

**February 2010 Reconnaissance Study of Pesticide Compounds in
Community Public Water Supply Wells**

**Minnesota Department of Agriculture
Minnesota Department of Health**

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Executive Summary

In February 2010 the Minnesota Department of Health in conjunction with the Minnesota Department of Agriculture conducted a reconnaissance study surveying community public water supply wells throughout Minnesota for the presence of eighty-nine pesticides and pesticide degradates. A total of eighty-three wells were sampled for the quality of source water prior to any applicable treatment and distribution to ultimate users. Analyses were performed by the Minnesota Department of Agriculture's analytical lab using gas chromatography mass spectrometry (GC) and liquid chromatography with tandem mass spectrometry.

Sampling showed that water from the community public water supply wells in the study posed no risk to public health. A small number of pesticide and pesticide degradates were detected in some wells, but all detections were well below established health reference values. The results of this study suggest the benefits of periodic reconnaissance to determine if community public water supply wells are impacted by pesticide use in Minnesota.

The study was performed utilizing currently funded MDA/MDH staff time. The analytical equipment was funded through a grant received from the Legislative-Citizen Commission on Minnesota Resources (LCCMR). All participation by community public water supplies was voluntary. This report contains the results and a discussion of this study.

Introduction

This report presents the results of a cooperative project between the Minnesota Departments of Agriculture (MDA) and the Minnesota Department of Health (MDH) to conduct a reconnaissance study of community water supply wells for pesticide and pesticide degradate compounds. The purpose for this work was to determine whether:

- these chemicals are found in community public water supply wells;
- vulnerability assessments conducted by the MDH on community public water supply wells help identify wells that may be at risk to pesticide contamination; and,
- monitoring should be expanded in the future to assess other community public water supply wells that may be at risk.

This study was designed as a reconnaissance survey and sample site selection was not random therefore results are not necessarily representative and cannot be extrapolated to other wells or regions. All community public water supplies that were selected for this study draw their drinking water from groundwater sources in an effort to fill gaps of data related to groundwater (there is much more data available regarding pesticides in surface water sources than there is for groundwater).

Background

Pesticides are chemicals that include herbicides (to manage weeds), insecticides (to manage insects), fungicides (to manage molds and fungi), and disinfectants (to manage germs and bacteria). Pesticide contamination of groundwater may result when there is rapid infiltration of precipitation or surface water into aquifers in areas where pesticides are being used. The MDA is responsible for regulating pesticide use and operates a monitoring network that evaluates the impacts of pesticide applications on groundwater. Much of this monitoring has been focused on shallow monitoring wells, and recently MDA has developed additional capacity to test for a broad range of pesticide and pesticide degradate compounds.

Community public water supply wells that are most likely to be at risk for pesticide contamination pump from aquifers that are 1) quickly recharged by precipitation or surface water and 2) 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 may be warranted. Also, the possible public health impacts of drinking water that contains pesticides and pesticide degradates needs to be assessed when they are detected. The MDH monitors the water that enters community public water supply distribution systems for a limited number of pesticide compounds but is working with the MDA on laboratory capabilities that MDA has recently developed.

Both agencies agreed that a reconnaissance evaluation of pesticide presence in the source water of community public water supply wells was warranted, and assumed the following roles.

The MDA provided:

- the bottles and labels needed for sample collection;
- the laboratory staff and equipment used to analyze water samples; and,
- analysis results to the MDH.

The MDH provided:

- identification of wells to sample and solicited cooperation from well owners;
- staff who collected samples and forwarded them to the MDA laboratory;
- a final report of testing results to each water supply along with the summary report; and,
- an evaluation of potential health risks associated with pesticides and pesticide degradates in community public water supply wells.

Both agencies cooperated to:

- ensure that water samples were delivered and analyzed according to schedule;
- share data and staff expertise that was used to support this study; and
- prepare this report of findings.

Well Selection

The time period for sample collection was limited to February 2010 as the MDA laboratory had only that month available for performing the analyses. Historical monitoring data for pesticides in Minnesota groundwater across seasons indicated no difference in results due to the season in which a well is 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.

