



MINNESOTA DEPARTMENT
OF AGRICULTURE



Groundwater Quality Monitoring

2012 Annual Work Plan

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*MONITORING and ASSESSMENT UNIT
ENVIRONMENTAL SECTION
PESTICIDE & FERTILIZER MANAGEMENT DIVISION*

Table of Contents

1.	INTRODUCTION	1
2.	GROUNDWATER MONITORING FRAMEWORK.....	2
3.	LABORATORY ANALYTICAL METHODS	3
4.	PMR SPECIFIC MONITORING	3
4.1.	PMRs 1, 5, 6, 7 and 8	3
4.2.	PMR 4.....	5
4.3.	PMR 9.....	7
4.4.	Urban	9
5.	MAINTENANCE OF NETWORK WELLS AND SITES.....	10
6.	2012 DATA ANALYSIS AND REPORTS.....	11
7.	QUALITY ASSURANCE SAMPLING.....	12
8.	APPENDIX	13

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1. INTRODUCTION

The purpose of this document is to describe planned groundwater monitoring activities of the Minnesota Department of Agriculture (MDA) Monitoring and Assessment Unit (MAU) for 2012. Direction for groundwater monitoring by MDA is derived from the Minnesota Pesticide Control Law (M.S. 18B) and the Minnesota Groundwater Protection Act (M.S. 103H). Specific information describing goals, objectives and practices pursued in implementing the charge to monitor groundwater by the MAU are described in the MAU's Groundwater Monitoring Design Document and its supporting material (QAPP, SOPs, etc). Planning and prioritization are essential to the practical implementation of monitoring to meet Departmental goals and objectives related to groundwater. Projects implemented by the MAU are pursued to optimize outcomes from limited resources, thus the MAU is constantly evaluating projects and procedures to try to maximize benefits and minimize costs.

2. GROUNDWATER MONITORING FRAMEWORK

The MDA groundwater monitoring program divides the state into ten Pesticide Monitoring Regions (PMRs), as shown in Figure 1. PMRs are based on areas with similar cropping practices, soil characteristics, hydrogeologic conditions, rainfall, and agro-ecosystem classifications. PMRs are delineated on county lines to facilitate the evaluation of the results by farmers, the general public and others.

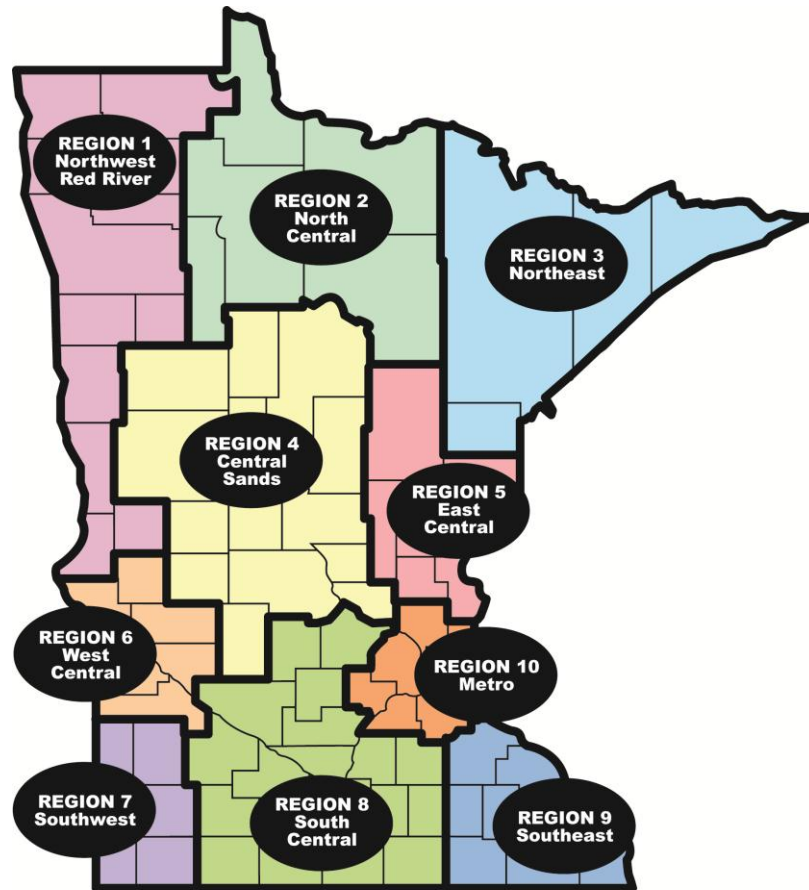


Figure 1. Pesticide Monitoring Regions (PMRs).

