Groundwater Monitoring for Pesticides and Nitrate in Greenfield Bench, Montana; Summary of Findings 1992-2015

Montana Department of Agriculture
Groundwater Protection Program
Helena, Montana

Introduction

The 1989 Montana Agricultural Chemical Groundwater Protection Act (MCA Title 80, Chapter 15, Sections 80-15-101 through 80-15-414) directs the Groundwater Protection Program (GWPP) of the Montana Department of Agriculture (MDA) to monitor the occurrence and concentration of agricultural chemicals in groundwater in Montana. The Montana Numeric Water Quality Standards for drinking established by the Montana Department of Environmental Quality (DEQ) are used as benchmarks for comparisons of any pesticide residues or nitrates detected.

GWPP monitoring is conducted by collecting groundwater samples and analyzing them for residues of pesticides (herbicides, insecticides, and fungicides) and fertilizers (as nitrate and nitrite). The program currently has two different methods for determining potential impacts to groundwater, a permanent monitoring well network across the state which is sampled twice per year, and special sampling projects where a specified region with vulnerable or susceptible groundwater is targeted for more intensive sampling than is provided by the permanent monitoring well network. Regional projects usually involve sampling from private wells and non-MDA monitoring wells (e.g. those established by the Bureau of Mines or DEQ).

The first GWPP regional monitoring project began in 1992 in the Greenfield Bench region of central Montana. Samples were obtained from monitoring, municipal, and private water-supply wells. In 1994 and 1995 imazamethabenz methyl, the active ingredient in the herbicide Assert, was detected in the monitoring wells. Sampling was expanded in 1996 as part of a wellhead protection project for the town of Fairfield. The 1996 sampling also revealed detections of imazamethabenz methyl as well as clopyralid, prometon and picloram in six additional wells. By the end of 1996 there were a total of thirteen wells with detectable pesticide concentrations, four of which were public water supply wells. These detections led to the development of the Greenfield Bench Specific Management Plan (SMP) that was active from June 22, 2001 until September 8, 2006. While the SMP was concluded in 2006, the sampling initiated by the SMP continued through 2015. The results of the last ~20 years of sampling activities in the region indicate that a new SMP is not necessary for this region, and that the existing sampling program should be scaled back in in favor of redirecting those resources to higher-priority areas. This report summarizes those results and lays out the rationale for that decision.

Background

Study Site

The Greenfield Bench (aka Fairfield Bench or “the Bench”) is located about 30 miles northwest of Great Falls, MT and encompasses approximately 85,000 acres in southern Teton and northern Cascade counties (Figure 1). The Bench is located on the semi-arid high plains of central Montana with an elevation of over 4000 feet. The region experiences a dry continental climate, with a mean annual precipitation of 12.4 inches (Miller et al 2002). Estimated mean evapotranspiration for the region ranged from 35 to 40 inches per year (Osborne, 1983.) The Bench is bordered to the south by the Sun River, to the north and east by Muddy Creek and to the west by Freezeout Lake. The soils on the Bench are classified within the Rothiemay clay loam series. The Rothiemay series is described as a fine-loamy, mixed Aridic Calciboroll. The soils are described as well drained and alluvial in origin.

The Greenfield Irrigation District diverts water below Gibson Reservoir to the Pishkun and Willow Creek Reservoirs to irrigate ~83,200 acres (as of 2015). The irrigation district extends from the Choteau-Augusta Highway on the west to Muddy Creek on the east. The Sun River flows through the southern portion with the north and south portions fringed by dry land strips.

Groundwater was sampled at 21 locations across the Greenfield Bench (Figure 1), including 1 MDA permanent monitoring location (F-1), two municipal water supplies for the City of Fairfield, MT (PWS-1 & PWS-2), and 17 private wells.

