4, 5, 7, 8, and 9). This would generally be expected since MDA monitoring wells are typically located adjacent to agricultural fields and represent the upper portion (water table) of shallow aquifers. No MDA groundwater monitoring occurs in PMRs 2 and 3 due to relatively low use of agricultural chemicals in these heavily forested regions. PMR 6 had a higher median metolachlor and degradate concentration in the CPWS wells, as did PMR 10. PMR 10 had the greatest difference in concentration (CPWS wells with a 232 ng/L median concentration and MDA monitoring wells at 15 ng/L median concentration). MDA monitoring well network had a much larger median metolachlor and degradates concentration at PMRs 4, 5, 8 and 9 than the CPWS. None of the metolachlor and degradate concentration medians were above an applicable reference value.

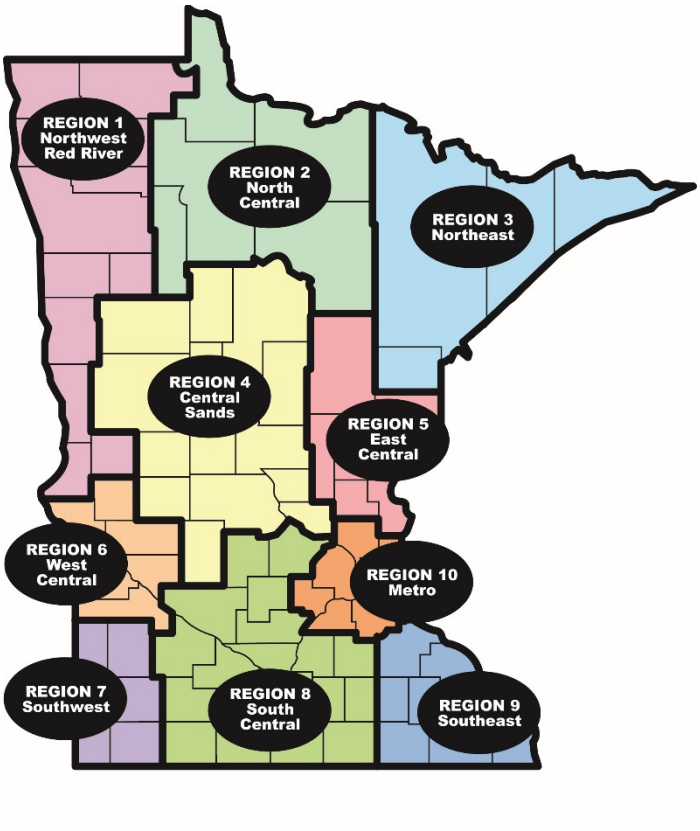

Figure 7. MDA's Pesticide Monitoring Regions (PMRs).

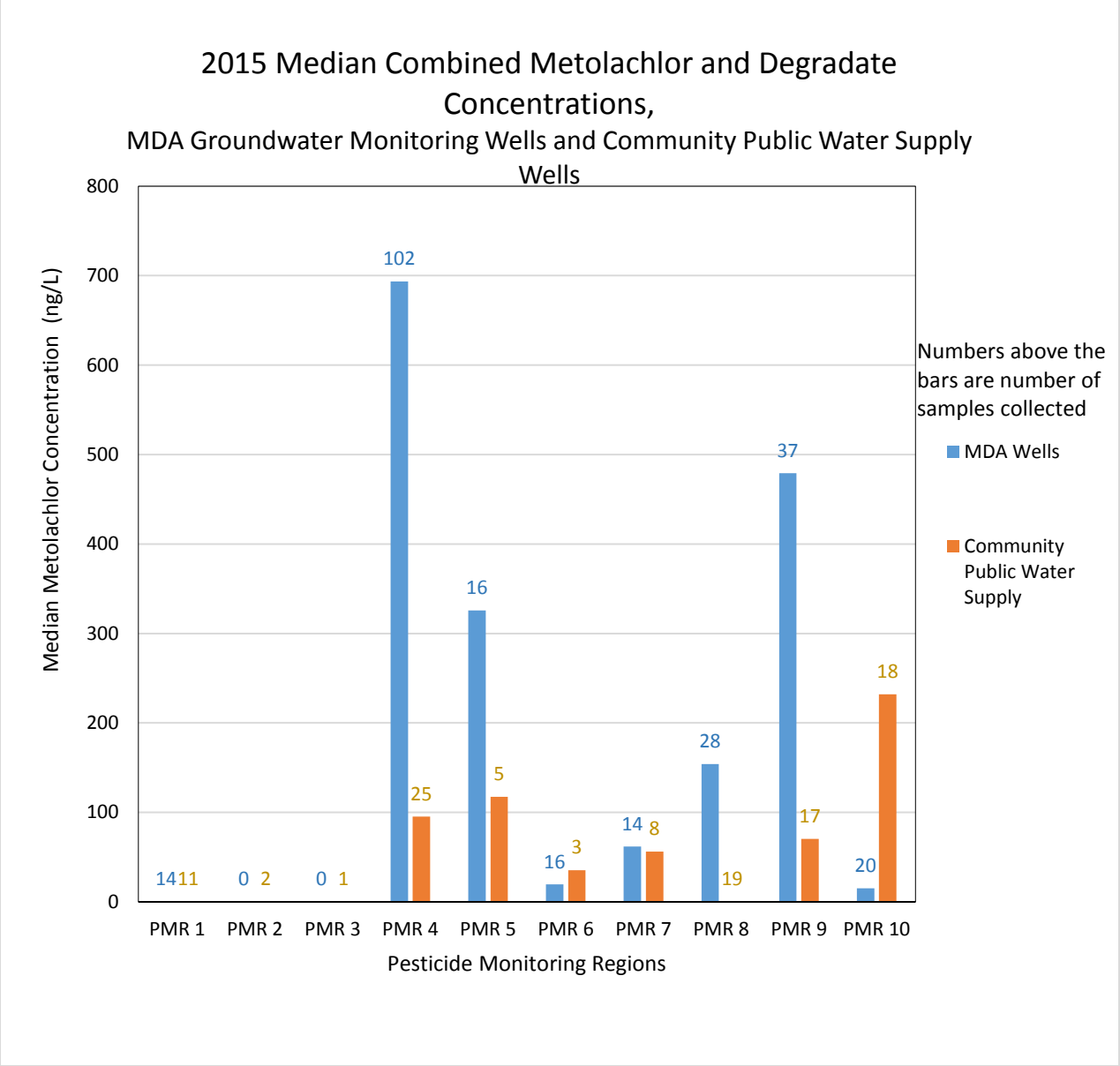

Figure 8. Comparison between 2015 CPWS results and MDA groundwater monitoring network results.

Comparison between 2010 and 2015 Pesticide Results

The first CPWS reconnaissance study evaluating pesticides occurred in 2010. At that time, the MDA Laboratory had a more limited analytical list consisting of 90 different pesticides and degradates. Also, there were only 83 wells sampled in 2010, as compared with 108 in 2015. These two studies were considered comparable, since many of the locations were sampled in both years. Eighty of the original 83 wells sampled in 2010 were resampled in 2015 as presented in Figure 9. Table 2 provides a comparison of summary statistics at the same sample locations for both 2010 and 2015. There were no pesticide detections above an applicable groundwater reference values in either the 2010 or the 2015 sampling results.

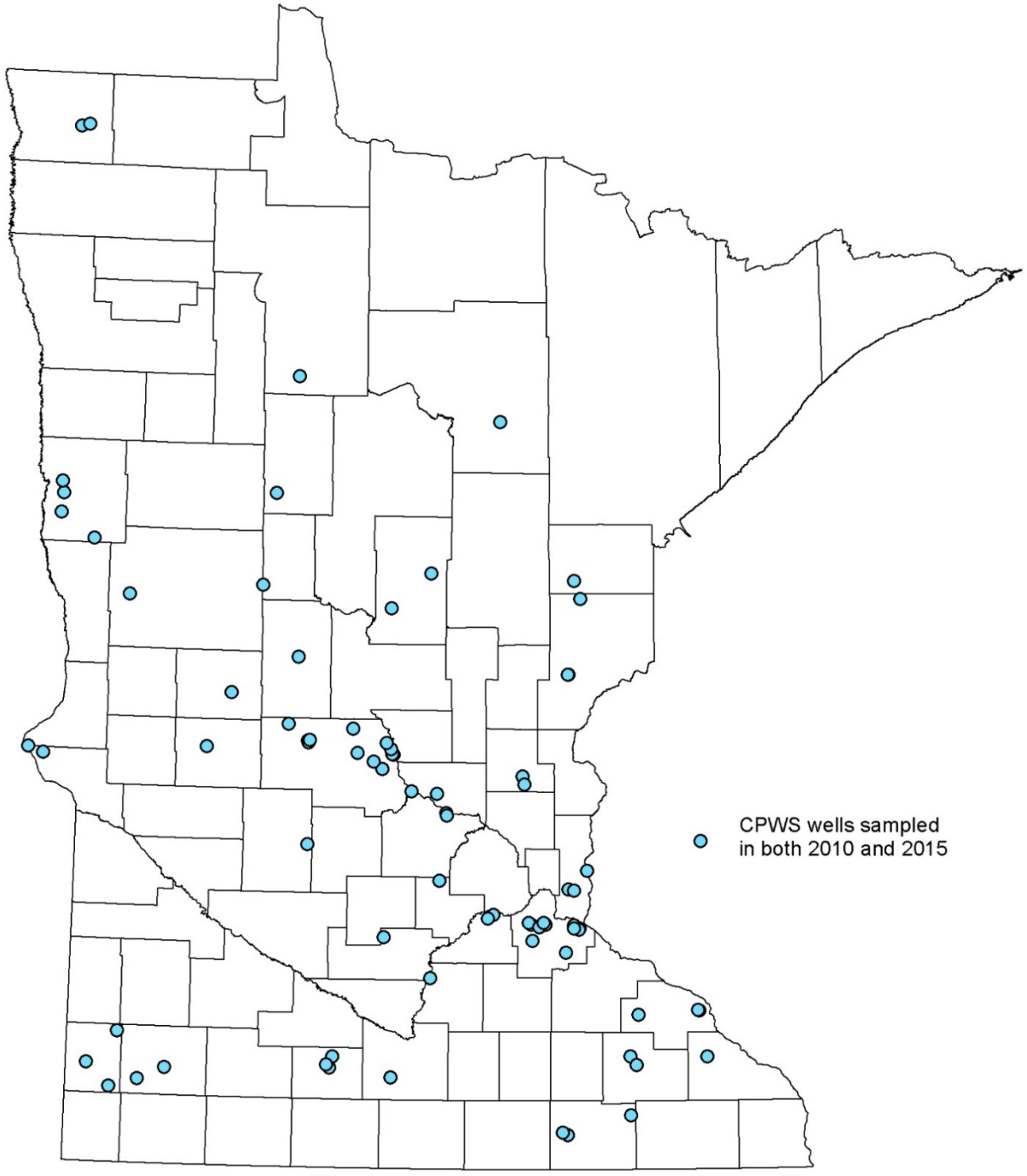

Figure 9. Location of CPWS wells sampled in 2010 and 2015.

Table 2. Summary of pesticide and pesticide degradate detections collected at the same CPWS location in 2010 and 2015.

Pesticide Analyte	2010 Detection Frequency (n=80)	2015 Detection Frequency (n=80)	2010 Median (ng/L)	2015 Median (ng/L)	2010 90th percentile (ng/L)	2015 90th percentile (ng/L)	2010 Maximum (ng/L)	2015 Maximum (ng/L)	Reference Value (ng/L)	Value Type†
2,4-D	1%	0%	nd	nd	nd	nd	**14.4**	nd	2,000	RA_{14}
Acetochlor ESA	19%	21%	nd	nd	**77.4**	**90.0**	**2,180**	**1,460**	300,000	HRL_{11}
Acetochlor OXA	5%	6%	nd	nd	nd	nd	**70.9**	**81.0**	100,000	HRL_{11}
Alachlor ESA	56%	49%	**53.5**	nd	**1,270**	**1,405**	**4,600**	**2,140**	50,000	RAA_{16}
Alachlor OXA	10%	13%	nd	nd	**3.60**	**35.1**	**187**	**111**	50,000	RAA_{16}
Atrazine	5%	4%	nd	nd	nd	nd	**90.0**	**81.0**	3,000	HRL_{MCL}
DACT Atrazine*	6%	na	nd	nd	nd	na	**104**	na	3,000	HRL
DEDI Atrazine*	na	5%	na	nd	na	nd	na	**82.6**	3,000**	Parent HRL_{MCL}
Desethylatrazine	5%	4%	nd	nd	nd	nd	**90.0**	**81.7**	3,000**	Parent HRL_{MCL}
Hydroxyatrazine	4%	1%	nd	nd	nd	nd	**7.84**	**10.5**	20,000	HBV_{05}
Bentazon	15%	8%	nd	nd	**1.18**	nd	**116**	**56.2**	30,000	HBV_{15}
Bromacil	0%	3%	nd	nd	nd	nd	nd	**76.2**	30,000	HBV_{14}
Dimethenamid ESA	3%	1%	nd	nd	nd	nd	**18.5**	**13.3**	300,000	RAA_{13}
Dimethenamid OXA	1%	0%	nd	nd	nd	nd	**14.9**	nd	300,000	RAA_{13}
Imazapyr	0%	1%	nd	nd	nd	nd	nd	**18.3**	900,000	RA_{14}
Metalaxyl	0%	1%	nd	nd	nd	nd	nd	**9.57**	20,000	RA_{14}
Metolachlor	1%	1%	nd	nd	nd	nd	**80.0**	**56.0**	300,000	HRL_{11}
Metolachlor ESA	70%	70%	**65**	**65.1**	**670**	**574**	**6,170**	**3,690**	800,000	HRL_{11}
Metolachlor OXA	38%	38%	nd	nd	**91.0**	**147**	**2,120**	**996**	800,000	HRL_{11}
Metribuzin DADK	0%	1%	nd	nd	nd	nd	nd	**607**	10,000	RAA_{12}
Picloram	1%	0%	nd	nd	nd	nd	**155**	nd	300,000	RA_{14}

nd = not detected, na = not applicable

† Reference value type information is found in Appendix 2.

* DACT and DEDI are the same compound. However, DACT was run via immunoassay in 2010 due to the compound not available for analysis through the MDA Laboratory at that time.

** In the absence of compound-specific toxicological information for pesticide degradates, MDH conservatively assumes by default that a pesticide degradate has the same toxicological effect as the pesticide parent compound and is as potent.

The comparison of the 2010 and 2015 CPWS well results presented in Table 2 indicates the three most frequently detected chemicals in 2010 were the same in 2015, metolachlor ESA at 70 percent in 2010, and 70 percent in 2015, alachlor ESA at 56 percent in 2010, and 49 percent in 2015, and metolachlor OXA at 38 percent in both years. Twenty-one pesticide compounds chemicals were detected between the two different years, which was 16 percent of the total 2015 list of pesticides tested. The only chemical to have a median concentration above non-detect in both 2010 and 2015 was metolachlor ESA (65 ng/L in 2010 and 65.1 ng/L in 2015).

Detection Maps

Figures 10 through 15 compare statewide detection patterns for the common detection pesticides between 2010 and 2015 for wells that were sampled during both time periods.

The figures indicate if concentrations were increasing or decreasing and the relative magnitude of the change. Maps for the non-common detection chemicals with detections can be found in Appendix 7.

Results for the common detection chemical acetochlor degradates ESA and OXA are presented in Figure 10. There were both increases and decreases in concentrations for both chemicals from 2010 to 2015. Acetochlor ESA had decreases up to 105 ng/L and increases up to 60 ng/L. Acetochlor OXA had a lower margin of change, with decreases up to 30 ng/L and increases up to 60 ng/L. These results were a very small percentage of the reference value (300,000 ng/L for acetochlor ESA and 100,000 ng/L for acetochlor OXA, Table 2). Stearns County showed the most decreases in acetochlor ESA between 2010 and 2015.