Specific monitoring designs for each region are based on the characteristics of the specific region. Water quality samples are collected and analyzed to facilitate evaluation of conditions within, and between, each region. Five PMRs (1, 5, 6, 7, and 8) are included in a common design. Two PMRs (4 and 9) have unique monitoring designs based on their distinctive land use, hydrogeology, or other important characteristics. A design for groundwater monitoring in PMR 10 has been completed, although funds are not yet available for implementation. PMRs 2 and 3 are not included in the monitoring program due to very small amounts of agricultural production in these heavily forested areas.

3. LABORATORY ANALYTICAL METHODS

During 2012 the MDA laboratory will utilize two analytical methods for analyzing water samples collected by the monitoring program. The two methods are GC-MS/MS and LC-MS/MS, which stands for gas chromatography with tandem mass spectrometry and liquid chromatography with tandem mass spectrometry, respectively. The list of chemical analytes for 2012 is located in the Appendix. Because the MDA Laboratory will be implementing the GC-MS/MS this year, this list of chemicals is subject to change as method validation continues throughout the year.

4. PMR SPECIFIC MONITORING

4.1. PMRs 1, 5, 6, 7 and 8

2012 sampling plan. The regional sampling network for regions 1, 5, 6, 7 and 8 consists of seven to twelve wells per PMR. Each well is sampled twice a year; once during April and once during October. Well locations are displayed in Figure 2.

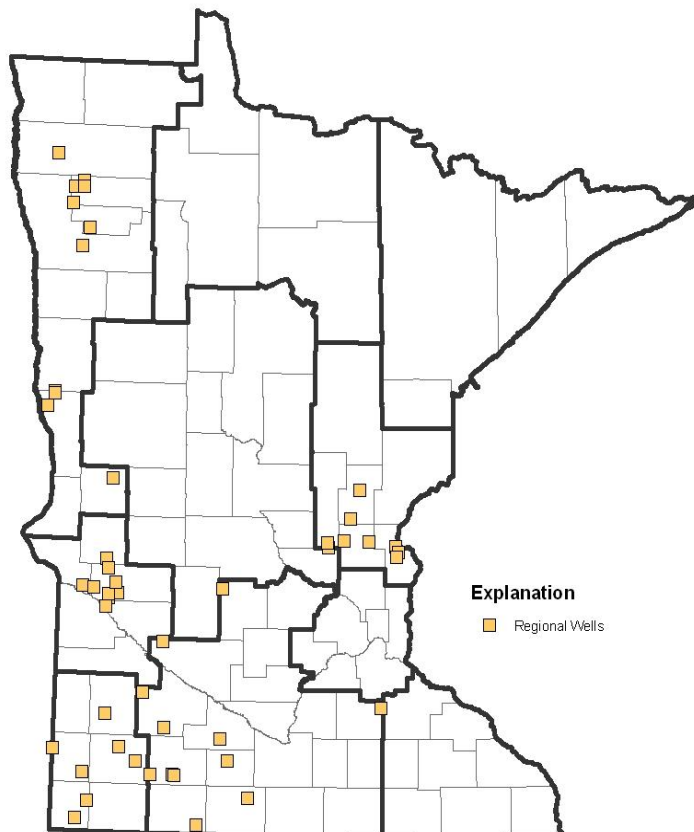


Figure 2. Groundwater Sites in PMRs 1, 5, 6, 7 and 8.