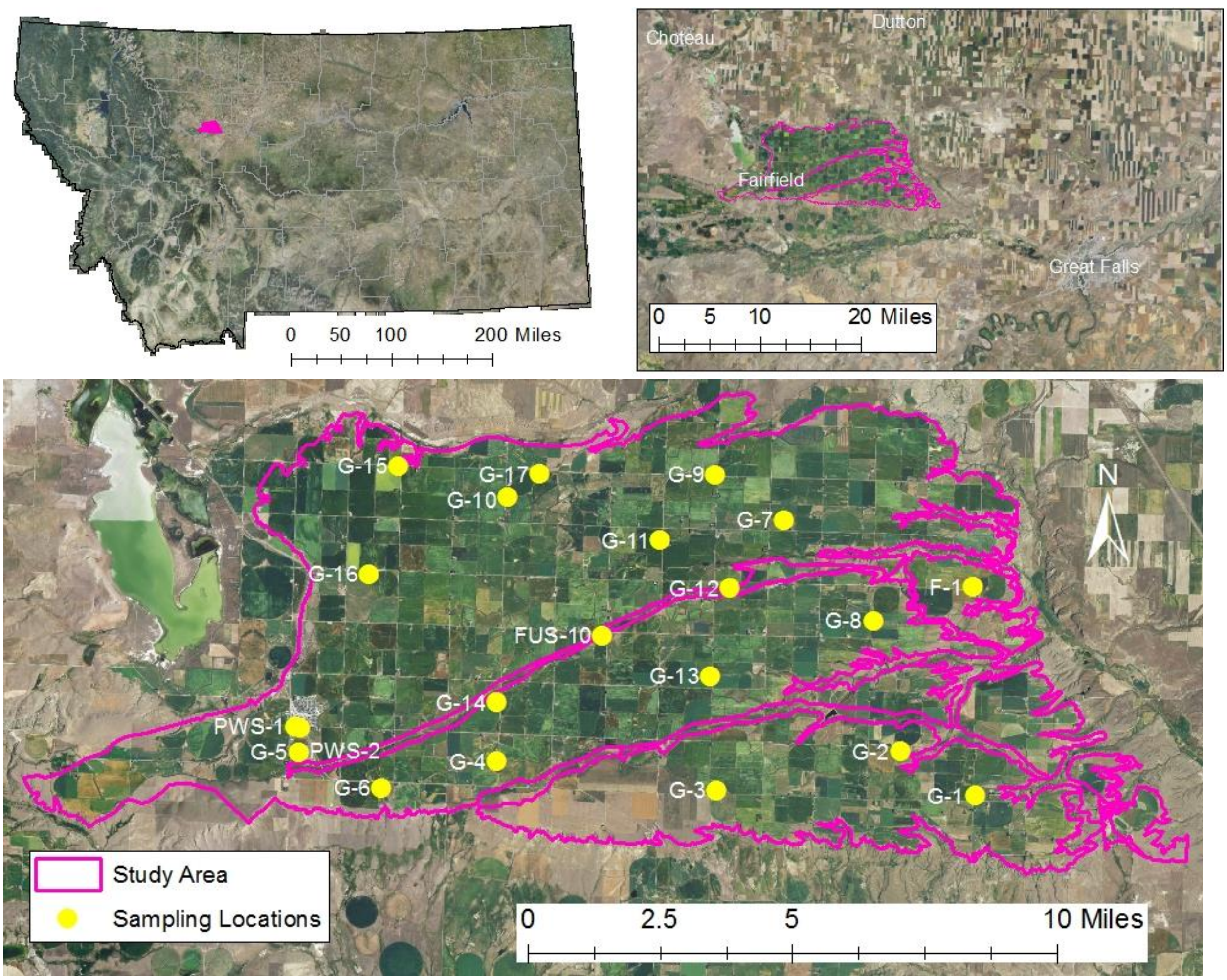

Figure 1: Location map of Greenfield Bench Study Area.

Geology

The bedrock of the Greenfield Bench consists of sedimentary rocks of the Cretaceous Colorado Group, including the Blackleaf and Marias River Formations described by Maughan (1961). The formations are primarily dark grey shales with interbeds of siltstone, sandstone, and bentonite clay layers. The Marias River Formation is the top of the bedrock and has an erosional surface formed before the deposition of the Tertiary and Quaternary aged gravels (Figure 2).