Figure 11 shows the results for both alachlor ESA and alachlor OXA. The difference between sample results with alachlor ESA ranged from a maximum decrease of 810 ng/L to a maximum increase of 320 ng/L. The difference between sample results for alachlor OXA ranged from a maximum decrease of 76 ng/L to a maximum increase of 21 ng/L. These increases or decreases were a small fraction of the reference value of 70,000 ng/L for both alachlor ESA and OXA (Table 2). The majority of the decreases between sample points were in alachlor ESA and located in central Minnesota and the Twin Cities metropolitan area. The highest increases were also found in the Twin Cities metropolitan area.

Figures 12 and Figure 13 show results for atrazine and two degradates. There was a small increase in atrazine concentration at one location in 2015 (20 ng/L) and two locations with a decrease in concentration (20 ng/L). Desethylatrazine results were similar, with two locations small increases in concentrations from 2010 to 2015 (35 ng/L) and three locations with small decreases (35 ng/L). The degradate hydroxyatrazine had the smallest change in concentration between the two years (either a 5 ng/L increase or decrease). The majority of results for atrazine and two degradates were non-detect in both 2010 and 2015.

Figures 14 and 15 depict results for metolachlor and its degradates. There was only one location with the parent metolachlor detected and that was a decrease in concentration between 2010 and 2015. Metolachlor ESA had that largest increases and decreases in the comparison of results between 2010 and 2015. The difference between sample results for metolachlor ESA ranged from a maximum decrease of 400 ng/L to a maximum increase of 600 ng/L. The difference between sample results for metolachlor OXA ranged from a maximum decrease of 200 ng/L to a maximum increase of 360 ng/L.

These increases or decreases were a small fraction of the reference value of 800,000 ng/L for both metolachlor ESA and OXA (Table 2). There was no general pattern in where the increases or decreases were found around the state for either metolachlor ESA or OXA.

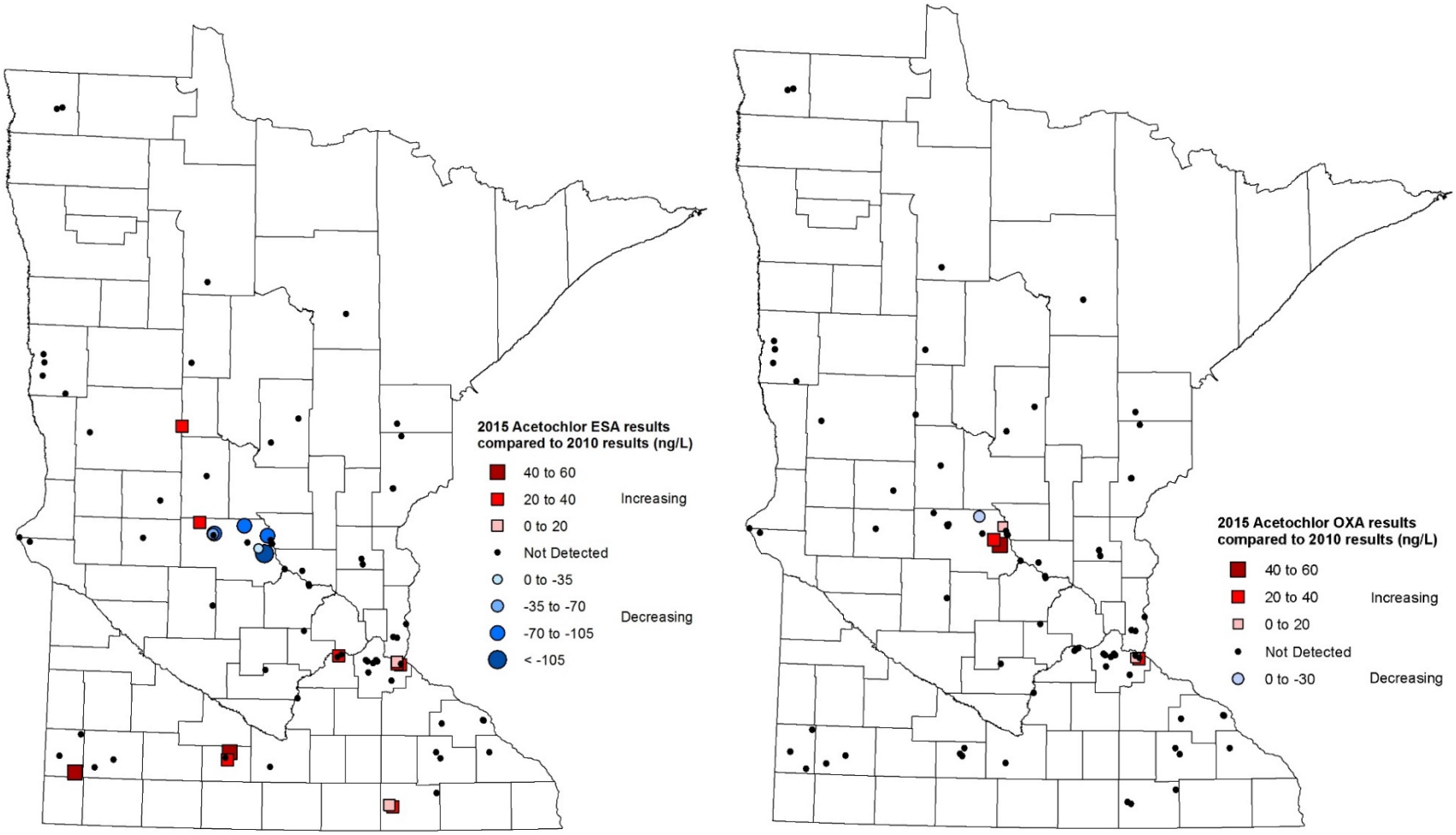

Figure 10. 2015 detections of acetochlor ESA and acetochlor OXA results compared with 2010 detections.

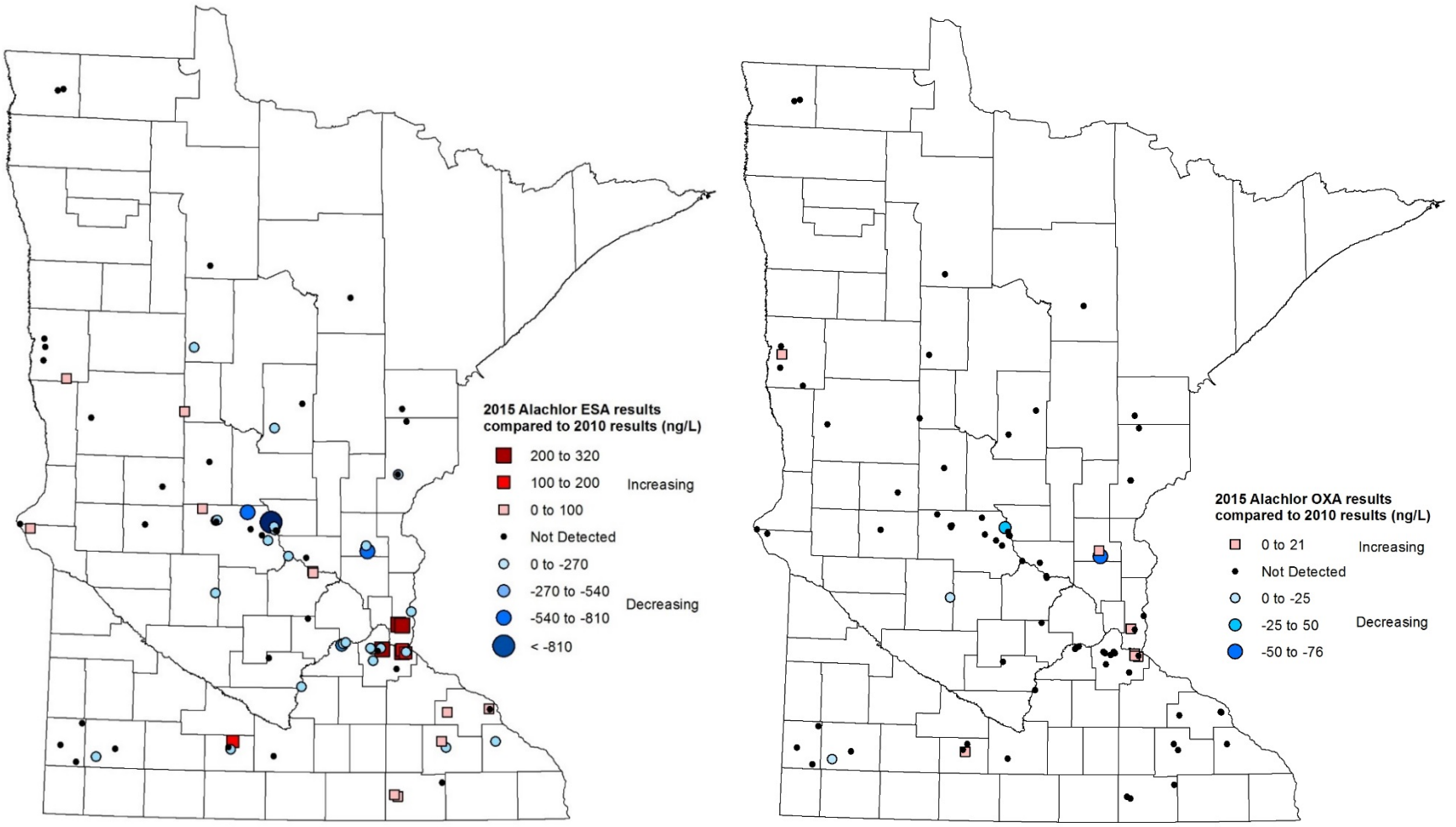

Figure 11. 2015 detections of alachlor ESA and alachlor OXA results compared with 2010 detections.

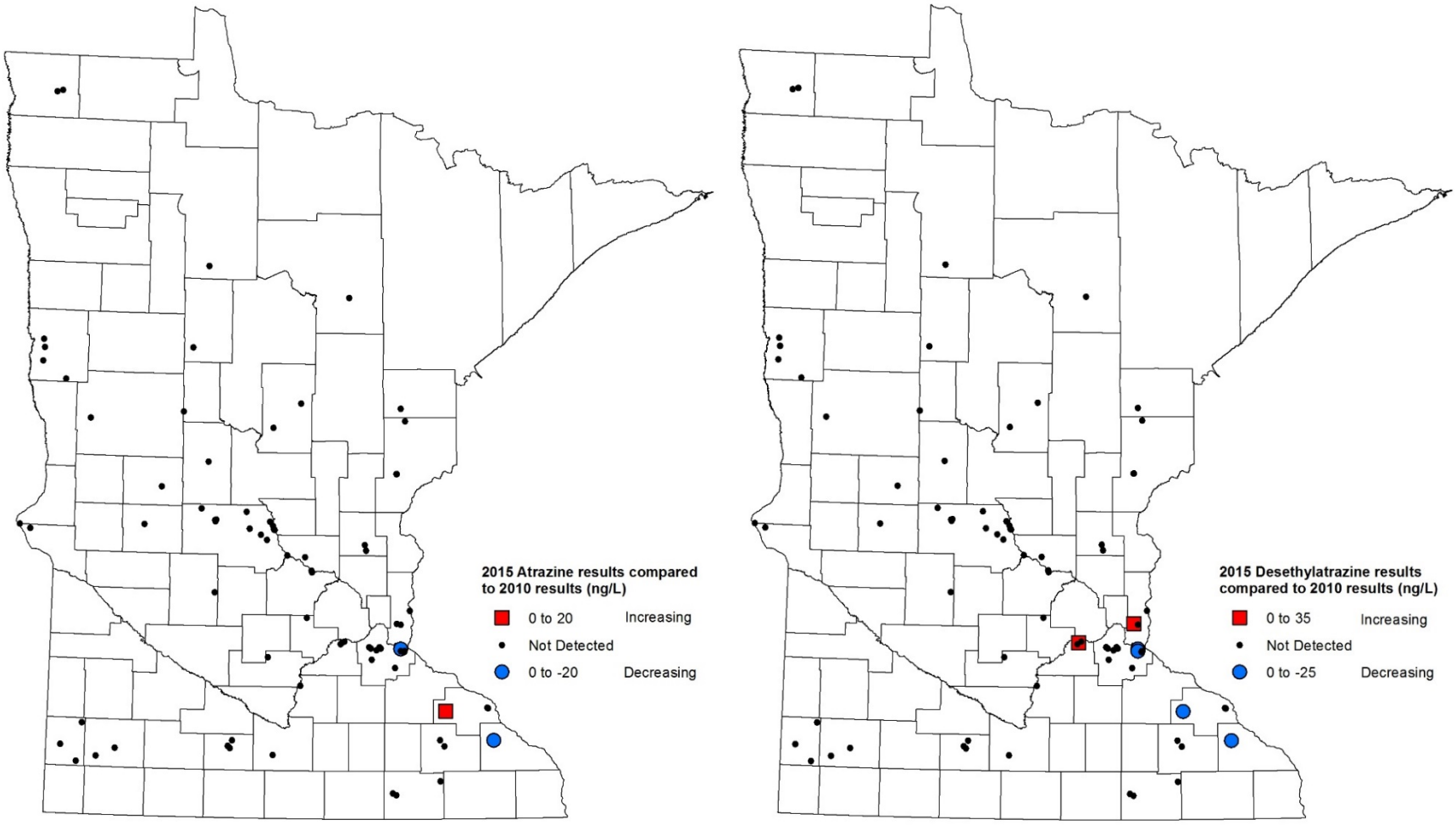

Figure 12. 2015 detections of atrazine and desethylatrazine results compared with 2010 detections.

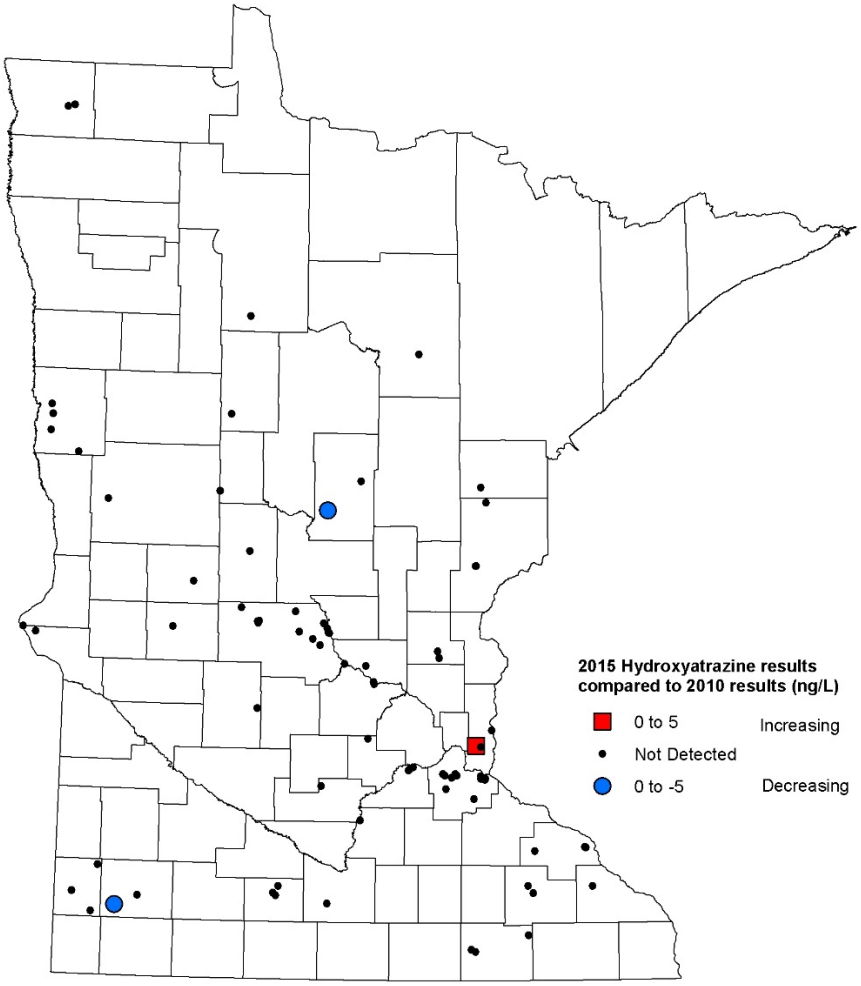

Figure 13. 2015 detections of hydroxyatrazine results compared with 2010 detections.