Table 1 lists the wells scheduled for sampling during 2012 in PMRs 1, 5, 6, 7 and 8. Based on previous experience, there is a strong possibility that all the wells may not be sampled due to sediment plugging, falling water tables due to drought conditions or other unpredictable problems. Each sample will consist of a liquid chromatography (LC-MS/MS) and a gas chromatography (GC-MS/MS) analysis. Nitrate-N samples will also be collected. See the Appendix for a summary of analyses to be conducted.

Table 1. Wells scheduled for sampling in PMRs 1, 5, 6, 7 and 8 during April and October 2012.

PMR	MDA#
1	26101
1	45006
1	57003
1	57005
1	57008
1	60201
1	84101
5	13101
5	13102
5	13103
5	30005
5	30008
5	33006
5	33101
5	48101
5	48102
6	6101
6	12101
6	75002
6	76042
6	76045
6	76101
6	76102
6	76103
6	76104
7	42101
7	51008
7	51101
7	59101
7	59102
7	67006
7	67102
8	8101
8	17007
8	17101
8	17102
8	17103
8	32101
8	46101
8	47101
8	64103
8	65101
8	66101
8	83101

4.2. PMR 4

2012 sampling plan. During 2012 the sampling network will consist of 80 sites containing nested wells. Samples will be collected from the shallowest well in the nest that intersects the water table and is able to produce enough water for a sample. Each site will be sampled once during 2012, in the second (spring) or fourth (fall) quarter of the year. Sites with a nested, deeper, automated level logger well will have samples collected from the shallowest well and from the deepest well twice during 2012; once during May and once in November. With the exception of the deep well sites, all sites are distributed to each sampling period by a randomization procedure. Site locations are displayed in Figure 3, and the sampling schedule are found in Table 2. Each sample will consist of analysis by GC-MS/MS and LC-MS/MS. Nitrate-N samples will also be collected. See the Appendix for a complete listing of analyses to be conducted.

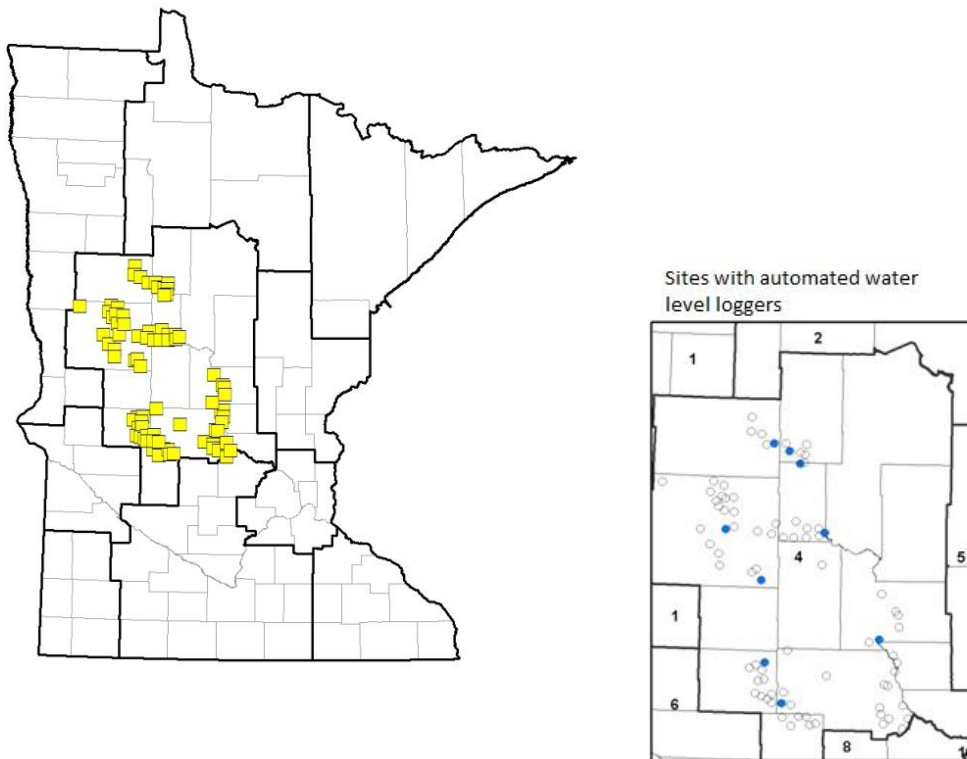


Figure 3. PMR 4 groundwater monitoring site locations.