The three gravel terraces that collectively comprise the Greenfield Bench are all Quaternary or Tertiary in age and are interpreted as gravelly deposition features of the ancestral Sun River. The first bench, the oldest and highest elevation, is Tertiary in age and has an average topographic gradient of 24 ft/mile. The second bench lies 120 feet below the first bench and has an average gradient of 19 ft/mile. The third bench lies about 75 feet below the second and has an average topographic gradient of 19 ft/mile (Osborne 1983). Data obtained from drill holes and domestic wells indicate that the gravel thickness ranges from 3 to 50 feet in the bench, with an average thickness of about 19 ft. Overall the gravels that cover the Greenfield Bench are moderately well sorted, poorly stratified gravel consisting primarily of quartzite and argillite pebbles and cobbles. These gravels are believed to be derived from Precambrian rocks exposed in the headwaters of the ancestral Sun River (Nimick, 1996). Larger stones are more common on the western end of the Bench, where boulders over one foot in diameter are often present (Osborne, 1983).

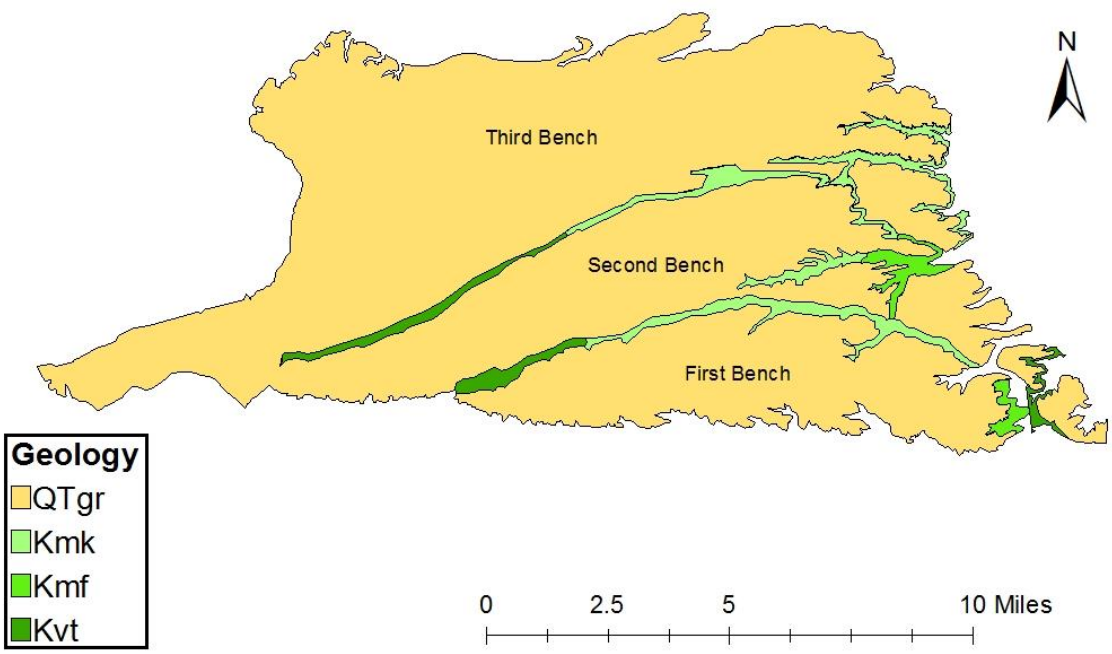

Figure 2: Geology map of Greenfield Bench Study Area.

Hydrology/ Hydrogeology

The terraced Quaternary gravels are the primary water-bearing units for municipal and domestic water uses on the Greenfield Bench. The sources of groundwater recharge to these units include: precipitation, canal losses, and on-farm irrigation. Discharge occurs through extraction by pumping wells, as groundwater discharge via drains and surface water features, and as evapotranspiration during the growing season from crop water demand. Osbourne (1983) estimated that about 65% of discharge occurred as groundwater baseflow into Muddy Creek. Groundwater is highly dependent on the seasonal effects of irrigation and precipitation; during irrigation season, groundwater levels may rise to the ground surface (Miller et al., 2002). Groundwater elevation and flow direction is estimated based on the Groundwater Information center (GWIC) well records for the Greenfield Bench. Groundwater elevations were determined from 427 well logs that recorded both surface elevation and static water level (Figure 3). From Figure 3, we can determine groundwater generally flows from the west- southwest to the east-northeast of the bench. These results are similar to observations by Miller et al. (2002).