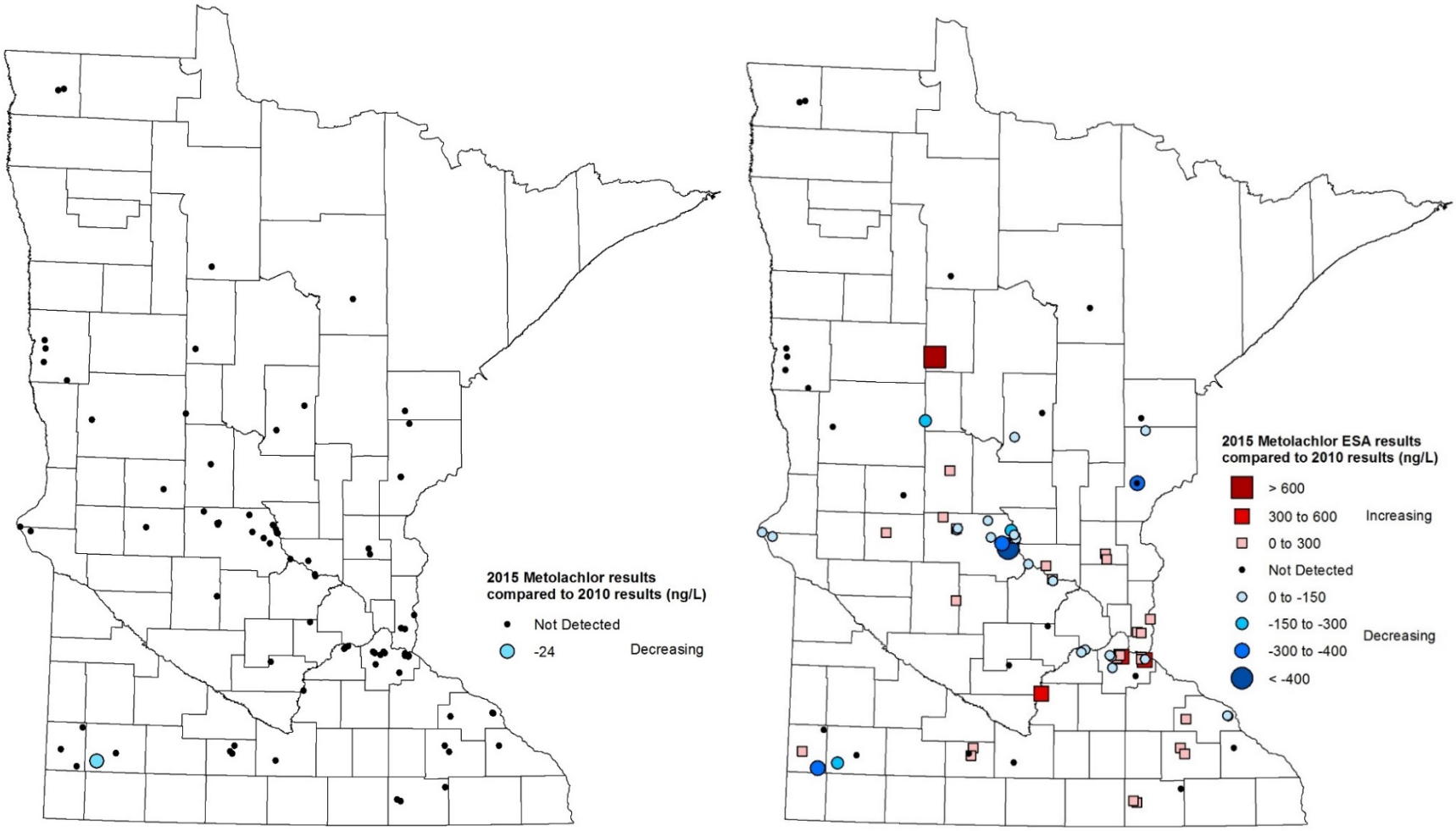

Figure 14. 2015 detections of metolachlor and metolachlor ESA results compared with 2010 detections.

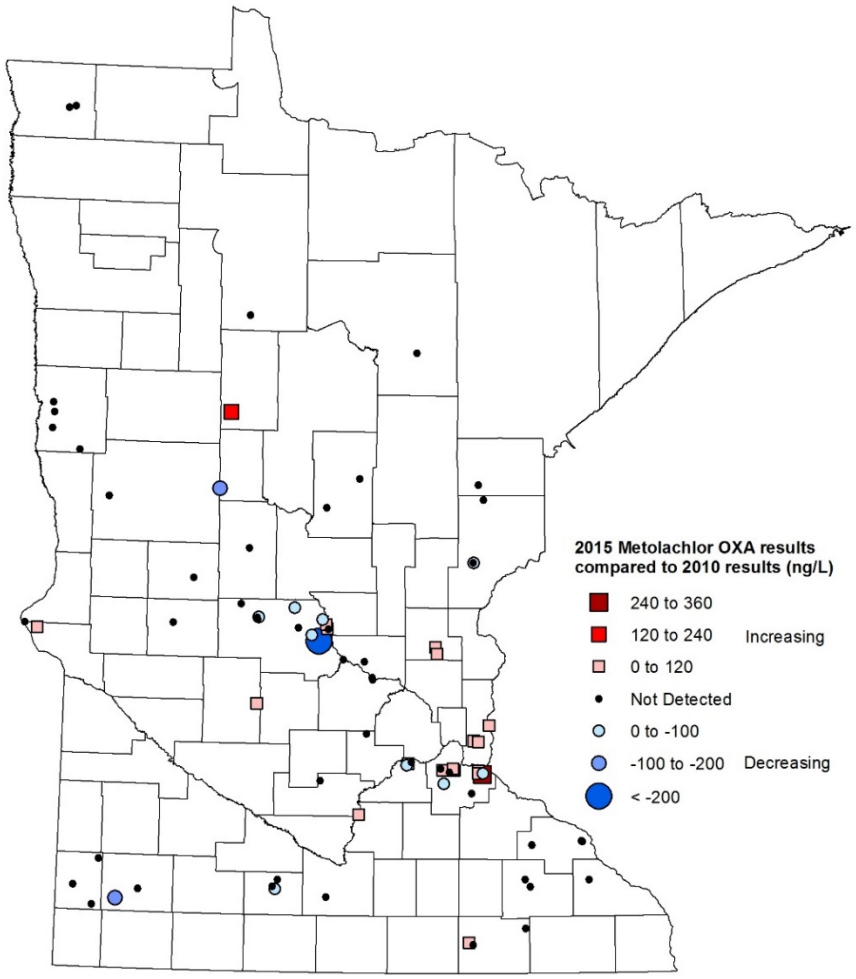

Figure 15. 2015 detections of metolachlor OXA.

Inorganic Compounds

Chloride/Bromide

Analysis performed by MDH PHL in 2015 indicated that none of the wells sampled contained chloride or bromide in excess of either USEPA primary or secondary drinking water standards. The mass ratio of chloride to bromide has previously been shown to predict the presence of total coliform bacteria in drinking water wells (MDH, 2012). Thus, it may be a good indicator of vulnerable hydrologic settings. This interpretation suggests that surface contaminants such as pesticides and pesticide degradates in source groundwater would be expected to co-occur where the chloride-bromide mass ratio was higher than values normally occurring in rain. Figures 16 and 17 depict the results of the chloride/bromide ratio from the CPWS study in 2010 and 2015.

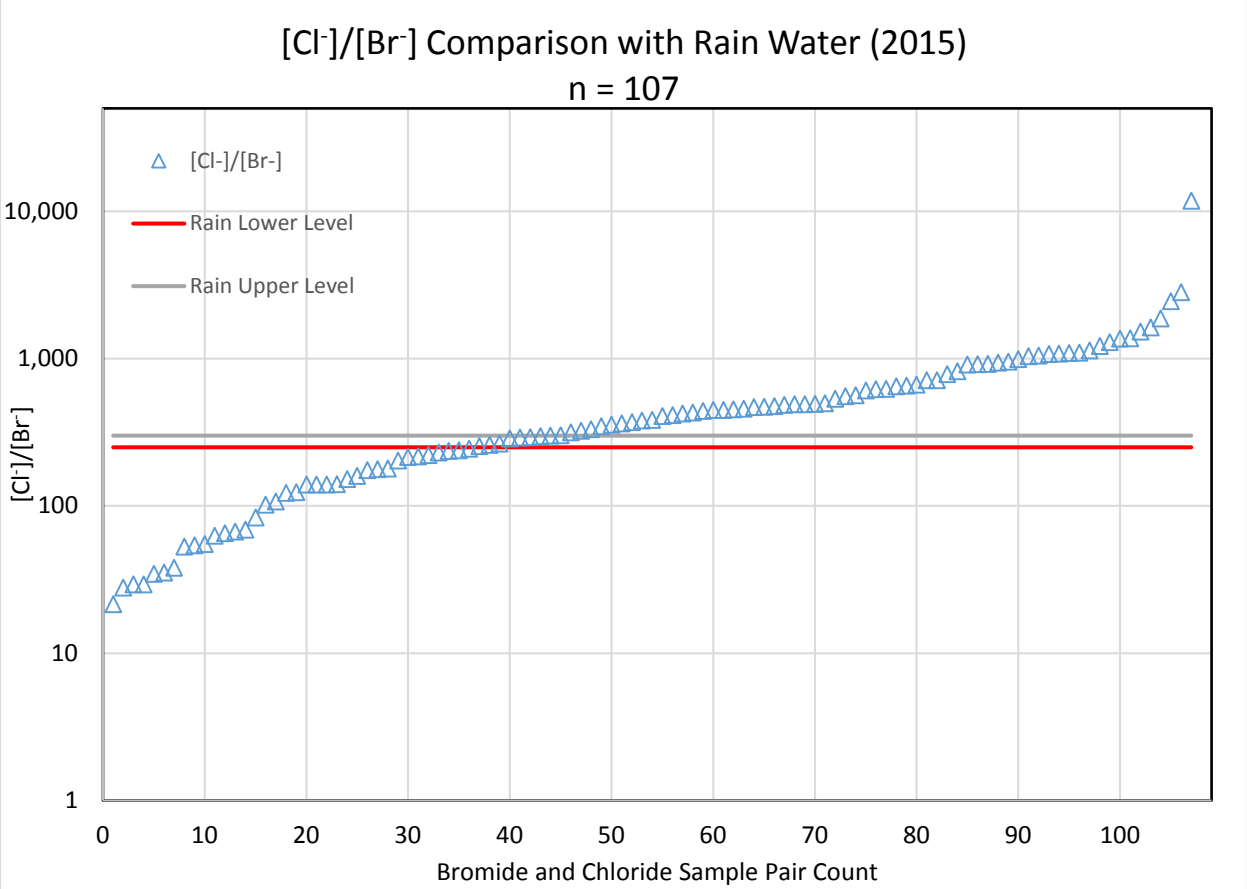

Figure 16. 2015 chloride and bromide results ratio in comparison with rain water.

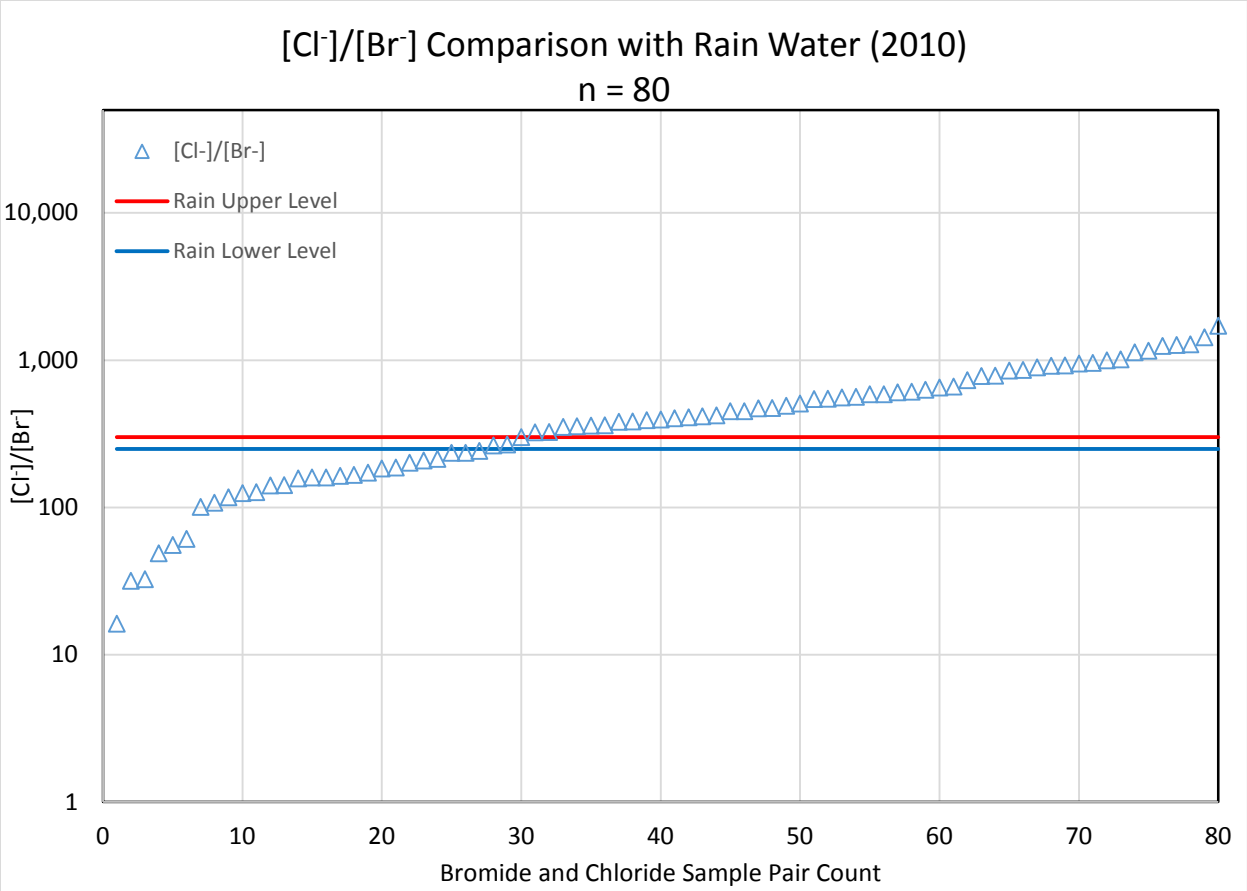

Figure 17. 2010 chloride and bromide results ratio in comparison with rain water.