The laboratory processing capabilities were optimized so that water samples from eighty-three wells could be collected for this reconnaissance project. Both agencies wanted 1) to focus most of the sampling on wells that would most likely be impacted by pesticide use, and 2) select approximately 10% of the wells to reflect pumping from aquifer settings that would be unlikely to be impacted. The latter set of wells would be used to confirm the well vulnerability assessment protocol used by the MDH, and to provide a control group for the reconnaissance study.

The MDH decided to begin well selection on the community public water supply systems that it had already scheduled for inspection during the first quarter of 2010 to maximize the efficiency of staff time required for sample collection. MDH Source Water Protection Unit staff selected wells for sampling from these community public 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) pump from geologically sensitive aquifers and 2) capture areas extended into land that is either cultivated or managed forest. Ten percent were selected for the control group and pump from geologically protected aquifers where cultivated land use occurs.

Well selection also included a statewide distribution of sampling sites to recognize the variability in 1) hydrogeologic settings and 2) well construction practices. Only wells for which the MDH has a well construction record were selected in order to confirm the hydrogeologic setting and well construction. The water that was sampled for this study came directly from the aquifer via the well and was sampled prior to any treatment process.

Community Public Water Supply Wells Sampled in this Study

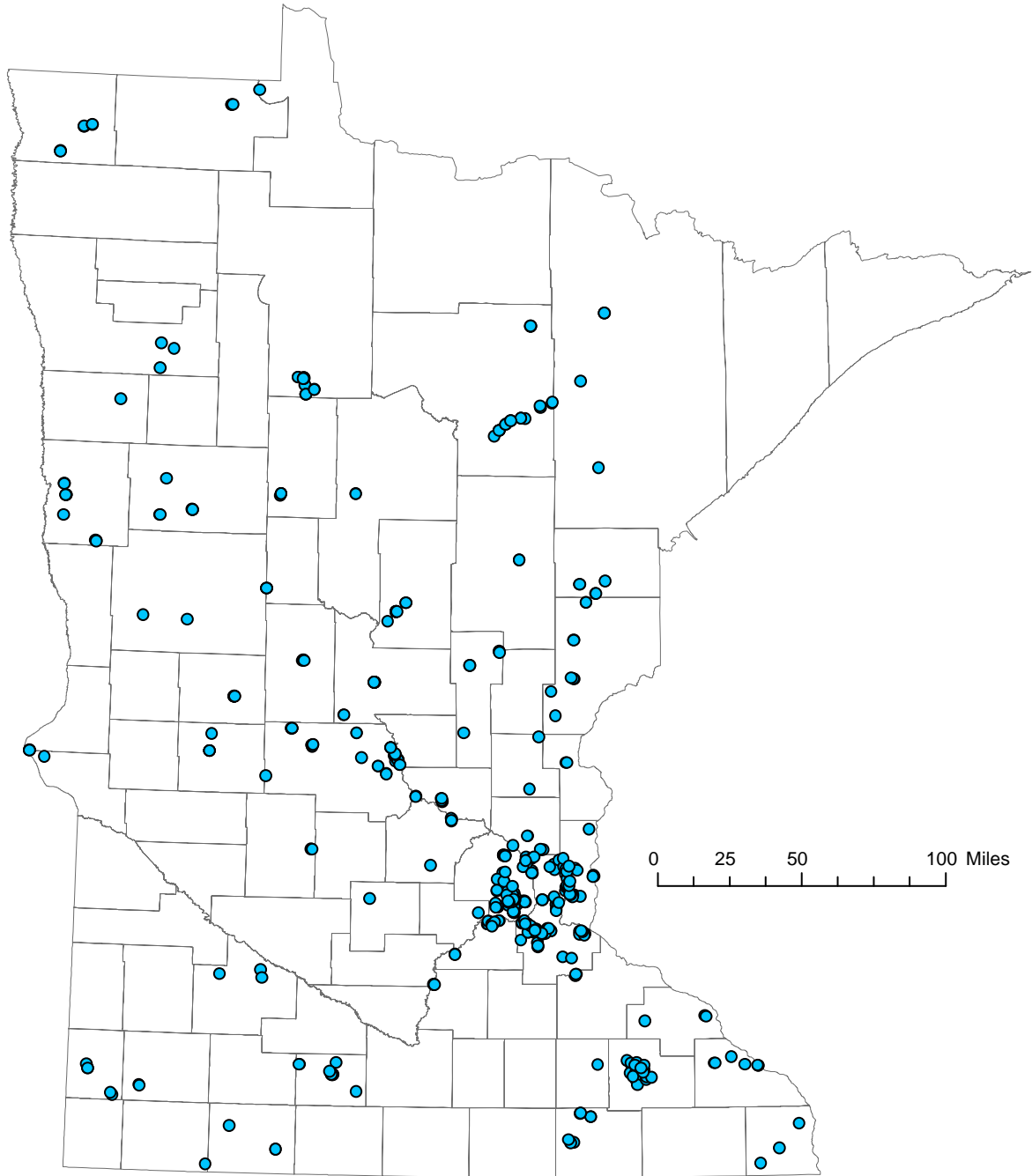


Figure 1. Location of Community Public Water Supply wells sampled in this study.

Well Sampling

MDH staff from the Drinking Water Protection Section collected water samples in February 2010. The project goal of sampling one hundred community public water supply wells was nearly achieved (total of 83 wells) with 90% of the wells pumping from aquifer settings that are designated by the MDH as being geologically sensitive and 10% that are not geologically sensitive. Water samples were collected directly from the well prior to any treatment processes.

Sample Analysis

Current analytical methods provide the capability of qualitatively identifying a chemical at concentrations lower than may be accurately quantified, i.e. below the Method Reporting Limit (MRL). The MRL represents the minimum concentration of an analyte that can be reliably quantified and reported by the laboratory. Analytes may be positively identified via qualitative procedures and reported as “Present” below the MRL. The MRL is a statistically