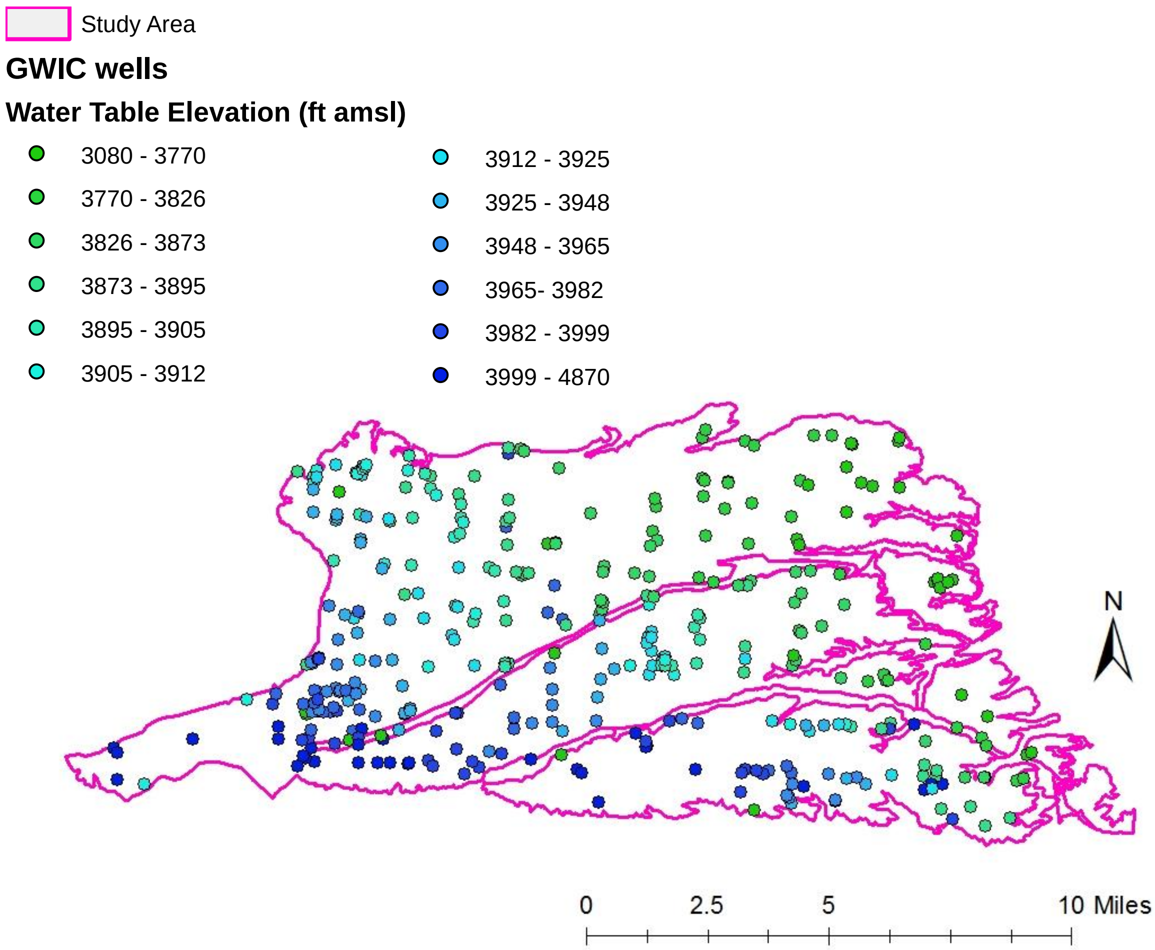

Figure 3: Groundwater elevation

Agriculture

The primary land use in the region is irrigated production of malting barley and to a lesser extent other small grains (mainly winter and spring wheat), alfalfa, non-alfalfa hay, and pasture. Figures 4 through 12 are from the 2016 USDA National Agricultural Statistics Service Cropland Data Layer and show little variation from year to year, with malting barley production covering >60% of the land area on the Greenfield Bench. The dominance of malting barley (and other small grains) production on the Greenfield Bench extends back into the 1990s.