A complete range of chloride to bromide concentration ratios ($[Cl^-]/[Br^-]$) at surveyed wells was plotted in comparison to the expected upper and lower limits of expected rainfall $[Cl^-]/[Br^-]$ values in 2015 and 2010 (Figures 16 and 17). In both studies a larger fraction of the CPWS wells had $[Cl^-]/[Br^-]$ values higher than the rainfall lower limit (250). The wells having $[Cl^-]/[Br^-]$ values above the rainfall upper limit (300) are generally more affected by surface contaminants. Table 3 shows the summary statistics in $[Cl^-]/[Br^-]$ ratios where pesticides were and were not detected in 2015. In general, $[Cl^-]/[Br^-]$ ratios were higher in wells with pesticide detections.

Table 3. 2015 comparison of chloride to bromide concentration ratios to pesticide detections.

	Pesticides Detected with Chloride and Bromide Results	No Pesticides Detected with Chloride and Bromide Results
Total Samples	72	35
Number of Pesticide Detections in 108 samples	236	0
Maximum $[Cl^-]/[Br^-]$	11,760	2,445
90^{th} Percentile $[Cl^-]/[Br^-]$	1,270	449
Mean $[Cl^-]/[Br^-]$	811	241
Median $[Cl^-]/[Br^-]$	490	122

*Non-detects were assigned detection level concentrations of 0.0050 mg/L bromide and/or 0.500 mg/L chloride for data calculation purposes (Appendix 5).

Nitrate

Every CPWS that was sampled had a nitrate-nitrogen analysis performed. Figure 18 and Figure 19 presents the locations and associated sample concentration of nitrate samples collected in 2015 and 2010, respectively.

Nitrate presence in groundwater samples may indicate impacts from land use and vulnerability caused by human activities. Samples collected at reconnaissance study sites in both 2015 and 2010 were analyzed for the sum of nitrate and nitrite nitrogen. Figures 20 and 21 show results from 2015 and 2010, respectively, in comparison to MCL and half-MCL levels.

Generally, MDH considers nitrate concentrations less than 1.0 mg/L as representing natural background levels (MDH, 1998). Nitrate concentrations of between 1.0 and 3.0 mg/L are viewed as transitional concentrations that may or may not represent anthropogenic influences, while concentrations of 3.0 mg/L and greater are elevated concentrations indicative of human activities. More than one-third of wells sampled in the 2010 and 2015 studies (41 and 35 percent, respectively) had nitrate plus nitrite results of at least 1.0 mg/L, while roughly one-fifth of wells (24 and 19 percent, respectively) were at or above 3.0 mg/L during the reconnaissance study periods.

Summary statistics indicate mean nitrate levels were greater than natural background at wells where pesticides were detected. In summary, nitrate concentrations were generally higher in water from wells with pesticide detections compared to those without pesticide detections (Table 4).

Table 4. 2015 Comparison of nitrate plus nitrite concentrations to pesticide detections.

	Pesticides Detected Nitrate plus Nitrite Results	No Pesticides Detected Nitrate plus Nitrite Results
Total Samples	72	36
Total Pesticide Detections	236	0
Maximum nitrate + nitrite	18.10 mg/L	2.08 mg/L
90^{th} Percentile nitrate + nitrite	5.88 mg/L	0.44 mg/L
Mean nitrate + nitrite	2.38 mg/L	0.47 mg/L
Median nitrate + nitrite	0.99 mg/L	0.40 mg/L

*Non-detects for nitrate –N were assigned the detection level of 0.04 mg/L for data calculation purposes (Appendix 4).

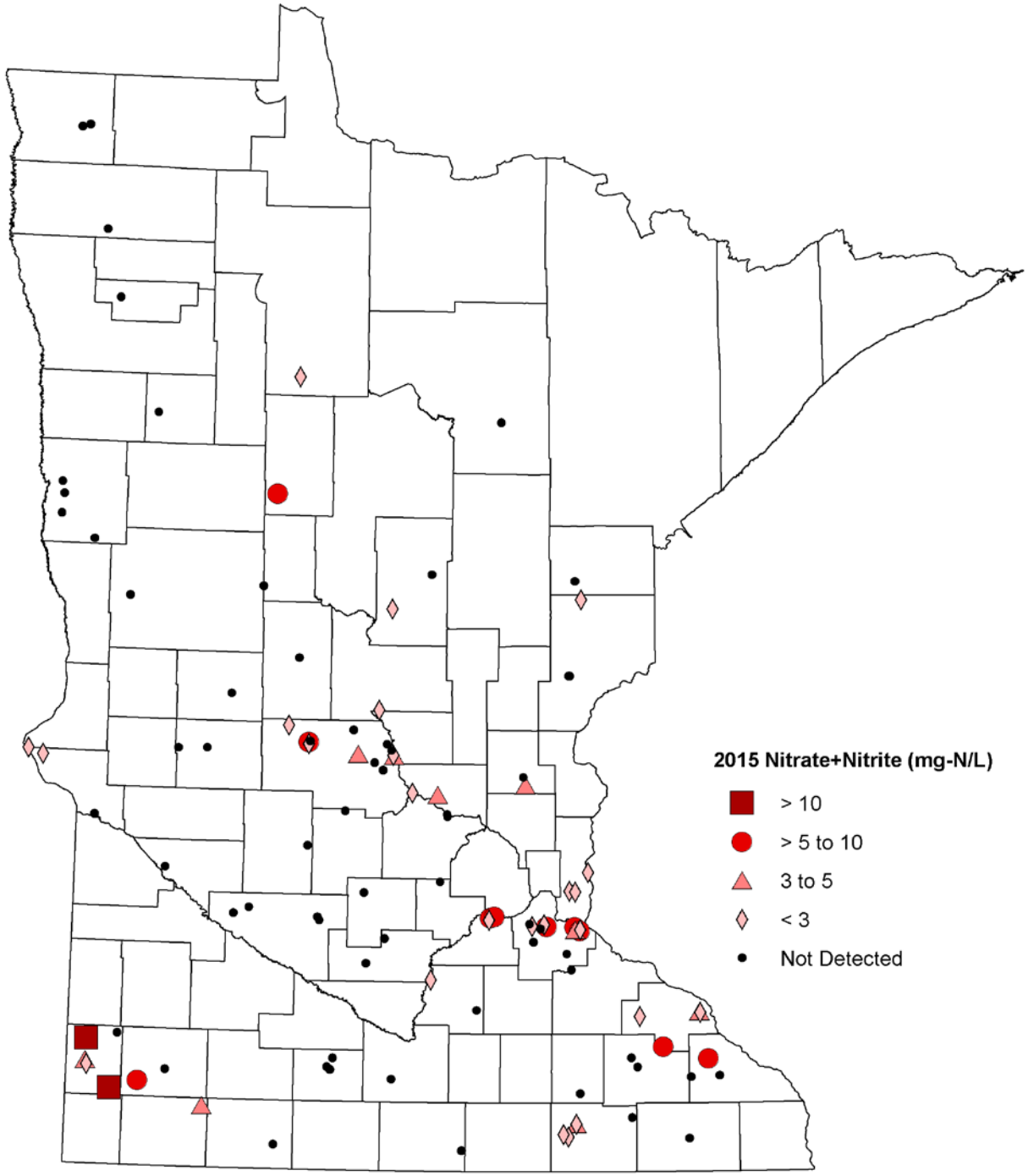

Figure 18. 2015 nitrate plus nitrite results.

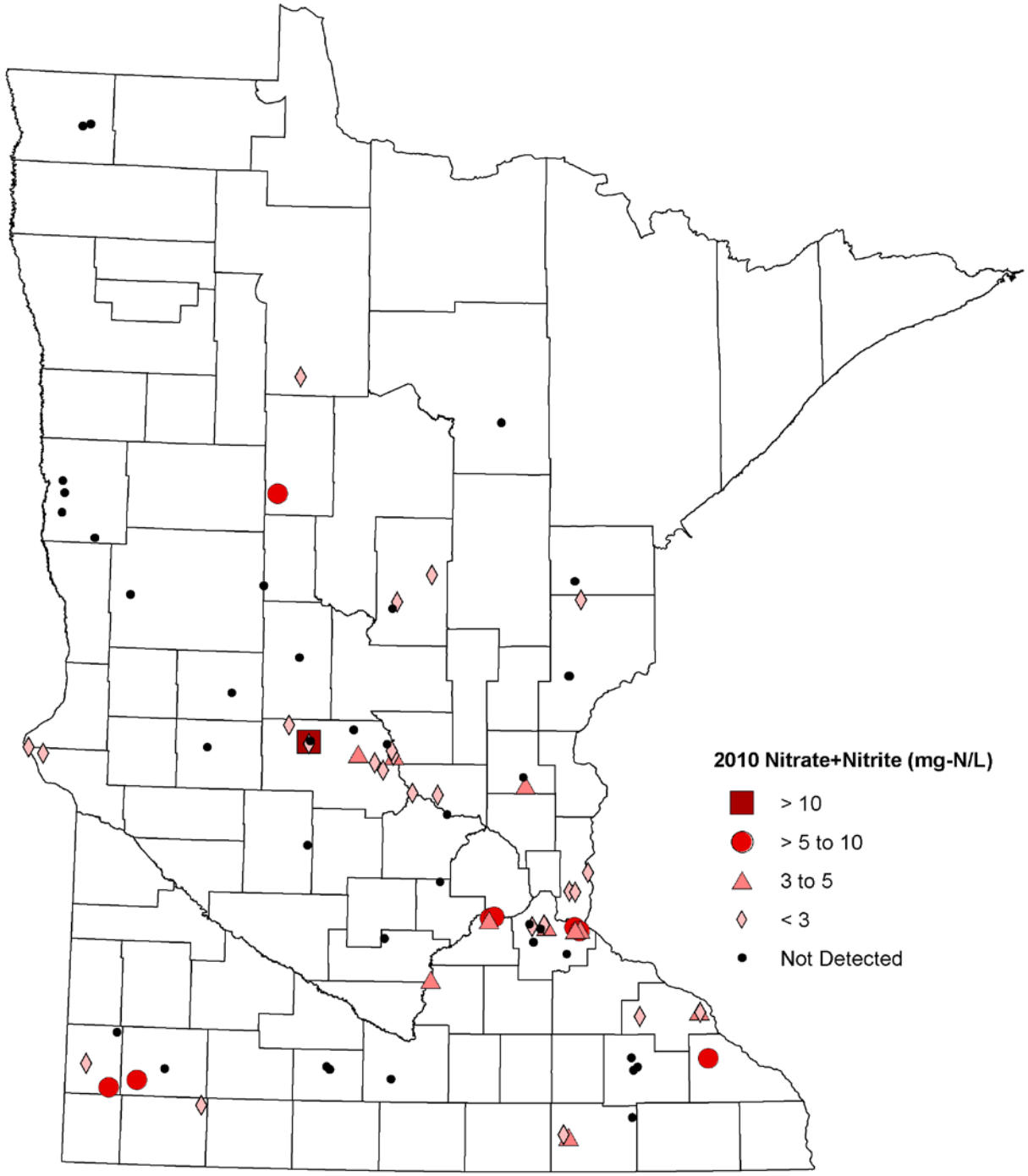

Figure 19. 2010 nitrate plus nitrite results.

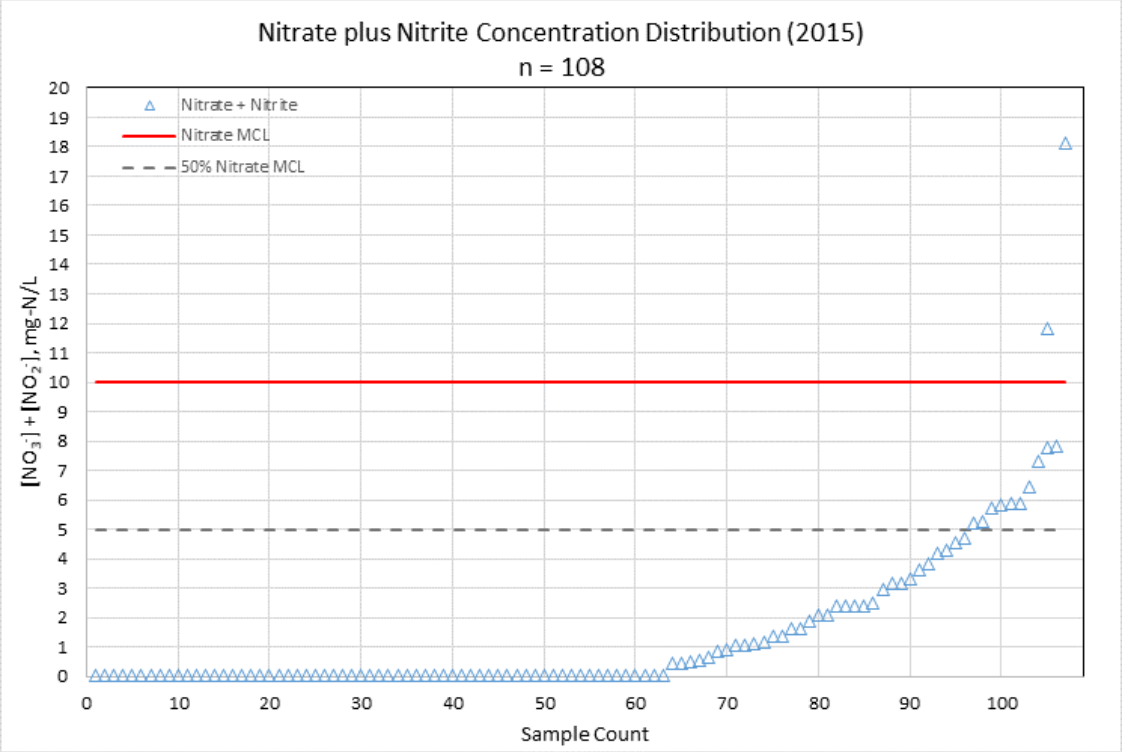

Figure 20. 2015 nitrate plus nitrite concentration distribution.

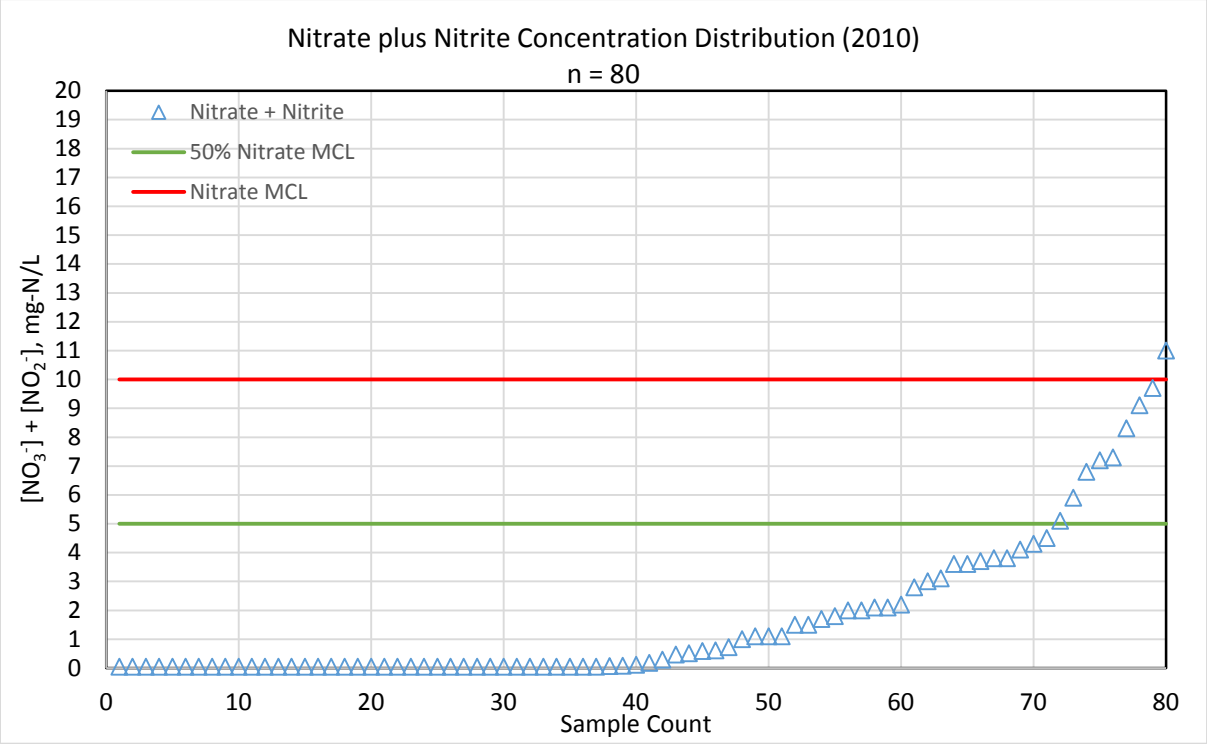

Figure 21. 2010 nitrate plus nitrite concentration distribution.