Table 2. 2012 schedule for sampling in PMR 4.

2 nd quarter (May 2012)	2 nd quarter (May 2012)	4 th quarter (Nov. 2012)	4 th quarter (Nov. 2012)
03-I2	56-J10*	03-I3	56-G3
03-K4*	56-K6	03-J3	56-J10*
29-A7	61-F5	03-J4	56-K5
29-A8*	61-G2*	03-K4*	61-F2
29-C8	61-G4	05-B2	61-F3
29-C9	61-H5	05-C3	61-F4
34-E1	73-A1	29-A8*	61-G2*
34-F2	73-A6*	29-B8	61-G3
49-D5	73-B6	29-C7	61-G5
49-D9*	73-E3	34-C1	61-G6
49-F6	73-I6	34-D1	61-H6
49-F7	73-J4	34-D2	73-A5
56-A1	73-K4	34-E2	73-A6*
56-E1	73-L6	49-D9*	73-J7
56-E2	73-M7	49-F8	73-K3
56-E7	80-A8	56-D6	73-K7
56-F3-1	80-B1*	56-E3	73-L8
56-F9	80-B8	56-F1	80-B1*
56-G4	80-D7	56-F2	80-B7
56-I6	80-D8	56-F4	80-C7
56-I9	80-E8*	56-F6	80-C8
56-I10		56-F8	80-E8*

*= sites with deep wells

Automated monitoring of water level will continue at nine sites within PMR 4 during 2012. The data loggers will be downloaded in May and November and the data will be summarized for the 2012 Annual Report.

4.3. PMR 9

2012 sampling plan. Spring sampling will follow the protocols developed when sampling of springs began in January 2000. The program will continue to monitor 13 of the 14 springs sampled during 2011 (Figure 4 is a location map of the springs, while Table 3 lists the springs to be sampled during 2012). Trout Valley spring is being dropped from the program following discovery that the contributing land is forested rather than agricultural. Each spring will be sampled four times during the year. Minnesota Department of Natural Resources (MDNR) fish hatchery springs will be sampled on a quarterly basis; the remaining 10 springs will be sampled by MDA staff four times, with three samples collected from May 15 through June 30 and a final sample during September. The sampling of springs is targeted to the middle four days of each two week sampling period regardless of prevailing weather conditions. In order to protect the biological integrity of water flowing through the hatcheries, MDNR hatchery springs will be sampled by MDNR hatchery personnel. MDA will notify MDNR hatchery personnel when samples need to be collected. MDA staff may either accompany hatchery personnel during sampling or may pick up samples from the hatcheries following sample collection. Sample custody will transfer from the MDNR to the MDA either immediately following the sample collection or when the MDA picks up the samples.

The currently monitored 14 domestic drinking water wells in the network will be maintained, with samples being collected once in September. PMR 9 drinking water wells are sampled in September to coincide with the fall sample collection from the springs.