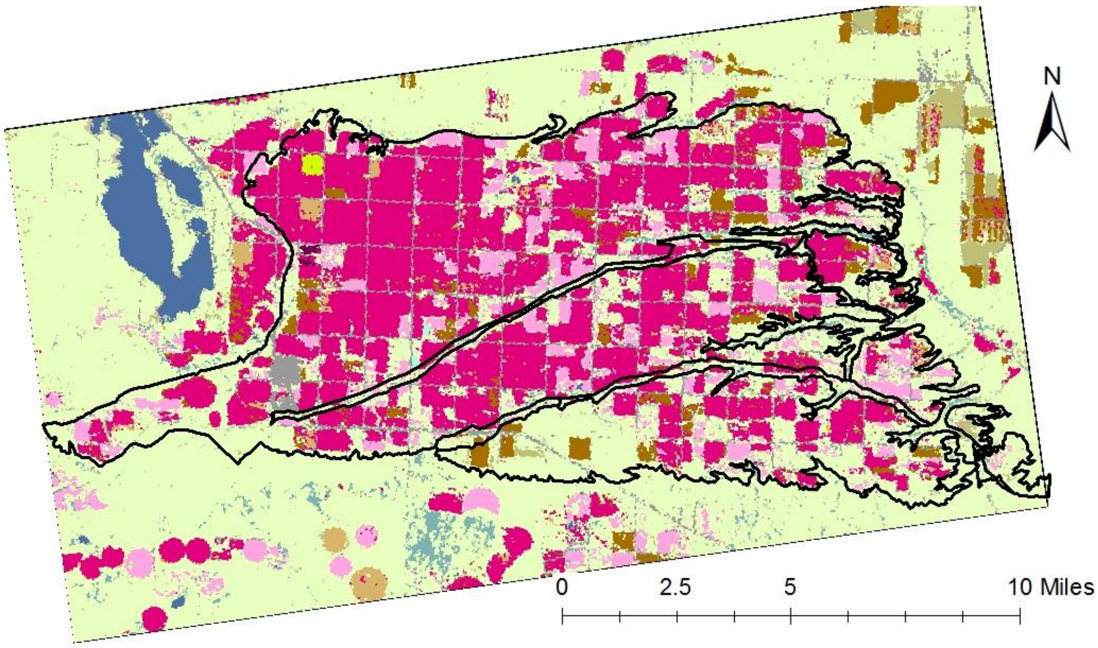

Figure 4: 2007 Crop Data Layer.