Co-Occurrence

Nitrate and Pesticide Co-Occurrence

Elevated nitrate in groundwater may sometimes be an indicator of the presence of other contamination caused by human activities. Previous work conducted by MDA has indicated there is often a correlation between nitrate concentration and pesticide presence and concentration in agricultural areas. A report published by MDA titled "Analysis of the Co-occurrence of Nitrate-Nitrogen and Pesticides in Minnesota Groundwater" (MDA, 2006) evaluated this relationship in MDA's groundwater monitoring data. A similar analysis evaluating the relationship between nitrate concentration ranges and pesticide detection probability is depicted in Figure 22 for the 2010 and 2015 CPWS data.

Nitrate concentrations were generally higher for wells with pesticide detections compared to those without pesticide detections (Table 4). Summary statistics indicate mean nitrate levels were greater than natural background at wells where this reconnaissance study found pesticides. It was also found that total pesticide concentrations and the number of pesticides detected generally increased as nitrate concentrations increased (Figures 23 and 24, respectively). However the relationship was not consistent and some wells with low or no nitrate indicated elevated pesticides and some wells with high nitrate had relatively low pesticide concentrations.

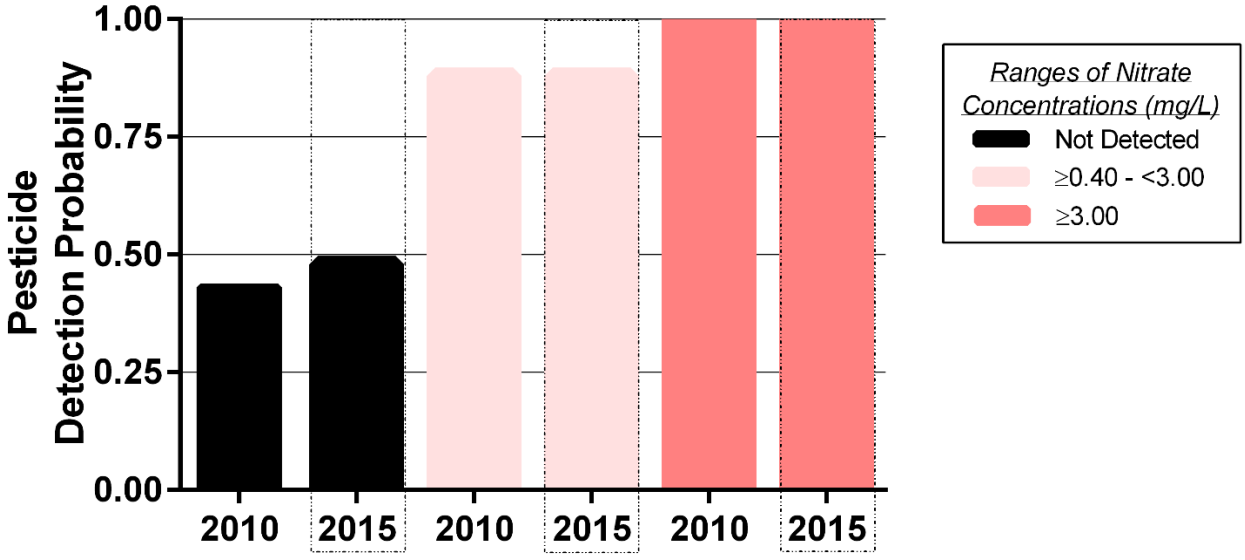

Figure 22. 2010 and 2015 pesticide detection probability based on nitrate concentration ranges.

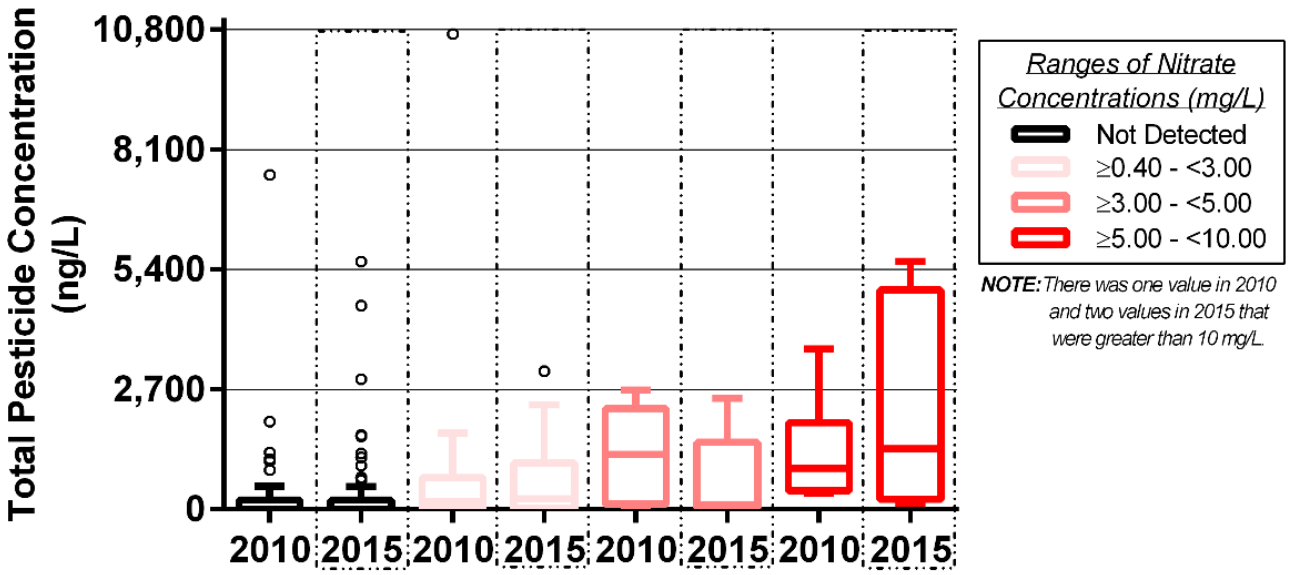

Figure 23. 2010 and 2015 total pesticide concentrations based on nitrate concentration ranges.

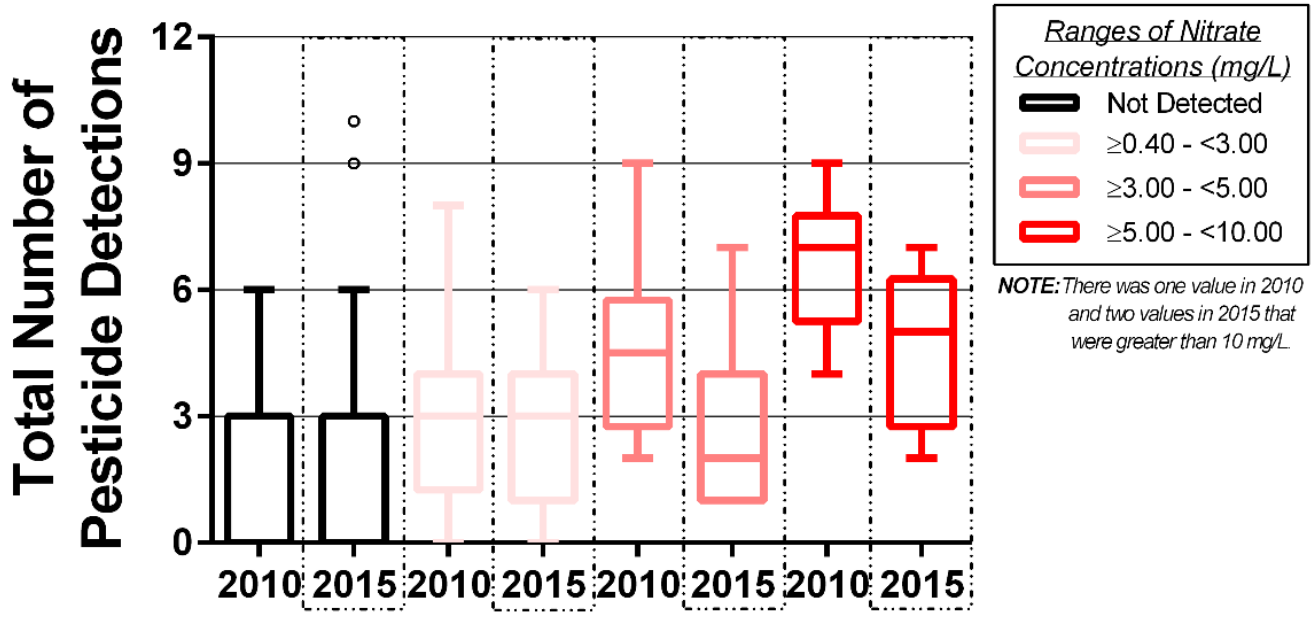

Figure 24. 2010 and 2015 total number of pesticide detections based on nitrate concentration ranges.

Summary

This report presents the results of a cooperative project between MDA and MDH to conduct a second reconnaissance study of CPWS wells for pesticide and pesticide degradate compounds, as well as the select inorganic compounds of nitrate as nitrogen (nitrate-N), chloride and bromide.

In summary, these are the main conclusions from the reconnaissance study:

- Pesticides were detected at low levels in 72 out of 108 samples resulting in an overall pesticide detection frequency of approximately 67 percent.
- A total of 19 (out of 135 possible) different pesticides and/or pesticide degradates were detected in the 2015 study.
- All detections were well below MDH or EPA established standards or established health reference values.
- Metolachlor ESA was the most frequently detected compound and was found in 63 percent of the sample wells sampled.
- The study results showed no known public health risks from pesticides in Minnesota CPWS wells sampled.
- No neonicotinoid pesticides were detected in the sample wells.
- Eighty wells that were sampled both in 2010 and 2015 were compared and overall detection frequency was similar. Only alachlor and bentazon showed a greater than five percent decrease in detection frequency between 2010 and 2015.
- In general, chloride/bromide ratios were higher in wells with pesticide detections.
- Pesticide and nitrate co-occurrence was briefly examined in this report. Generally, when nitrate was detected in a well, the probability of detecting pesticides at that same location was greater.
- MDH conducted a cumulative assessment of the chemicals detected in the CPWS samples and found that the concentrations do not pose a health risk of concern when combining chemicals that have a common health endpoint and common duration period.

Future Work

MDH intends to further evaluate the data to determine if the data set will be useful in comparing contaminant levels in wells from vulnerable areas to wells in non-vulnerable areas. Vulnerability assessments are conducted by MDH and communities in order to identify opportunities to protect the community source of drinking water from contamination. This analysis has not been completed at the time this report was published.

Future monitoring of these systems for pesticides is recommended to evaluate the occurrence of pesticides and pesticide degradates in CPWS wells over time. Further ideas to expand the study include using a randomized well selection approach which would allow for more representative data and sampling from selected surface water systems.

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Minnesota Department of Health, Groundwater Virus Monitoring Study accessed on-line on 1/6/2016 http://www.health.state.mn.us/divs/eh/water/dwp_cwl/virus/index.html (accessed January 6, 2016)

Appendix

Appendix 1: Definitions and acronyms

Chronic Standard, Criterion, or Advisory Value
The highest water concentration of a chemical to which organisms can be exposed without causing chronic toxicity. It is established for an individual chemical based on toxicity to aquatic life ("toxicity-based") or toxicity to human life ("human health-based") when sufficient information exists to establish one or both of these numbers. The more stringent of the two numbers is used as the chronic standard, criterion or advisory value for purposes of implementation of Minnesota Rules Chapter 7050 ("Waters of the State"). The underlying exposure assumptions (e.g., timeframes for exposure comparisons) and applicability of any numbers are established by the Minnesota Pollution Control Agency (MPCA) and may vary depending on the state classification of the water body, the nature of the data comparisons being made, and the regulatory status of the number being used for comparison.

Health Based Value (HBV)
Identical to a Health Risk Limit (HRL) except the value is issued on an interim basis for specific situations and until such time that the basis of its derivation and calculation are reviewed and subject to rule-making.

Health Risk Limit (HRL)
The concentration of a substance or chemical (i.e., one that has been determined to be a potential private well drinking water contaminant) in drinking water that can produce a potential toxicological result due to systemic or carcinogenic effect in humans upon consumption. The underlying exposure assumptions (e.g., volume of water consumed and timeframes for exposure comparisons) and the general applicability of any HRL are established for Minnesota by MDH and adopted by rule of the MDH Commissioner.

Maximum Contaminant Level (MCL)
The highest level of a contaminant that is allowed in CPWS drinking water. This value is established by the U.S. Environmental Protection Agency (EPA) considering health risks and best available treatment technology while taking cost into consideration.

Method Reporting Limit (MRL)
Represents the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory.

Rapid assessment (RA)
Rapid Assessment (chronic), a non-promulgated value established by MDH in the year indicated.

Risk assessment advice (RAA)
Technical guidance concerning exposures and risks to human health. This may be quantitative or qualitative. A RAA generally contains greater uncertainty than a HBV or HRL because available information is more limited.

ABBREVIATIONS

AMPA	aminomethylphosphonic acid
CPWS	Community Public Water System
GC-MS/MS	Gas Chromatography with tandem Mass Spectrometry
HA	Health Advisory
HBV	Health Based Value
HRL	Health Risk Limit
LC-MS/MS	Liquid Chromatography with tandem Mass Spectrometry
MCL	Maximum Contaminant Level
MDA	Minnesota Department of Agriculture
MDA Laboratory	MDA Laboratory Services
MDH	Minnesota Department of Health
MN DNR	Minnesota Department of Natural Resources
MPCA	Minnesota Pollution Control Agency
MRL	Method Reporting Limit
na	Not applicable
nd	Not detected
ng/L	Nanograms per liter (equivalent to one parts per trillion or ppt)
OW	Office of Waters (USEPA)
ppt	parts per trillion (equivalent to nanograms of chemical per liter of water sample or ng/L)
PMR	Pesticide Monitoring Region
PHL	Minnesota Public Health Laboratory
PWS	Public Water System
RAA	Risk Assessment Advice
RA	Rapid Assessment

SDWA	Safe Drinking Water Act
USEPA	United States Environmental Protection Agency

Appendix 2: 2015 MDA pesticide analyte list and reference values.

Key to value types and symbols in groundwater reference values

The values selected were discussed MDH while preparing this report, and appropriate human health-based groundwater reference may change pending MDH evaluation of toxicity information.

Human health-based groundwater reference values:

HBV – Health Based Value (chronic), a non-promulgated value established by MDH in the year indicated.

HRL – Health Risk Limit (chronic) promulgated by MDH in the year indicated or set in 2007 to the United States Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) as required by state law.

MCL – Maximum Contaminant Level, established by USEPA for the regulation of public water supplies. If available, used in the absence of an HRL, HBV, RAA or RA.

RA – Rapid Assessment (chronic), a non-promulgated value established by MDH in the year indicated.

RAA – Risk Assessment Advice (chronic), a non-promulgated value established by MDH in the year indicated.