determined level above which a result is reported at a known confidence level, i.e. there is certainty that value of the result is not due to random noise in the system. An Estimated Reporting Limit (ERL) is an estimate of the lowest concentration that a given method may be capable of reporting when final validation of the method is complete; used for reporting mass estimates for analytes of interest before the analytical method is fully developed and validated.

The MDA has adopted the following method of reporting and analyzing analytical results:

Water sample pesticide results reported from the MDA Laboratory Services Division as meeting qualitative or estimated requirements but not quantified (i.e., “Present at less than the Method Reporting Limit” (MRL) or “Present at less than the Estimated Reporting Limit” (ERL)) are entered into the database as “P”. For the purposes of statistical analysis and evaluation, results reported as “P” were assigned a numerical value of one-half the MRL or ERL. Values entered into the database as non-detect (ND) were assigned a numerical value of zero for purposes of statistical analysis and evaluation. If statistical analysis calculations result in a value of zero, the result is reported as “non-detect.” In situations where statistical analysis results in a value between zero and the MRL the value is reported as “P”.

It is well known that pesticide parent materials decompose by various means to other compounds called degradates. Degradates of a pesticide parent material are evaluated independently and, where appropriate, in sum with the parent compound.

Water samples are analyzed for pesticides and inorganic compounds in the laboratory where they are referred to as analytes. A pesticide may be included in a “target analyte” list for a given water sample based on the relative expectation of detecting the pesticide. This expectation may depend on the mobility of the pesticide in soil or water, the general use of the pesticide in the monitoring area or other programmatic reasons or concerns.

A target pesticide analyte list helps MDA monitoring efforts focus limited resources on the chemicals of greatest concern to water resources. The target analyte list typically includes many of the most commonly used pesticide products or degradates or analytes that can easily be detected with available equipment. Some pesticide active ingredients on the target analyte list are not registered for use in Minnesota. The chemical analysis may also detect additional pesticides that fall into the same chemical class as pesticides on the target analyte list. Therefore,

pesticides that are not part of the target analyte list may be detected, quantified (if possible) and reported as non-target analyte detections.