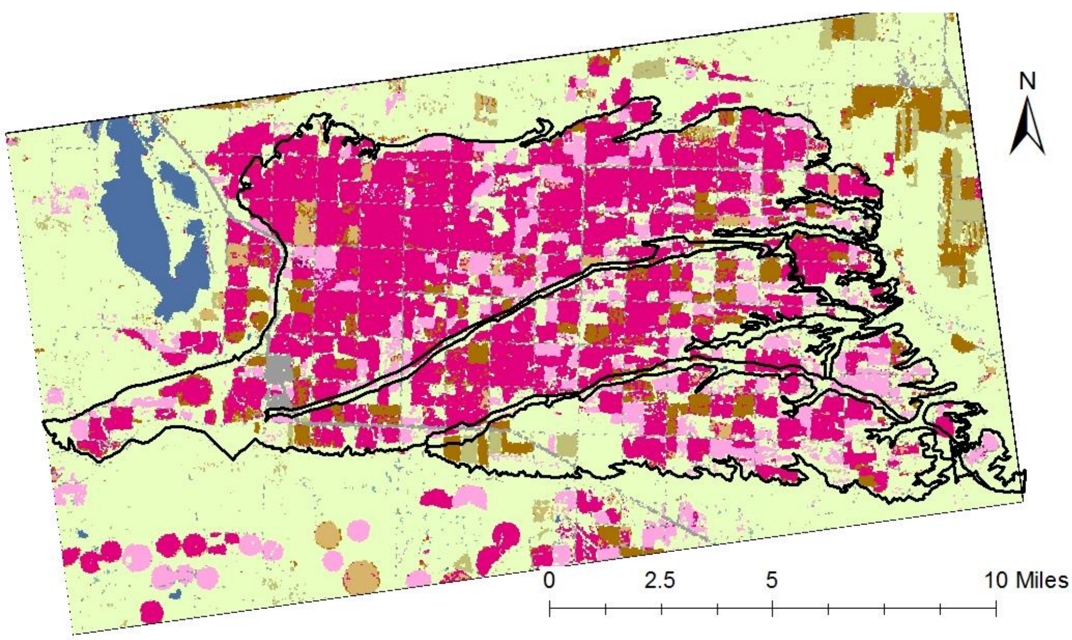

Figure 5: 2008 Crop Data Layer.

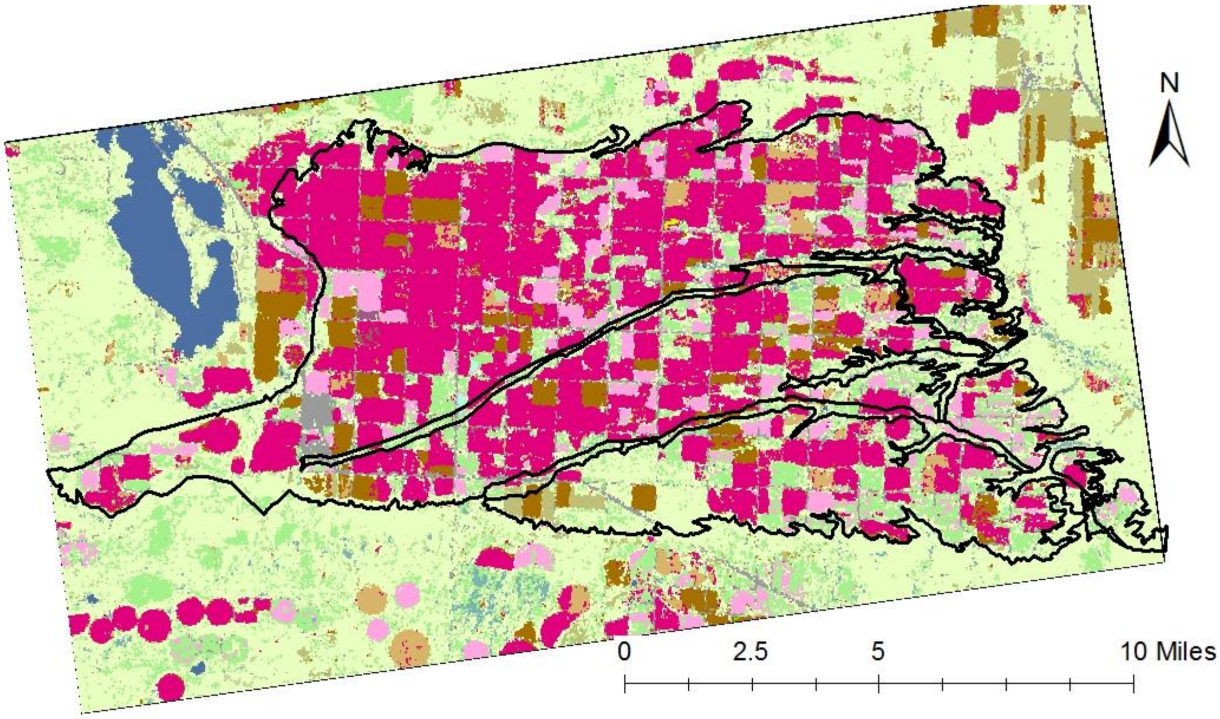

Figure 6: 2009 Crop Data Layer.