In keeping with the Minnesota Pesticide Management Plan, MDA seeks a published chronic reference value in the absence of an MCL, HRL, HBV, RAA, or RA, if available. Further, the lowest published reference value will be utilized for comparison to the results, even though a different, more current value may exist in literature.

***** – In the absence of compound-specific toxicological information for pesticide degradates, MDH conservatively assumes by default that a pesticide degradate has the same toxicological effect as the pesticide parent compound and is as potent.

Please visit MDH website for the most current MDH health-based reference values for groundwater. The USEPA maintains the current drinking water standards, advisories and human health benchmarks for pesticides and other contaminants.

For all other reference values, health effects information is available from MDA or MDH. Guidance can also be found at MDH website for evaluating concurrent exposures to multiple chemicals.

Note: The analyte bromoxynil was added to the LC-MS/MS list after the samples for this study were analyzed. Bromoxynil was not included in the following list.

Pesticide Analyte	Reference Value (ng/L)	Value Type
2,4,5-T	10,000	RA_{14}
2,4,5-TP	50,000	HRL_{MCL}
2,4-D	2,000	RA_{14}
2,4-DB	5,000	RA_{14}
Acetamiprid	100,000	RA_{14}
Acetochlor	9,000	HRL_{09}
Acetochlor ESA	300,000	HRL_{11}
Acetochlor OXA	100,000	HRL_{11}
Alachlor	2,000	HRL_{MCL}
Alachlor ESA	50,000	RAA_{16}
Alachlor OXA	50,000	RAA_{16}
Aldicarb Sulfone	3,000	RA_{14}
Aldicarb Sulfoxide	2,000	RA_{14}
Atrazine	3,000	HRL_{MCL}
DEDI Atrazine	3,000*	Parent
Deisopropylatrazine	3,000*	Parent
Desethylatrazine	3,000*	Parent
Hydroxyatrazine	20,000	HBV_{05}
Azoxystrobin	300,000	RA_{14}
Benfluralin	8,000	RA_{14}
Bensulfuron-methyl	50,000	RA_{14}
Bensulide	10,000	RA_{16}
Bentazon	30,000	HRL_{15}
Bifenthrin	3,000	RA_{14}
Boscalid	300,000	RA_{14}
Bromacil	30,000	RA_{14}
Carbaryl	10,000	RA_{14}
Carbendazim	9,000	RA_{14}
Carbofuran	100	RA_{14}
Chlorantraniliprole	1,000,000	RA_{14}
Chlorimuron-ethyl	20,000	RA_{14}
Chlorothalonil	30,000	HRL_{94}
Chlorpyrifos	600	HBV_{13}
Chlorpyrifos Oxon	400	RAA_{13}
Clomazone	70,000	RA_{14}
Clopyralid	200,000	RA_{14}
Clothianidin	200,000	HBV_{16}
Cyanazine	1,000	HRL_{09}
Cyantraniliprole	2,000	RA_{15}
Cyfluthrin	6,000	RA_{14}
Diazinon	80	RA_{14}
Diazinon Oxon	80*	Parent
Dicamba	200,000	HRL_{93}
Dichlobenil	40,000	RA_{14}
Dichlorprop	60,000	RA_{14}
Dichlorvos	1,000	RA_{14}

Pesticide Analyte	Reference Value (ng/L)	Value Type
Dicrotophos	30	RA_{14}
Difenoconazole	10,000	RA_{14}
Dimethenamid	300,000	HRL_{15}
Dimethenamid ESA	300,000	RAA_{13}
Dimethenamid OXA	300,000	RAA_{13}
Dimethoate	3,000	RA_{14}
Dinotefuran	5,000	RA_{14}
Disulfoton	300	RA_{14}
Disulfoton Sulfone	300*	Parent
Diuron	2,000	RA_{14}
EPTC	40,000	HBV_{15}
Esfenvalerate	2,000	RA_{14}
Ethalfluralin	10,000	RA_{14}
Ethofumesate	800,000	RA_{14}
Flufenacet OXA	2,000	RA_{14}
Flumetsulam	400,000	RA_{14}
Flutriafol	10,000	RA_{14}
Fluxapyroxad	40,000	RA_{16}
Fonofos	500,000	RA_{14}
Halosulfuron-methyl	20,000	RA_{14}
Hexazinone	10,000	RA_{14}
Imazamethabenz-methyl	60,000	RA_{14}
Imazamethabenz Acid	60,000*	Parent
Imazamox	20,000,000	RA_{14}
Imazapic	30,000	RA_{14}
Imazapyr	900,000	RA_{14}
Imazaquin	60,000	RA_{14}
Imazethapyr	900,000	RA_{14}
Imidacloprid	90,000	RA_{14}
Isoxaflutole	7,000	RA_{14}
Isoxaflutole DKN	7,000*	Parent
lambda-Cyhalothrin	200	RA_{14}
Linuron	1,000	HRL_{93}
Malathion	100,000	RA_{14}
MCPA	3,000	HRL_{93}
MCPB	7,000	RA_{14}
MCPP	4,000	RA_{14}
Mesotrione	5,000	RA_{14}
Metalaxyl	20,000	RA_{14}
Methoxychlor	10,000	RA_{14}
Metolachlor	300,000	HRL_{11}
Metolachlor ESA	800,000	HRL_{11}
Metolachlor OXA	800,000	HRL_{11}
Metribuzin	10,000	HRL_{13}
Metribuzin DA	10,000	RAA_{12}
Metribuzin DADK	10,000	RAA_{12}

Pesticide Analyte	Reference Value (ng/L)	Value Type
Metribuzin DK	10,000	RAA_{12}
Metsulfuron-methyl	400,000	RA_{14}
Myclobutanil	40,000	RA_{14}
Nicosulfuron	300,000	RA_{14}
Norflurazon	4,000	RA_{14}
Norflurazon-desmethyl	4,000*	Parent
Oxadiazon	6,000	RA_{14}
Oxydemeton-methyl	300	RA_{14}
Parathion-methyl	80	RA_{14}
Parathion-methyl Oxon	80	Parent
Pendimethalin	40,000	RA_{14}
Phorate	1,000	RA_{14}
Picloram	300,000	RA_{14}
Picoxystrobin	10,000	RA_{15}
Prometon	10,000	RA_{14}
Prometryn	100,000	RA_{14}
Propachlor	15,000	RA_{14}
Propachlor ESA	15,000*	Parent
Propachlor OXA	15,000*	Parent
Propazine	10,000	HBV_{95}
Propiconazole	90,000	RA_{14}
Pyraclostrobin	100,000	HBV_{11}
Pyroxasulfone	5,000	RA_{14}
Saflufenacil	40,000	RA_{14}
Sedaxane	20,000	RA_{16}
Siduron	200,000	RA_{14}
Simazine	4,000	HRL_{MCL}
Sulfometuron-methyl	100,000	RA_{14}
Tebuconazole	30,000	RA_{14}
Tebuprimiphos	100	RA_{14}
Tembotrione	600	RA_{14}
Terbufos	100	RA_{14}
Tetraconazole	30,000	RA_{14}
Thiacloprid	3,000	RA_{16}
Thiamethoxam	20,000	RA_{14}
Thifensulfuron-methyl	70	RA_{14}
Thiobencarb	20,000	RA_{14}
Tolfenpyrad	10,000	RA_{16}
Triallate	10,000	RA_{14}
Triasulfuron	10,000	RA_{14}
Triclopyr	80,000	RA_{14}
Trifluralin	9,000	RA_{14}
zeta-Cypermethrin	50,000	RA_{14}

Appendix 3: 2015 List of pesticide and pesticide degradate in groundwater with associated method reporting limits (MRLs).

Pesticide Analyte	Type	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
2,4,5-T	Herbicide		50
2,4,5-TP	Herbicide		50
2,4-D	Herbicide		8.3
2,4-DB	Herbicide		20
Acetamiprid	Insecticide		25
Acetochlor	Herbicide	30	
Acetochlor ESA	Herbicide Degradate		30
Acetochlor OXA	Herbicide Degradate		33.3
Alachlor	Herbicide	30	
Alachlor ESA	Herbicide Degradate		41.6
Alachlor OXA	Herbicide Degradate		33.3
Aldicarb Sulfone	Insecticide Degradate		15
Aldicarb Sulfoxide	Insecticide Degradate		50
Atrazine	Herbicide	30	
DEDI Atrazine	Herbicide Degradate		50
Deisopropylatrazine	Herbicide Degradate	150	
Desethylatrazine	Herbicide Degradate	50	
Hydroxyatrazine	Herbicide Degradate		6.7
Azoxystrobin	Fungicide		10
Benfluralin	Herbicide	25	
Bensulfuron-methyl	Herbicide		16.7
Bensulide	Herbicide		250
Bentazon	Herbicide		5
Bifenthrin	Insecticide	20	
Boscalid	Fungicide		50
Bromacil	Herbicide		30
Carbaryl	Insecticide		25
Carbendazim	Fungicide		10
Carbofuran	Insecticide		13.3
Chlorantraniliprole	Insecticide		50
Chlorimuron-ethyl	Herbicide		20
Chlorothalonil	Fungicide	50	
Chlorpyrifos	Insecticide	40	

Pesticide Analyte	Type	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
Chlorpyrifos Oxon	Insecticide Degradate		40
Clomazone	Herbicide	15	
Clopyralid	Herbicide		41.6
Clothianidin	Insecticide		25
Cyanazine	Herbicide		25
Cyantraniliprole	Insecticide		100
Cyfluthrin	Insecticide	100	
Diazinon	Insecticide	30	
Diazinon Oxon	Insecticide Degradate	75	
Dicamba	Herbicide		50
Dichlobenil	Herbicide	5	
Dichlorprop	Herbicide		50
Dichlorvos	Insecticide	15	
Dicrotophos	Insecticide		25
Difenoconazole	Fungicide		25
Dimethenamid	Herbicide	15	
Dimethenamid ESA	Herbicide Degradate		6.7
Dimethenamid OXA	Herbicide Degradate		10
Dimethoate	Insecticide	100	
Dinotefuran	Insecticide		25
Disulfoton	Insecticide	60	
Disulfoton Sulfone	Insecticide		20
Diuron	Herbicide		13.3
EPTC	Herbicide	10	
Esfenvalerate	Insecticide	150	
Ethalfluralin	Herbicide	50	
Ethofumesate	Herbicide	50	
Flufenacet OXA	Herbicide Degradate		8.3
Flumetsulam	Herbicide		50
Flutriafol	Fungicide		10
Fluxapyroxad	Fungicide		10 (estimated)
Fonofos	Insecticide	15	
Glyphosate	Herbicide		3100
AMPA	Herbicide Degradate		5160

Pesticide Analyte	Type	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
Halosulfuron-methyl	Herbicide		30
Hexazinone	Herbicide		10
Imazamethabenz-methyl	Herbicide		5
Imazamethabenz Acid	Herbicide Degradate		10
Imazamox	Herbicide		13.3
Imazapic	Herbicide		10
Imazapyr	Herbicide		8.3
Imazaquin	Herbicide		16.7
Imazethapyr	Herbicide		6.7
Imidacloprid	Insecticide		20
Isoxaflutole	Herbicide		40
Isoxaflutole DKN	Herbicide Degradate		50
lambda-Cyhalothrin	Insecticide	75	
Linuron	Herbicide		20
Malathion	Insecticide	50	
MCPA	Herbicide		5
MCPB	Herbicide		20
MCPP	Herbicide		50
Mesotrione	Herbicide		50
Metalaxyl	Fungicide		8.3
Methoxychlor	Insecticide	50	
Metolachlor	Herbicide	25	
Metolachlor ESA	Herbicide Degradate		10
Metolachlor OXA	Herbicide Degradate		10
Metribuzin	Herbicide	75	
Metribuzin DA	Herbicide Degradate	500 (estimated)	
Metribuzin DADK	Herbicide Degradate	500 (estimated)	
Metribuzin DK	Herbicide Degradate	500 (estimated)	
Metsulfuron-methyl	Herbicide		23.3
Myclobutanil	Fungicide		10
Nicosulfuron	Herbicide		26.6
Norflurazon	Herbicide		20
Norflurazon-desmethyl	Herbicide Degradate		50
Oxadiazon	Herbicide	75	
Oxydemeton-methyl	Insecticide		20

Pesticide Analyte	Type	GC-MS/MS MRL (ng/L)	LC-MS/MS MRL (ng/L)
Parathion-methyl	Insecticide	100	
Parathion-methyl Oxon	Insecticide Degradate		25
Pendimethalin	Herbicide	75	
Phorate	Insecticide	25	
Picloram	Herbicide		41.6
Picoxystrobin	Fungicide		50
Prometon	Herbicide	100	
Prometryn	Herbicide		3.3
Propachlor	Herbicide	30	
Propachlor ESA	Herbicide Degradate		30
Propachlor OXA	Herbicide Degradate		10
Propazine	Herbicide	25	
Propiconazole	Fungicide		10
Pyraclostrobin	Fungicide		25
Pyroxasulfone	Herbicide		50
Saflufenacil	Herbicide		15
Sedaxane	Fungicide		75
Siduron	Herbicide		6.7
Simazine	Herbicide	75	
Sulfometuron-methyl	Herbicide		8.3
Tebuconazole	Fungicide		10
Tebuprimiphos	Fungicide	30	
Tembotrione	Herbicide		50
Terbufos	Insecticide	30	
Tetraconazole	Fungicide		10
Thiacloprid	Insecticide		50
Thiamethoxam	Insecticide		25
Thifensulfuron-methyl	Herbicide		16.7
Thiobencarb	Herbicide		8.3
Tolfenpyrad	Insecticide	100	
Triallate	Herbicide	50	
Triasulfuron	Herbicide		23.3
Triclopyr	Herbicide		50
Trifluralin	Herbicide	50	
zeta-Cypermethrin	Insecticide	500	

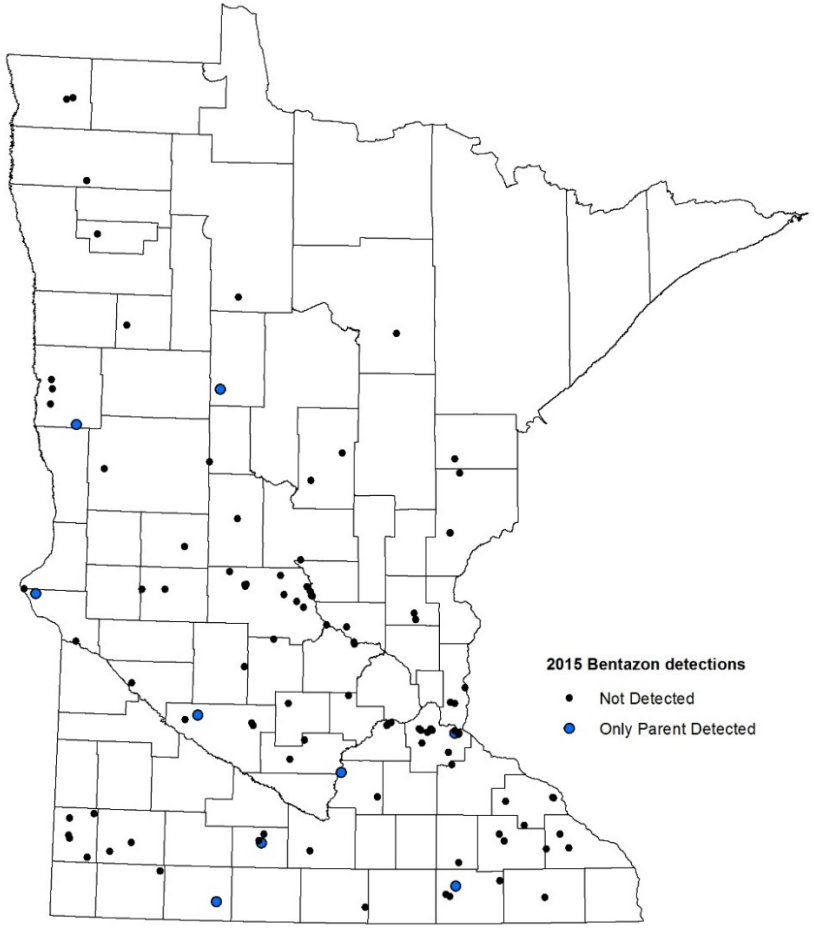
Appendix 4: Inorganics analyzed by MDA Laboratory Services