A list of target analytes along with common trade names, method reporting limits, and analyses method can be found in Appendix 1 of this report.

Groundwater Reference Values and Standards

Some of the pesticides and pesticide degradates have federal Safe Drinking Water Act (SDWA) Maximum Contaminant Levels (MCLs). MDH has also developed state drinking water criteria known as Health Risk Limits (HRLs), Health Based Values (HBVs), and Risk Assessment Advice (RAAs) for some of these pesticides and pesticide degradates.

MDH considers drinking water with concentrations at or below these health limits and values safe to consume over a lifetime. If pesticides or pesticide degradates with established health standards are detected in any public water supply wells, these criteria can be used to evaluate the potential health risks.

Definitions

MDH Health Risk Limit (HRL)

A health risk limit (HRL) is the concentration of a groundwater contaminant, or a mixture of contaminants, that can be consumed with little or no risk to health and which has been promulgated under rule (Minnesota Administrative Rules, Parts 4717.7810 through 4717.7900). A HRL is expressed as a concentration in micrograms per liter ($\mu\text{g/L}$). The underlying exposure assumptions (e.g., volume of water consumed and timeframes for exposure comparisons) are established for Minnesota by the MDH and adopted by rule of the MDH Commissioner. Derivation of HRL values does not consider economic factors or technological factors.

MDH Health Based Value (HBV)

A Health Based Value (HBV) also represents a concentration of a chemical (or a mixture of chemicals) that is likely to pose little or no risk to human health. MDH develops HBVs when Minnesota agencies need guidance for chemicals that do not have HRLs. MDH may also calculate HBVs to update an existing value if there is significant new scientific information about how toxic that chemical is. HBVs are calculated using the methodology set in the Health Risk Limits Rules.

MDH Risk Assessment Advice (RAA)

RAA is advice that MDH issues to Minnesota agencies. MDH provides RAA to assist the agencies in evaluating potential health risks to humans from exposures to a chemical. Generally, RAA contains greater uncertainty than HRLs, and HBVs because the available information is more limited.

United States Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL)

A value set by the USEPA as the maximum amount of chemical allowed in a federally regulated public water supply, considering health, economic or other factors including technological factors such as treatment cost and feasibility.

Findings

MDH uses U.S. Environmental Protection Agency (U.S. EPA) Maximum Contaminant Levels (MCLs) for public drinking water supplies; and Health Risk Limits (HRLs), Health Based Values (HBVs), and Risk Assessment Advice (RAAs) for private drinking water supplies and for public drinking water supplies if a U.S. EPA MCL does not exist. These health standards are typically applied when evaluating risk of drinking water consumed after any applicable treatment and/or prior to distribution.

The concentration of a pesticide or pesticide degradate was compared to the available MCL, HRL, HBV and/or RAA. In the absence of compound-specific toxicological information for pesticide degradates, the MDH uses a conservative default approach by assuming 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. If a HRL or HBV exists for a pesticide degradate, then the degradate concentration is compared to that value.

Community public drinking water, systems that show pesticide concentrations consistently above the MCLs are given a Notice of Violation. The data collected with this study shows no systems exceeded any reference values (MCL, HRL, HBV, RAA).

There are situations when a sample of groundwater may contain a mixture of multiple chemicals. Chemicals in combination may cause adverse effects that would not be predicted based on separate exposures to the individual concentrations of each chemical present. Therefore, evaluating the safety of a mixture of chemicals based on individual groundwater reference values or standards may not provide an adequate margin of safety. The procedure for evaluating multiple chemicals is provided in the MDH HRLs Rules for Groundwater. Chemicals that affect the same health endpoint (e.g., liver system, kidney system) are typically evaluated together. For each chemical a ratio is calculated by comparing the groundwater concentration of the chemical to the groundwater reference value or standard for that chemical. The ratios are then summed within each health endpoint group. A total sum of 1 or less indicates that the combined exposure does not pose a health risk. A total sum in excess of 1 indicates a health concern.