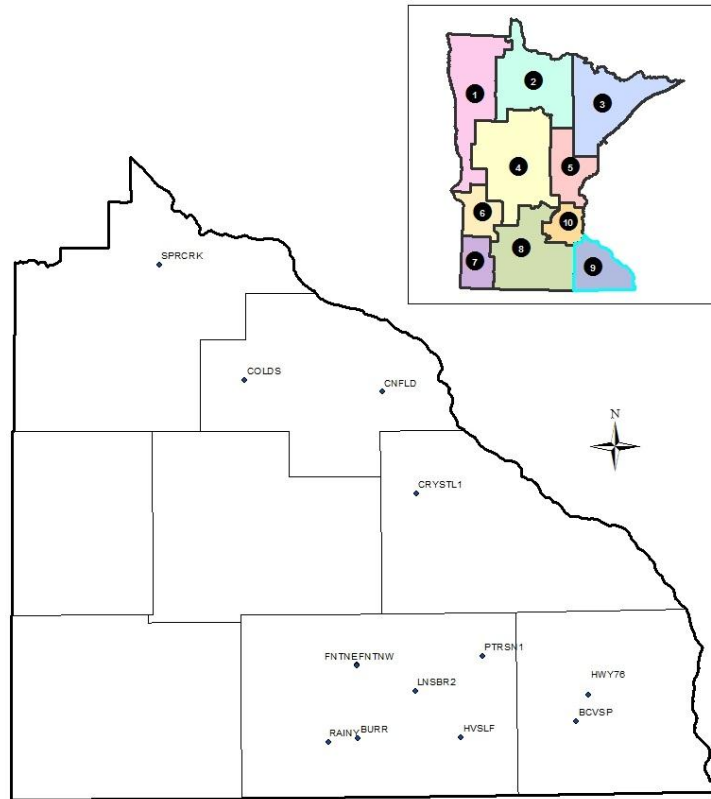


Figure 4. PMR 9 SE MN spring locations.

Table 3. Springs to be sampled during 2012.

Spring Name	County	Schedule
Big BCVSP	Houston	May 15 – June 30 (1 bi-weekly); late September
Canfield	Wabasha	May 15 – June 30 (1 bi-weekly); late September
Cold South	Wabasha	May 15 – June 30 (1 bi-weekly); late September
Fountain E	Fillmore	May 15 – June 30 (1 bi-weekly); late September
Fountain W	Fillmore	May 15 – June 30 (1 bi-weekly); late September
Burr Oak	Fillmore	May 15 – June 30 (1 bi-weekly); late September
Rainy	Fillmore	May 15 – June 30 (1 bi-weekly); late September
Spring Creek	Goodhue	May 15 – June 30 (1 bi-weekly); late September
Hvoslef	Fillmore	May 15 – June 30 (1 bi-weekly); late September
Highway 76	Houston	May 15 – June 30 (1 bi-weekly); late September
Crystal Springs	Winona	Quarterly (March, May, August, November)
Lanesboro	Fillmore	Quarterly (March, May, August, November)
Peterson	Fillmore	Quarterly (March, May, August, November)

4.4. Urban

2012 sampling plan As stated in the MDA/MPCA groundwater monitoring Memorandum of Agreement (MOA) (see MDA website), urban sampling is included in a groundwater monitoring program operated by the Minnesota Pollution Control Agency (MPCA). Based on MDA established criteria, the MPCA judiciously selects a subset of wells that are being sampled for their program and an additional sample is collected for pesticide analysis. Some urban well up-gradient areas contain significant amounts of agricultural land that is in the process of conversion to suburban development. These sites are best considered mixed-use, although summary statistics will be prepared for all urban sites together.

Samples collected from urban settings undergo analysis for the pesticides found in the available analytical suites. These analytical methods allow for the analysis of pesticides used in urban and suburban environments, as well as agricultural pesticides. Samples for urban use pesticides are typically collected from urban centers within PMRs 4, 9 and 10 (Figure 5), although sites in PMR 2 have been sampled in the past.

Approximately 20 samples for analysis by GC-MS/MS and LC-MS/MS will be collected from urban sites selected in collaboration with MPCA staff. Samples are collected by MPCA and submitted to the MDA laboratory for pesticide analysis. One set of samples from each well will be collected during the summer months of July and August, if possible, but may be collected as late as October.