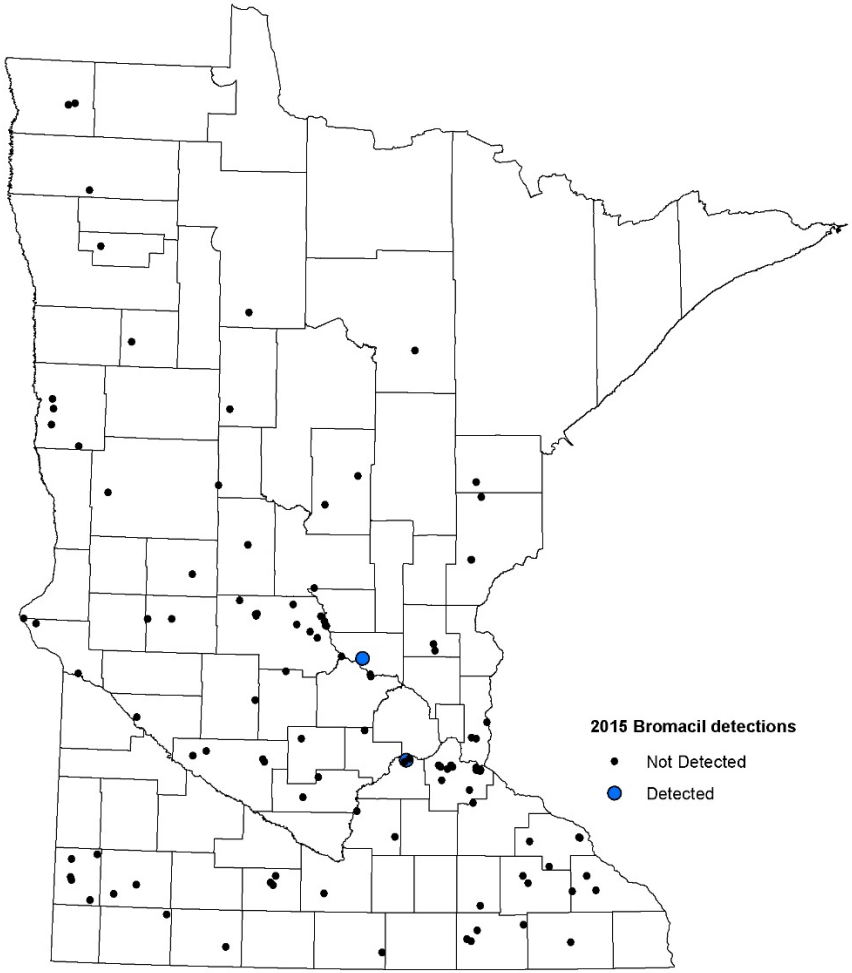
Compound	Method	MRL (mg/L)
Nitrate/Nitrite-Nitrogen	Std. Meth. 4500	0.40
Bromide	EPA 300.0, Rev 2.1	0.50
Chloride	EPA 300.0, Rev 2.1	0.50

Appendix 5: Inorganics analyzed by MDH Public Health Laboratory

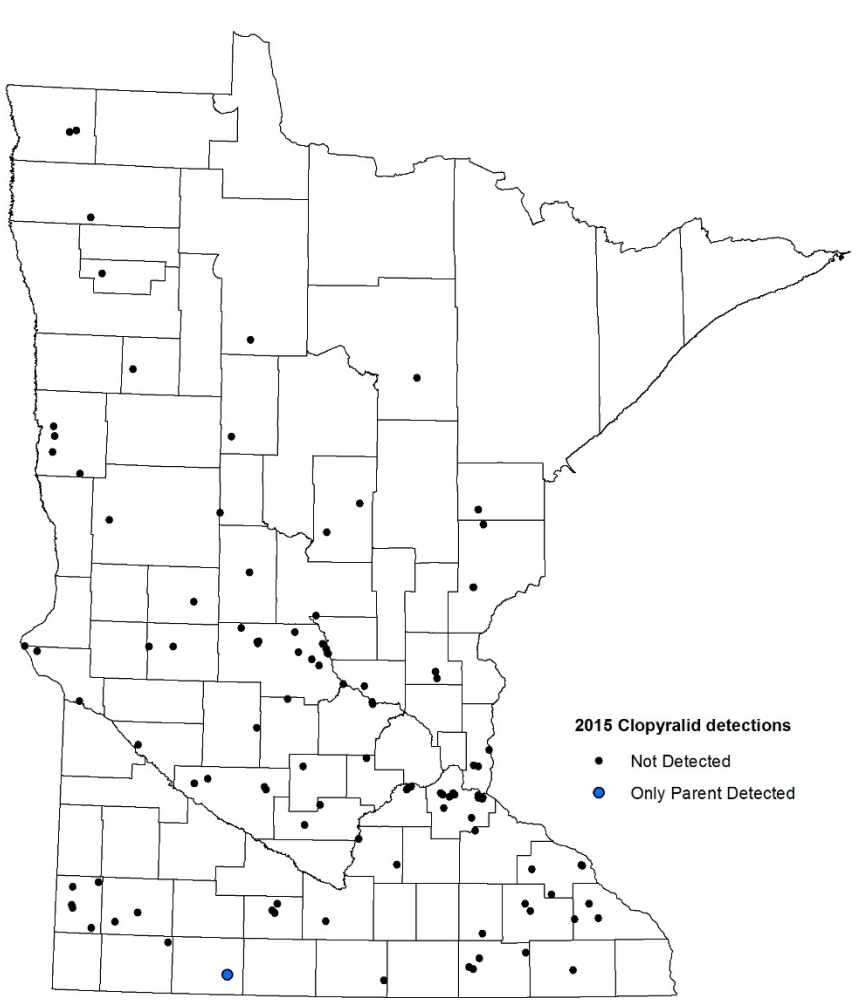
Compound	Method	MRL (mg/L)
Bromide	EPA 300.1	0.0050
Chloride	EPA 300.1	0.500

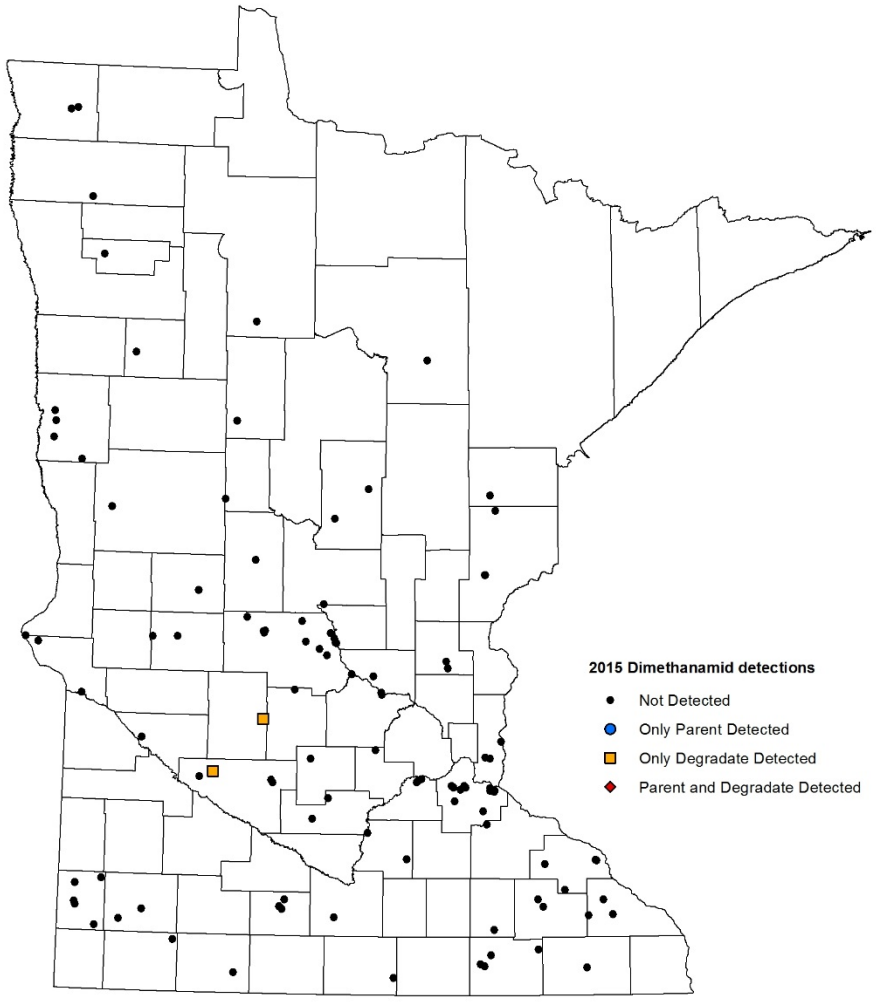
Appendix 6: Additional 2015 detection maps