A conservative screening assessment (likely to overestimate the potential risk) can be conducted in which the maximum concentration detected is compared to the reference value or standard and all ratios (regardless of health endpoint) are summed (the result is a "health index"). Utilizing this screening approach a total sum of approximately 0.2 can be calculated for the pesticide and pesticide degradate concentrations reported in Table 1 (0.2 is the sum of figures in the column labeled "ratio"). This conservative screening shows that the health index is five times lower than MDH's level of concern. As a result of these findings, further risk analyses of this data set is not needed. In addition, the screening assessment is conservative because, for those public water supplies implementing one or more treatment steps to source water prior to distribution, concentrations of some contaminants in delivered drinking water may be even lower than the concentrations reported.

MDH also sampled the wells for chloride, bromide, and nitrate/nitrite-nitrogen. Analysis by the MDH lab showed that none of the wells sampled contained any of these compounds in excess of either USEPA primary or secondary drinking water standards.

Table 1. Summary of pesticide and pesticide degradate detections in groundwater sampled as part of in this study. (83 samples analyzed)

Common Name	Number of Samples with Detections	Median (µg/L)	75% (µg/L)	90% (µg/L)	Range (µg/L) (min - max)	Groundwater Reference Value or Standard (µg/L)	Reference Value Exceedances	Ratio of Maximum to Groundwater Value*
2,4-D	1	ND	ND	ND	ND – 0.01	70 ^a	0	0.0001
Acetochlor ESA	16	ND	ND	0.086	ND – 2.18	300 ^b	0	0.007
Acetochlor OXA	5	ND	ND	ND	ND – 0.07	100 ^b	0	0.0007
Alachlor ESA	48	0.437	0.234	1.24	ND – 4.66	70 ^c	0	0.07
Alachlor OXA	8	ND	ND	ND	ND – 0.19	70 ^c	0	0.003
Atrazine	5	ND	ND	ND	ND – 0.09	3 ^a	0	0.03
Bentazon	14	ND	ND	0.001	ND – 0.12	200 ^d	0	0.0006
DACT Atrazine	5	ND	ND	ND	ND – 0.10	3 ^e	0	0.03
Deethylatrazine	5	ND	ND	ND	ND – 0.05	3 ^e	0	0.02
Dimethenamid ESA	2	ND	ND	ND	ND – 0.02	40 ^f	0	0.0005
Dimethenamid OXA	1	ND	ND	ND	ND – 0.15	40 ^f	0	0.004
Hydroxyatrazine	4	ND	ND	ND	ND – 0.05	20 ^d	0	0.003
Imazapyr	1	ND	ND	ND	ND – 0.01	6000 ^g	0	0.000002
Metolachlor	1	ND	ND	ND	ND – 0.08	300 ^b	0	0.0003
Metolachlor ESA	59	0.064	0.212	0.667	ND – 6.17	800 ^b	0	0.008
Metolachlor OXA	32	ND	0.032	0.089	ND – 2.12	800 ^b	0	0.003
Picloram	1	ND	ND	ND	ND – 0.16	500 ^h	0	0.0003

ND = not detected

^a EPA MCL

^b MDH HBV (derived utilizing 2009 promulgated methods)

^c MDH RAA (derived utilizing 2009 promulgated methods)

^d MDH HBV (derived utilizing pre-2009 methods)

^e MDH HRL for parent compound (derived utilizing pre-2009 methods)-recommended for evaluating degradates

^f MDH HBV for parent compound (derived utilizing pre-2009 methods)-recommended for evaluating degradates

^g Based on EPA RED (Reregistration Eligibility Document) Reference Dose (RfD) value and MDH methodology.

^h MDH HRL (derived utilizing pre-2009 methods)

*MDH's level of concern would be when the ratio of maximum to groundwater value is equal to or above 1.