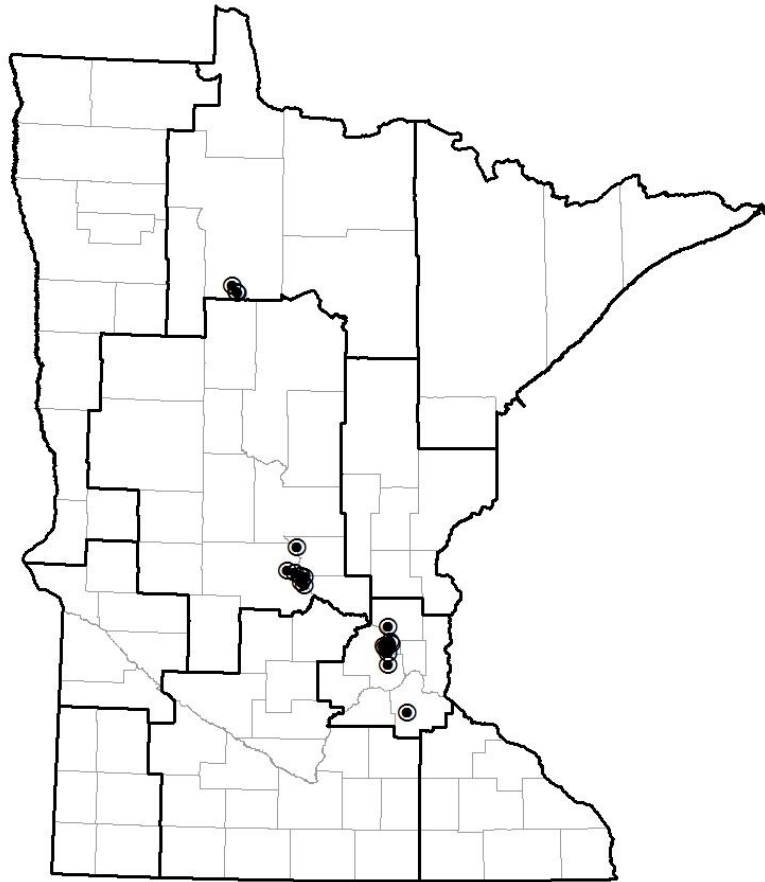


Figure 5. Typical locations for urban groundwater monitoring sites (actual locations vary by year).

5. MAINTENANCE OF NETWORK WELLS AND SITES

Replacement wells. Occasionally wells in the network may need to be replaced, closed or discontinued for various reasons. When necessary, replacement wells will be located as close to the existing well as possible. If a replacement well cannot be installed near the existing well, a new site, based on site selection criteria in the program design document, will be selected. Wells will also need major maintenance or repair on an unknown frequency. There are 16 sites identified for replacement, closure, abandonment or major maintenance and repair during the 2012 calendar year as indicated in Table 4. It is not known if funding will be available for any replacement wells during 2012.

Table 4. Sites to be closed, dropped, repaired or replaced during 2012.

PMR	County	Site	Well(s)	Close/replace/repair/drop	Reason
4	Todd	77-E3	639580 639581	Close	Land use change; wells fenced off in summer 2011
4	Morrison	49-C9	676380	Close	Land use change - now urban
4	Stearns	73-J8	616527 616528	Close	Denied future access by land owner
4	Otter Tail	56-F3-2	623640 623641	Close	Land use change - now urban
5	Isanti	30005	243879	Drop	Poor location, bad wells
6	Chippewa	12101	733730	Repair, close or replace	Broken break-away
9	Winona	Trout Valley	Trout Valley	Drop	Not ag land use - Forested

Installation of wells at new locations. Additional wells at previously unmonitored locations may be installed as resources allow. At the time of the publication of this document, funds for installation of wells at new sites were uncertain.

Evaluation of existing wells. Existing monitoring wells installed by other state or federal agencies remain the most cost effective means of collecting groundwater samples. The program will continue to assess existing wells of which it becomes aware. When a suitable, functioning well is discovered, it may or may not be immediately added to the program due to laboratory sample load constraints. All such wells will be added to a list the program will maintain for future reference when expansion of the network becomes possible or necessary. The search for additional existing wells will continue during 2012.

6. 2012 DATA ANALYSIS AND REPORTS

The program develops an annual report every year. During 2012, analysis of data for the 2011 report will begin in January with a report completion goal of April 30, 2012. Goals and objectives of the annual report are largely established by the information needs of the MDA pesticide management program. Additional reports covering specific components of the groundwater program may be completed during the year. Although no specific reports have yet been established, the program is considering detailed reports on various aspects of the monitoring program. Possible reports may include a detailed analysis of trends over time in pesticide concentrations and occurrence, and the analysis of spatial trends within and between regions.