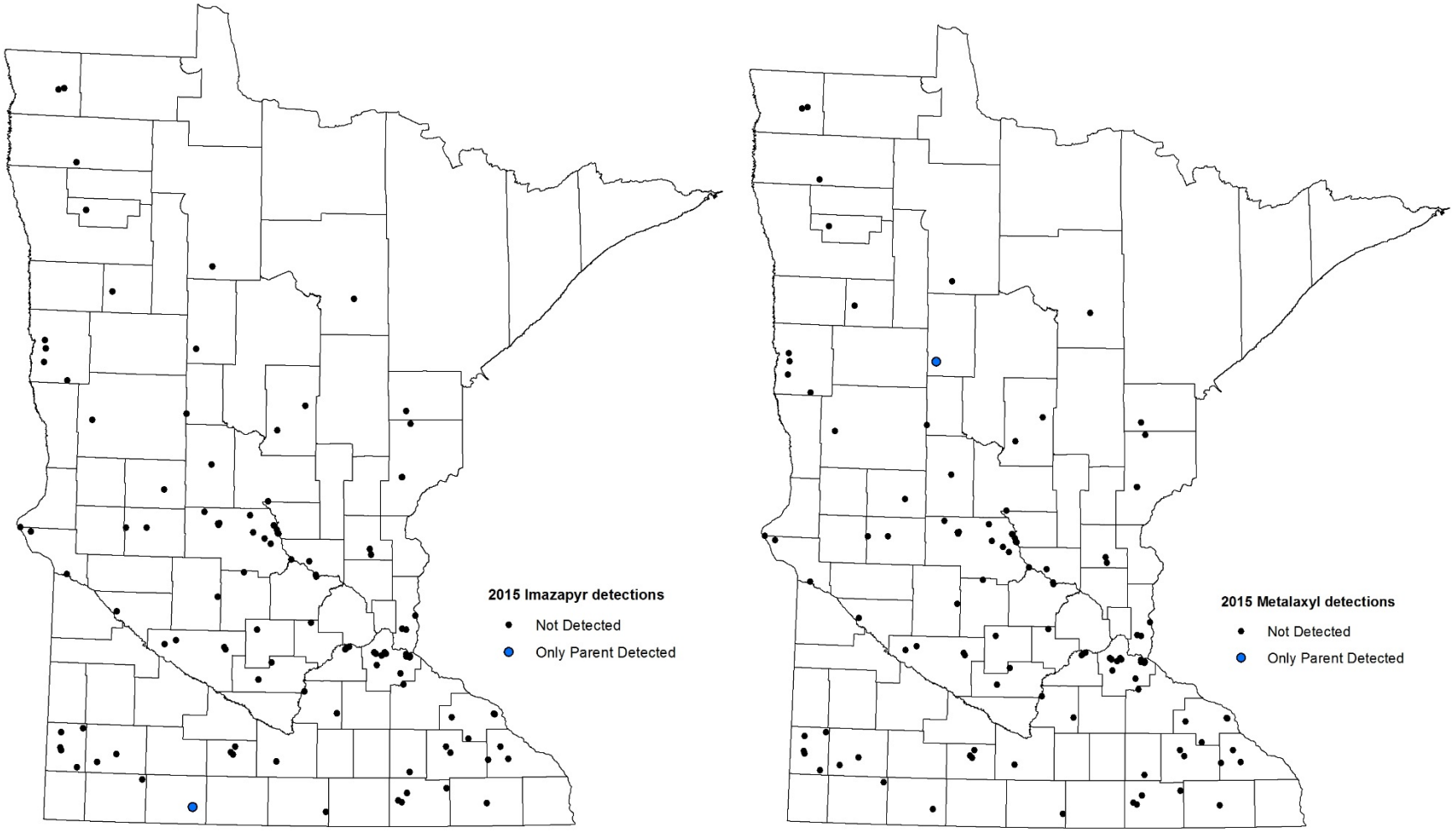


2015 Detections of bentazon and bromacil.



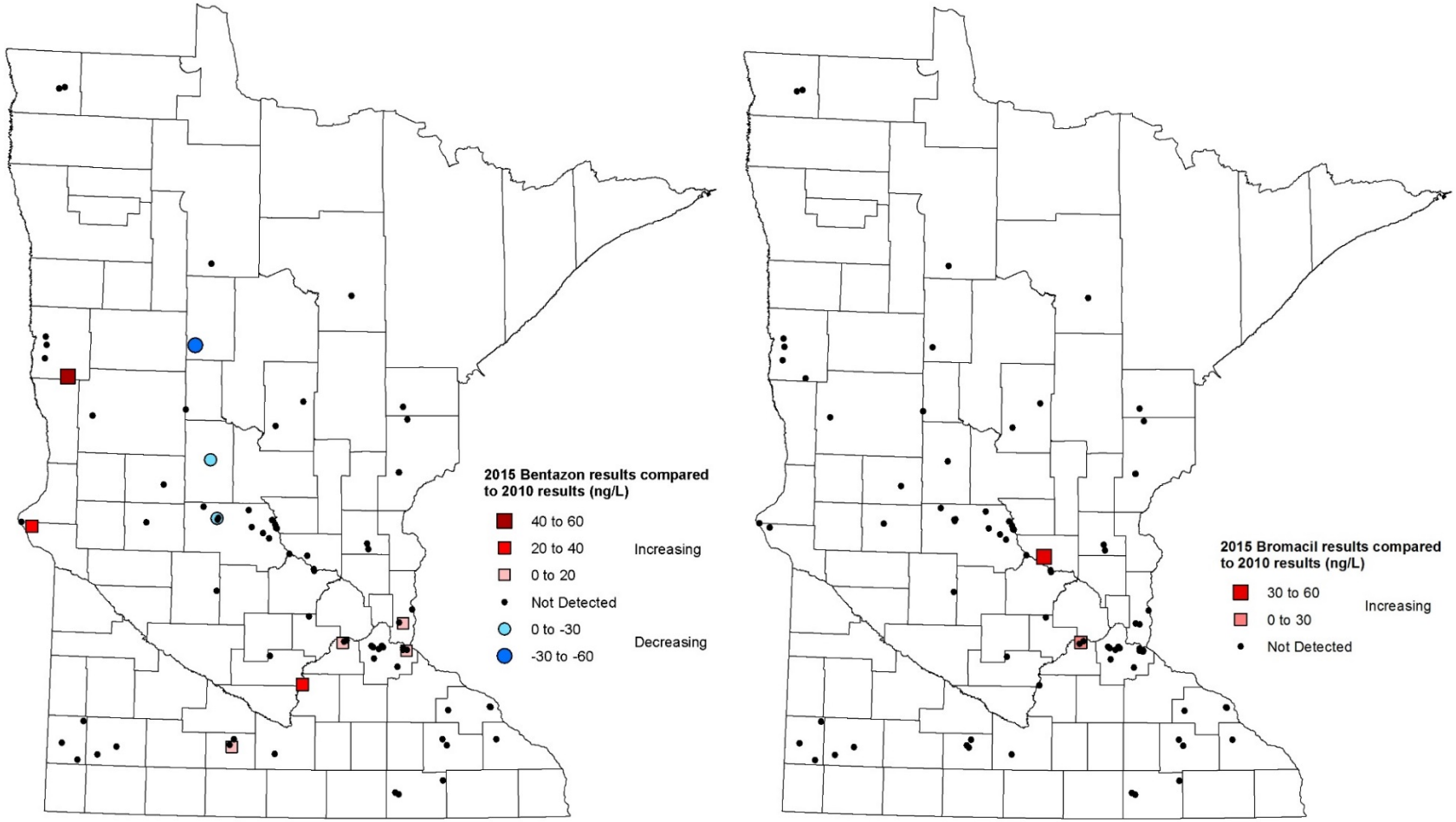


2015 Detections of clopyralid and dimethenamid and degradates.

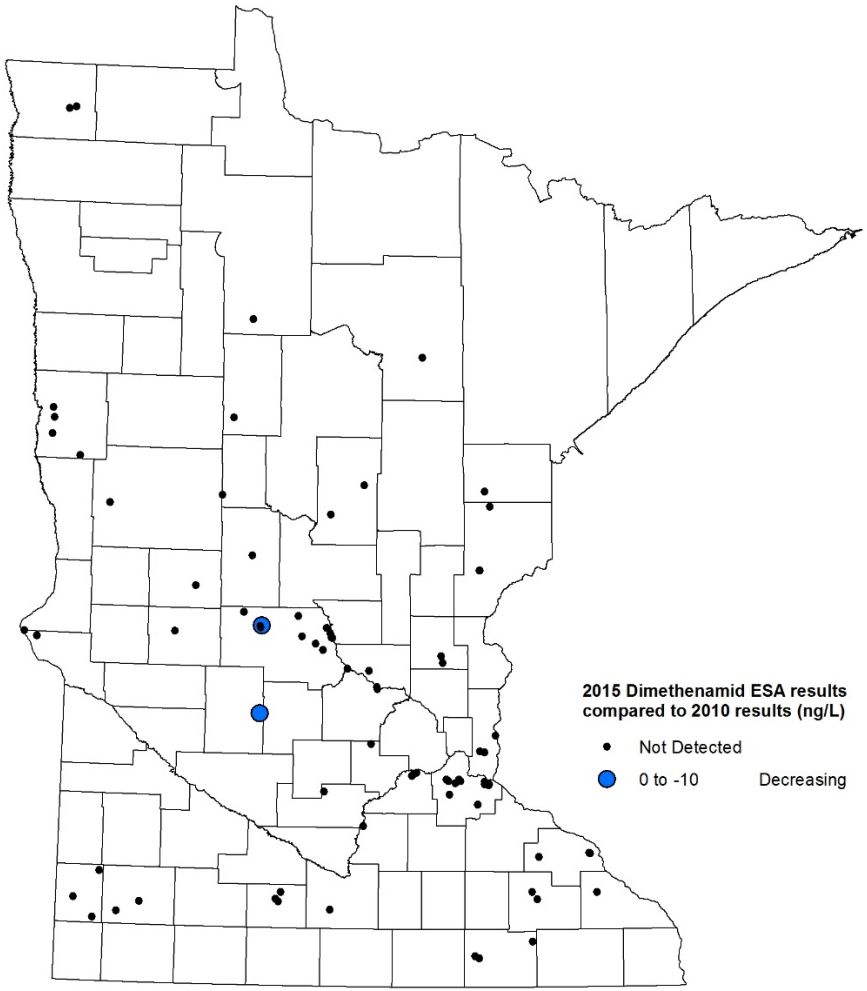


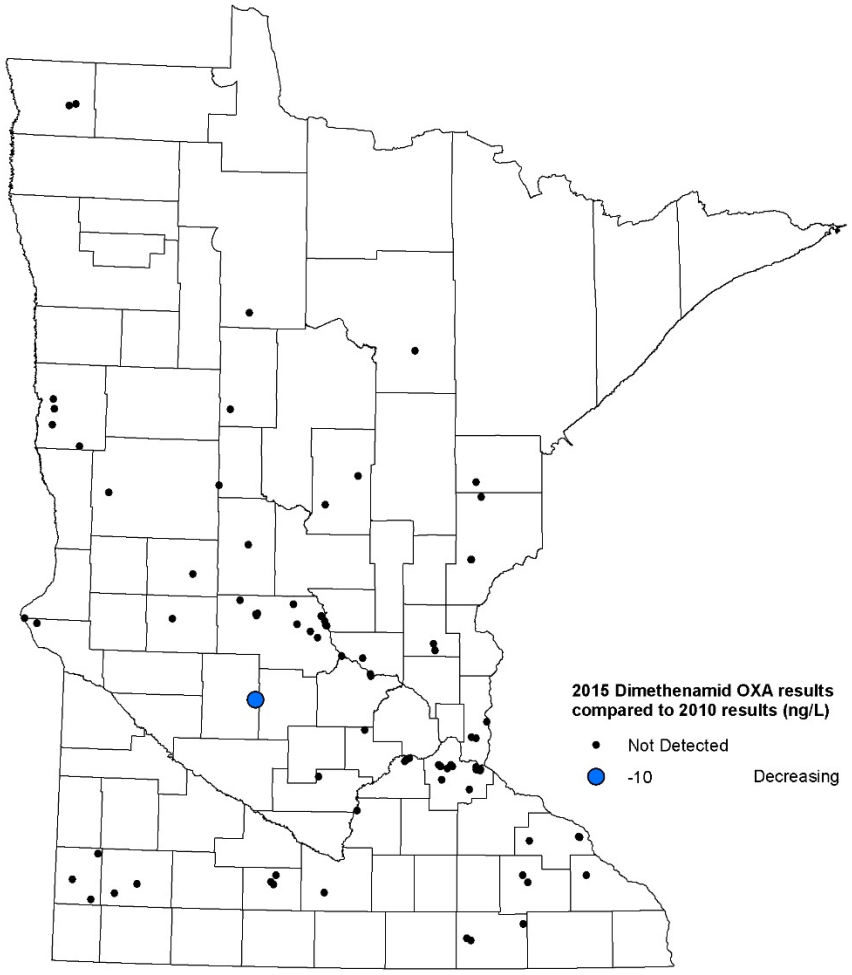
2015 Detections of imazapyr and metalaxyl.

Appendix 7: Additional 2015 detections compared with 2010 detections.

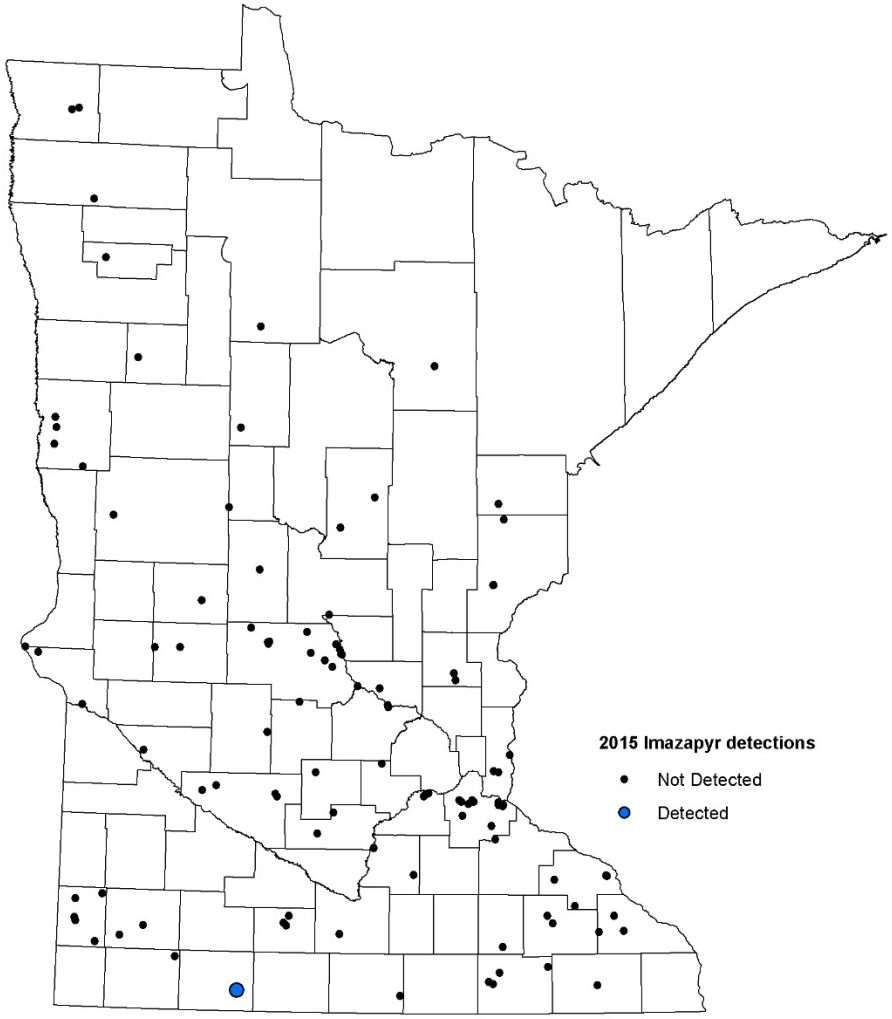


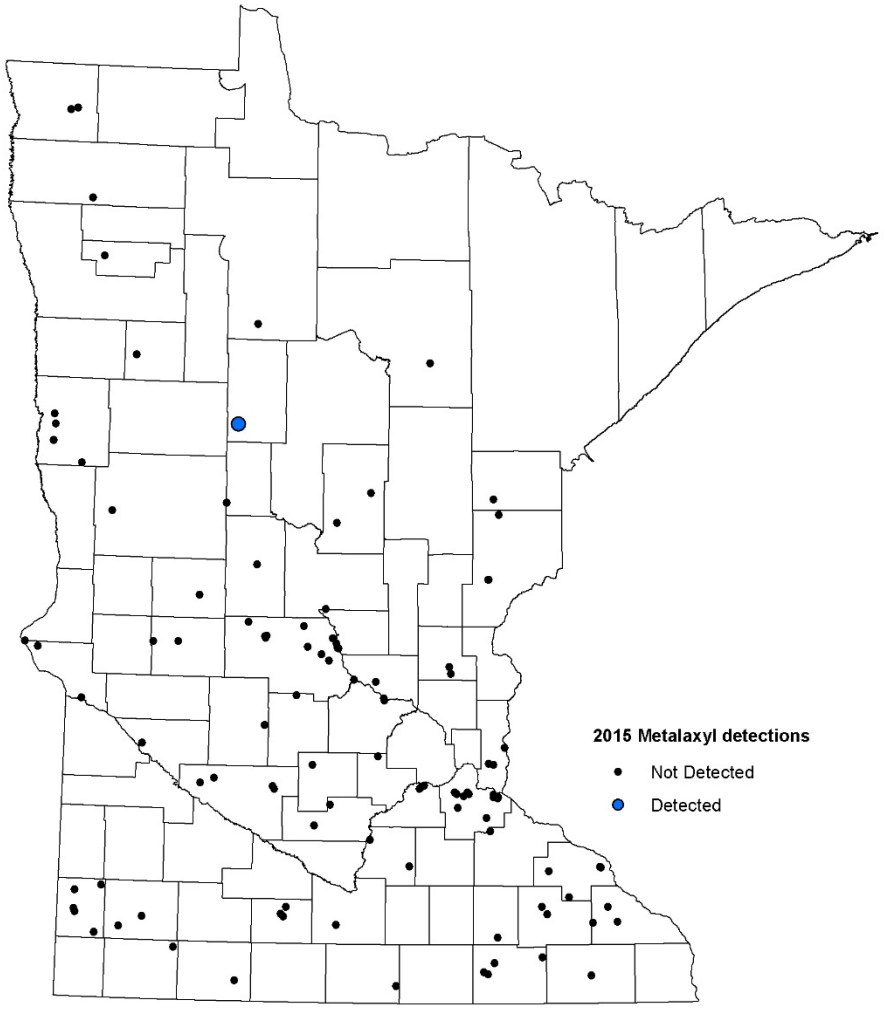
2015 detections of bentazon and bromacil results compared with 2010 detections.



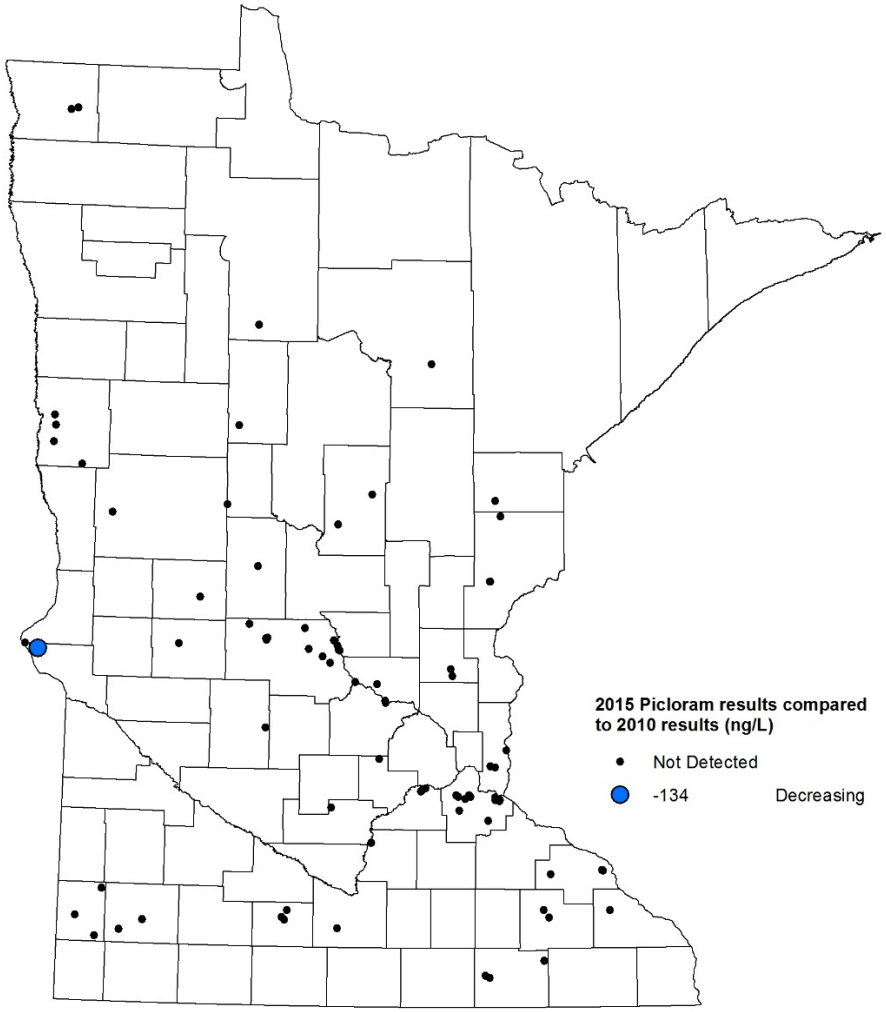


2015 detections of dimethenamid ESA and dimethenamid OXA results compared with 2010 detections.





2015 detections of imazapyr and metalaxyl results compared with 2010 detections.



2015 detections of picloram results compared with 2010 detection.