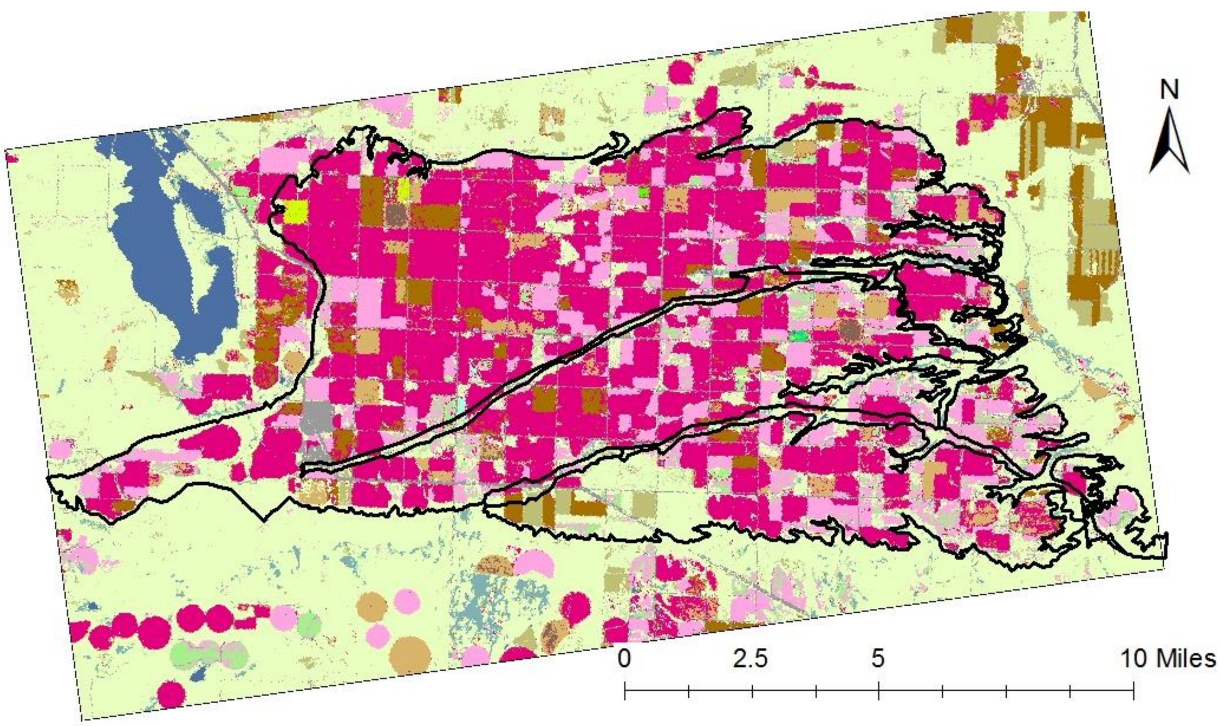

Figure 7: 2010 Crop Data Layer.