7. QUALITY ASSURANCE SAMPLING

The groundwater monitoring program collects additional samples used to ensure the quality of the program's results. Samples to be collected in 2012 include field blanks, replicates (sometimes referred to as duplicates), field equipment blanks, and field equipment post-cleaning blanks all of which are submitted to the laboratory as regular samples. Field blanks and replicates will each be collected at a rate of 1 in 20 regular samples (5%). Field equipment blanks are collected once during each sampling round (2 times per year) by each field staff. Field equipment post-cleaning blanks, following laboratory based cleaning of the field equipment, are collected at the beginning of each sampling round by each field staff. Approximately 14 sets of field blanks, 14 sets of replicates, 12 sets of field equipment blanks and 12 sets of field equipment post-cleaning blanks will be collected during 2012. Data from the quality assurance samples will be checked against regular sample results as they become available. Results will additionally be shared with the analytical laboratory for the purposes of their internal quality control process.

8. APPENDIX

Appendix A1. 2012 list for GC-MS (gas chromatography mass spectrometry) and LC-MS/MS (liquid chromatography with tandem mass spectrometry) pesticide and pesticide degradates analyzed in groundwater with associated method reporting limit (MRL).

Common Name	Type	1 ug/L = 1,000 ng/L	
		GC-MS	LC-MS/MS
		MRL (ug/L)	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		13.3
Acetamiprid	Insecticide		25
Acetochlor	Herbicide	0.05	
Acetochlor ESA	Degradate		30
Acetochlor OXA	Degradate		33.3
Alachlor	Herbicide	0.05	
Alachlor ESA	Degradate		41.6
Alachlor OXA	Degradate		33.3
Aldicarb sulfone	Insecticide		15
Aldicarb sulfoxide	Insecticide		50
Atrazine	Herbicide	0.05	
DEDI Atrazine	Degradate		50
Deisopropylatrazine	Degradate	0.2	
Desethylatrazine	Degradate	0.05	
Hydroxyatrazine	Degradate		6.7
Azoxystrobin	Fungicide		10
Bensulfuron-methyl	Herbicide		16.7
Bentazon	Herbicide		0.8
Boscalid	Fungicide	0.3	
Bromacil	Herbicide		20
Carbaryl	Insecticide		25
Carbofuran	Insecticide		13.3
Chlorantraniliprole	Insecticide		50
Chlorimuron-ethyl	Herbicide		20
Chlorothalonil	Fungicide	0.12	
Chlorpyrifos	Insecticide	0.04	

Appendix B1.continued. 2012 list for GC-MS (gas chromatography mass spectrometry) and LC-MS/MS (liquid chromatography with tandem mass spectrometry) pesticide and pesticide degradates analyzed in groundwater with associated method reporting limit (MRL).

Common Name	Type	1 ug/L = 1,000 ng/L	
		GC-MS	LC-MS/MS
		MRL (ug/L)	MRL (ng/L)
Clomazone	Herbicide	0.1	
Clopyralid	Herbicide		41.6
Clothianidin	Insecticide		25
Cyanazine	Herbicide	0.2	
Cyfluthrin	Insecticide	0.5	
Diazinon	Insecticide	0.12	
Dicamba	Herbicide		50
Dichlorprop	Herbicide		50
Difenoconazole	Fungicide		25
Dimethenamid	Herbicide	0.05	
Dimethenamid ESA	Degradate		6.7
Dimethenamid OXA	Degradate		10
Dimethoate	Insecticide	0.22	
Disulfoton	Insecticide	0.15	
Disulfoton Sulfone	Insecticide		20
Diuron	Herbicide		13.3
EPTC	Herbicide	0.23	
Esfenvalerate	Insecticide	0.2	
Ethalfuralin	Herbicide	0.15	
Flufenacet OXA	Herbicide		8.3
Flumetsulam	Herbicide		50
Fonofos	Insecticide	0.1	
Halosulfuron-methyl	Herbicide		30
Hexazinone	Herbicide		10
Imazamethabenz-methyl	Herbicide		5
Imazamethabenz Acid	Degradate		10
Imazamox	Herbicide		13.3
Imazapic	Herbicide		10
Imazapyr	Herbicide		8.3
Imazaquin	Herbicide		16.7

Appendix C1.continued. 2012 list for GC-MS (gas chromatography mass spectrometry) and LC-MS/MS (liquid chromatography with tandem mass spectrometry) pesticide and pesticide degradates analyzed in groundwater with associated method reporting limit (MRL).