Discussion and Conclusions

This report presents the results of a cooperative project between the MDA and MDH to conduct a reconnaissance testing of community water supply wells for pesticide and pesticide degradate compounds. The purpose for this work was to determine whether:

- these chemicals are found in the source water of community public water supply wells prior to any applicable treatment and distribution to ultimate users;
- vulnerability assessments conducted by the MDH on community public water supply wells help identify wells that may be at risk to pesticide contamination;
- monitoring should be expanded in the future to assess other community public water supply wells that may be at risk; and,
- pesticide detection concentrations were of health concern.

MDH intends to further evaluate the data to determine if the data set 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.

Comparisons of samples collected as part of this study to current health standards show no exceedances, and future monitoring is anticipated to evaluate the occurrence of pesticides and pesticide degradates in community public water supply wells. Staff determined that additional monitoring should be pursued depending on resource availability within the MDH and MDA. MDH considered many possible future modifications to the methods used for this study. Some ideas discussed include using a randomized well selection approach which allow for more representative data, and sampling during other times of the year. The MDH would also like to pursue sampling for pesticide compounds in surface water systems to determine the connection between pesticide detections and time of year (MDA evidence suggest surface water systems may show seasonal difference in pesticide concentrations detected).

Additional information on statewide monitoring results for pesticides and pesticide degradates can be found at <http://www.mda.state.mn.us/chemicals/pesticides/maace.aspx>, along with information related to protecting drinking water sources at <http://www.mda.state.mn.us/en/protecting/waterprotection/pesticides.aspx>.

Questions regarding this study can be sent to Karla Peterson, MDH Community Public Water Supply Unit, at karla.peterson@state.mn.us, or John Hines, MDA Monitoring Unit, at john.w.hines@state.mn.us.

Acknowledgements

The Minnesota Department of Agriculture and the Minnesota Department of Health would like to thank all of the community public water supplies that voluntarily participated in this study.

Appendix 1. Analyte List for this Study

Common Name	Type	MRL	Analysis Method
2,4-D	Herbicide	8.3 ppt	LC
24-DB	Herbicide	13.3 ppt	LC
Acetochlor	Herbicide	0.05 ppb	GC
Acetochlor ESA	Degradate	30 ppt	LC
Acetochlor OXA	Degradate	33.3 ppt	LC
Alachlor	Herbicide	0.05 ppb	GC
Alachlor ESA	Degradate	41.6 ppt	LC
Alachlor OXA	Degradate	33.3 ppt	LC
Atrazine	Herbicide	0.05 ppb	GC
Deethylatrazine	Degradate	0.05 ppb	GC
Deisopropylatrazine	Degradate	0.2 ppb	GC
Diaminochlorotriazine(DACT)	Degradate	50 ppt	LC
Hydroxyatrazine	Degradate	6.7 ppt	LC
Bensulfuron Methyl	Herbicide	16.7 ppt	LC
Bentazon	Herbicide	0.8 ppt	LC
Boscalid	Fungicide	0.3 ppb	GC
Bromacil	Herbicide	20 ppt	LC
Carbaryl	Insecticide	25 ppt	LC
Carbofuran	Insecticide	13.3 ppt	LC
Chlorimuron Ethyl	Herbicide	20 ppt	LC
Chlorothalonil	Fungicide	0.12 ppb	GC
Chlorpyrifos	Insecticide	0.04 ppb	GC
Clomazone	Herbicide	0.1 ppb	GC
Clopyralid	Herbicide	41.6 ppt	LC
Cyanazine	Herbicide	0.2 ppb	GC
Cyfluthrin	Insecticide	0.5 ppb	GC
Diazinon	Insecticide	0.12 ppb	GC
Dimethenamid	Herbicide	0.05 ppb	GC
Dimethenamid ESA	Degradate	6.7 ppt	LC
Dimethenamid OXA	Degradate	10 ppt	LC
Dimethoate	Insecticide	0.22 ppb	GC
Disulfoton	Insecticide	0.15 ppb	GC
Disulfoton Sulfone	Insecticide	20 ppt	LC
Diuron	Herbicide	13.3 ppt	LC
EPTC	Herbicide	0.23 ppb	GC
Esfenvalerate	Insecticide	0.2 ppb	GC
Ethalfuralin	Herbicide	0.15 ppb	GC
Flufenacet OXA	Degradate	8.3 ppt	LC
Fonofos	Insecticide	0.1 ppb	GC

Common Name	Type	MRL	Analysis Method
Imazamethabenz Acid	Degradate	10 ppt	LC
Imazamethabenz Methyl	Herbicide	5 ppt	LC
Imazamox	Herbicide	13.3 ppt	LC
Imazapic	Herbicide	10 ppt	LC
Imazapyr	Herbicide	8.3 ppt	LC
Imazaquin	Herbicide	16.7 ppt	LC
Imazethapyr	Herbicide	6.7 ppt	LC
Lambda Cyhalothrin	Insecticide	0.2 ppb	GC
Linuron	Herbicide	20 ppt	LC
Malathion	Insecticide	0.09 ppb	GC
MCPA	Herbicide	5 ppt	LC
MCPB	Herbicide	10 ppt	LC
Metalaxyl	Fungicide	8.3 ppt	LC
Methyl Parathion	Insecticide	0.12 ppb	GC
Metolachlor	Herbicide	0.07 ppb	GC
Metolachlor ESA	Degradate	10 ppt	LC
Metolachlor OXA	Degradate	10 ppt	LC
Metribuzin	Herbicide	0.1 ppb	GC
Metribuzin DA	Degradate	1 ppb	GC
Metribuzin DADK	Degradate	1 ppb	GC
Metribuzin DK	Degradate	1 ppb	GC
Metsulfuron Methyl	Herbicide	23.3 ppt	LC
Myclobutanil	Fungicide	0.2 ppb	GC
Neburon	Herbicide	10 ppt	LC
Nicosulfuron	Herbicide	26.6 ppt	LC
Oxadiazon	Herbicide	0.05 ppb	GC
Pendimethalin	Herbicide	0.08 ppb	GC
Phorate	Insecticide	0.12 ppb	GC
Picloram	Herbicide	41.6 ppt	LC
Prometon	Herbicide	0.1 ppb	GC
Prometryn	Herbicide	3.3 ppt	LC
Propachlor	Herbicide	0.1 ppb	GC
Propachlor OXA	Degradate	10 ppt	LC
Propazine	Herbicide	0.1 ppb	GC
Propiconazole	Fungicide	0.2 ppb	GC
Pyraclostrobin	Fungicide	0.23 ppb	GC
Siduron	Herbicide	6.7 ppt	LC
Simazine	Herbicide	0.1 ppb	GC
Sulfometuron Methyl	Herbicide	8.3 ppt	LC
Tebuconazole	Fungicide	0.2 ppb	GC

Common Name	Type	MRL	Analysis Method
Terbufos	Insecticide	0.19 ppb	GC
Tetraconazole	Fungicide	0.15 ppb	GC
Thifensulfuron Methyl	Herbicide	16.7 ppt	LC
Thiobencarb	Herbicide	8.3 ppt	LC
Triallate	Herbicide	0.1 ppb	GC
Triasulfuron	Herbicide	23.3 ppt	LC
Trifluralin	Herbicide	0.17 ppb	GC
Zeta-Cypermethrin	Insecticide	0.5 ppb	GC

*Pesticide analytes (active ingredients or their degradates) may be associated with one or more trade names for products packaged and sold to pesticide applicators. *In addition, some pesticide analytes may be associated with products that are not registered for sale or used in Minnesota. For a searchable database of currently registered products and pesticide active ingredients, consult the Minnesota Department of Agriculture website at <http://state.ceris.purdue.edu/doc/mn/statemn.html>*

Compound	Method	MRL (mg/L)
Nitrate/Nitrite-Nitrogen	EPA 353.2	0.05
Bromide	EPA 300.1	0.005
Chloride	EPA 300.1	0.50