Common Name	Type	1 ug/L = 1,000 ng/L	
		GC-MS MRL (ug/L)	LC-MS/MS MRL (ng/L)
Imazethapyr	Herbicide		6.7
Imidacloprid	Insecticide		20
Isoxaflutole	Herbicide		40
Isoxaflutole DKN	Degradate		50
Lambda Cyhalothrin	Insecticide	0.2	
Linuron	Herbicide		20
Malathion	Insecticide	0.09	
MCPA	Herbicide		5
MCPB	Herbicide		10
MCPP	Herbicide		50
Mesotrione	Herbicide		50
Metalaxyl	Fungicide		8.3
Metolachlor	Herbicide	0.07	
Metolachlor ESA	Degradate		10
Metolachlor OXA	Degradate		10
Metribuzin	Herbicide	0.1	
Metribuzin DA	Degradate	1 (estimated)	
Metribuzin DADK	Degradate	1 (estimated)	
Metribuzin DK	Degradate	1 (estimated)	
Metsulfuron-methyl	Herbicide		23.3
Myclobutanil	Fungicide	0.2	
Neburon	Herbicide		10
Nicosulfuron	Herbicide		26.6
Norflurazon	Herbicide		20
Oxadiazon	Herbicide	0.05	
Parathion-methyl	Insecticide	0.12	
Pendimethalin	Herbicide	0.08	
Phorate	Insecticide	0.12	
Picloram	Herbicide		41.6
Prometon	Herbicide	0.1	
Prometryn	Herbicide		3.3

Appendix D1.continued. 2012 list for GC-MS (gas chromatography mass spectrometry) and LC-MS/MS (liquid chromatography with tandem mass spectrometry) pesticide and pesticide degradates analyzed in groundwater with associated method reporting limit (MRL).

Common Name	Type	1 ug/L = 1,000 ng/L	
		GC-MS	LC-MS/MS
		MRL (ug/L)	MRL (ng/L)
Propachlor	Herbicide	0.1	
Propachlor ESA	Degradate		30
Propachlor OXA	Degradate		10
Propazine	Herbicide	0.1	
Propiconazole	Fungicide	0.2	
Propoxur	Insecticide		10
Pyraclostrobin	Fungicide	0.23	
Saflufenacil	Herbicide		15
Siduron	Herbicide		6.7
Simazine	Herbicide	0.1	
Sulfometuron-methyl	Herbicide		8.3
Tebuconazole	Fungicide	0.2	
Tebuprimiphos	Fungicide	0.1	
Tembotrione	Herbicide		50
Terbufos	Insecticide	0.19	
Tetraconazole	Fungicide	0.15	
Thiamethoxam	Insecticide		25
Thifensulfuron-methyl	Herbicide		16.7
Thiobencarb	Herbicide		8.3
Triallate	Herbicide	0.1	
Triasulfuron	Herbicide		23.3
Triclopyr	Herbicide		50
Trifluralin	Herbicide	0.17	
zeta-Cypermethrin	Insecticide	0.5	

Appendix B. 2012 Analysis Goals by PMR or Special Project

Setting	PMR #	GC-MS	LC-MS/MS	Nitrate-N
Ag	1	14	14	14
Ag	2	0	0	0
Ag	3	0	0	0
Ag	4	83	83	83
Ag	5	16	16	16
Ag	6	18	18	18
Ag	7	14	14	14
Ag	8	22	22	22
Ag	9	69	69	69
Ag	10	0	0	0
Urban	Urban (multiple PMRs)	20	20	0
Deep Well	4	16	16	16
Total	All	272	272	252