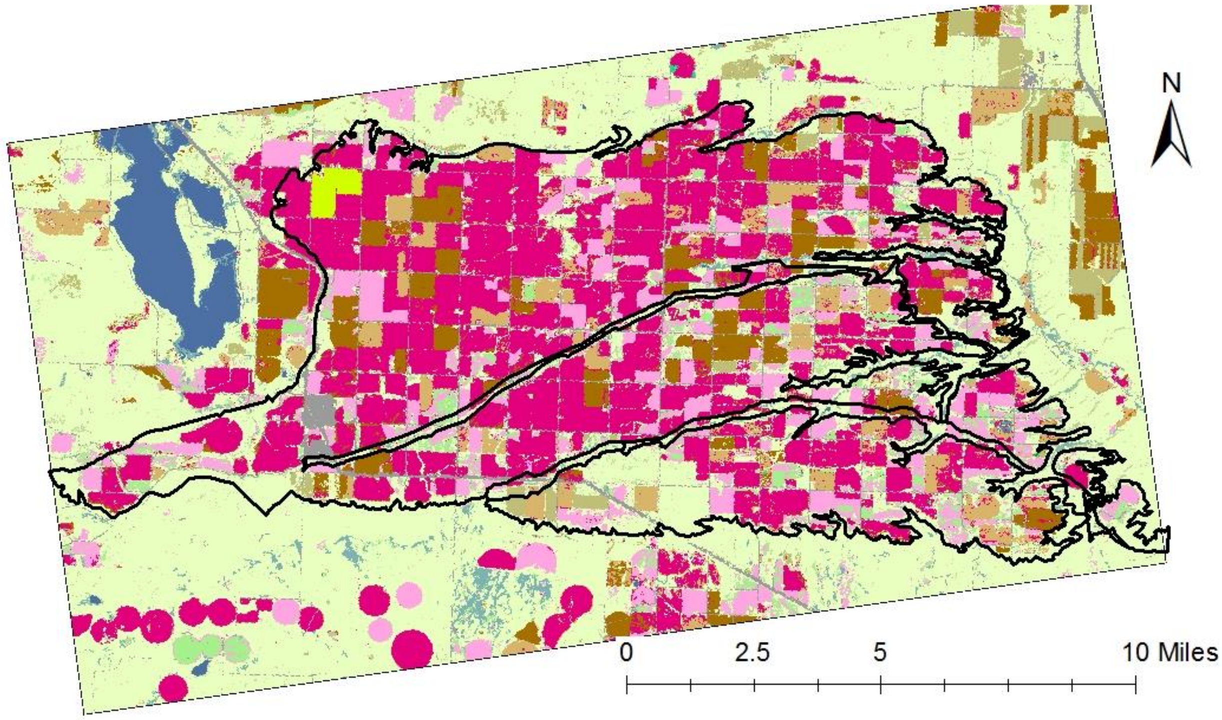

Figure 8: 2011 Crop Data Layer.

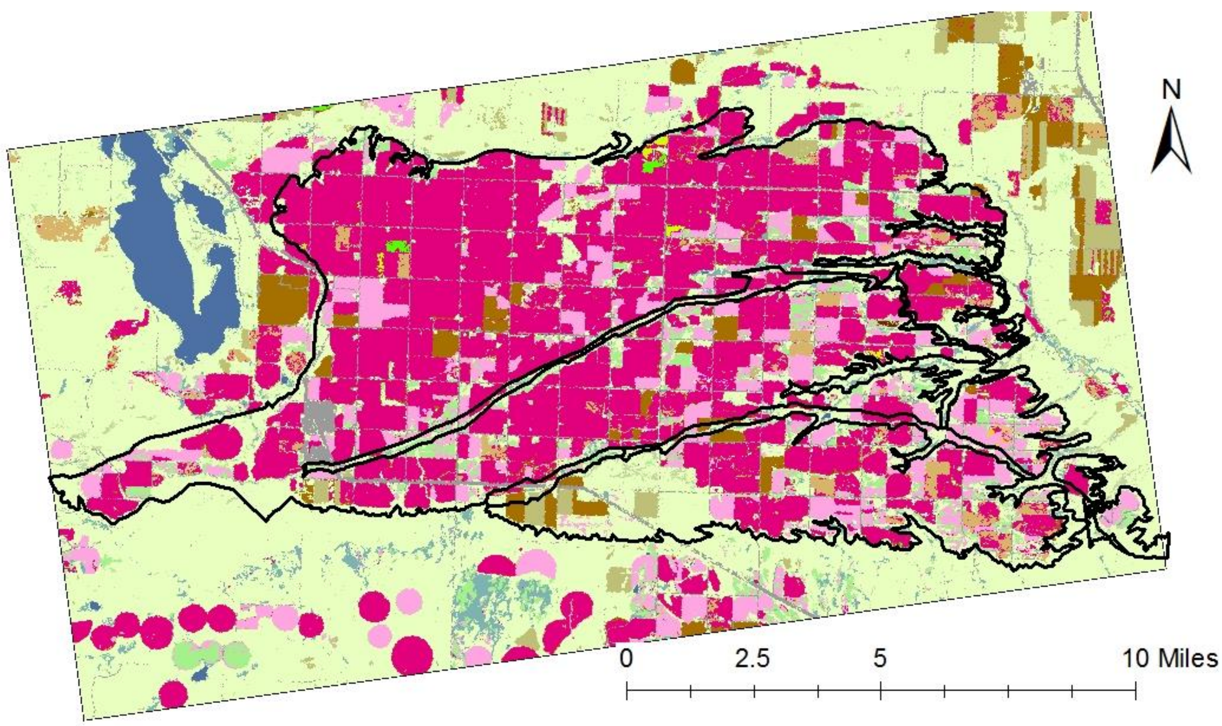

Figure 9: 2012 Crop Data Layer.

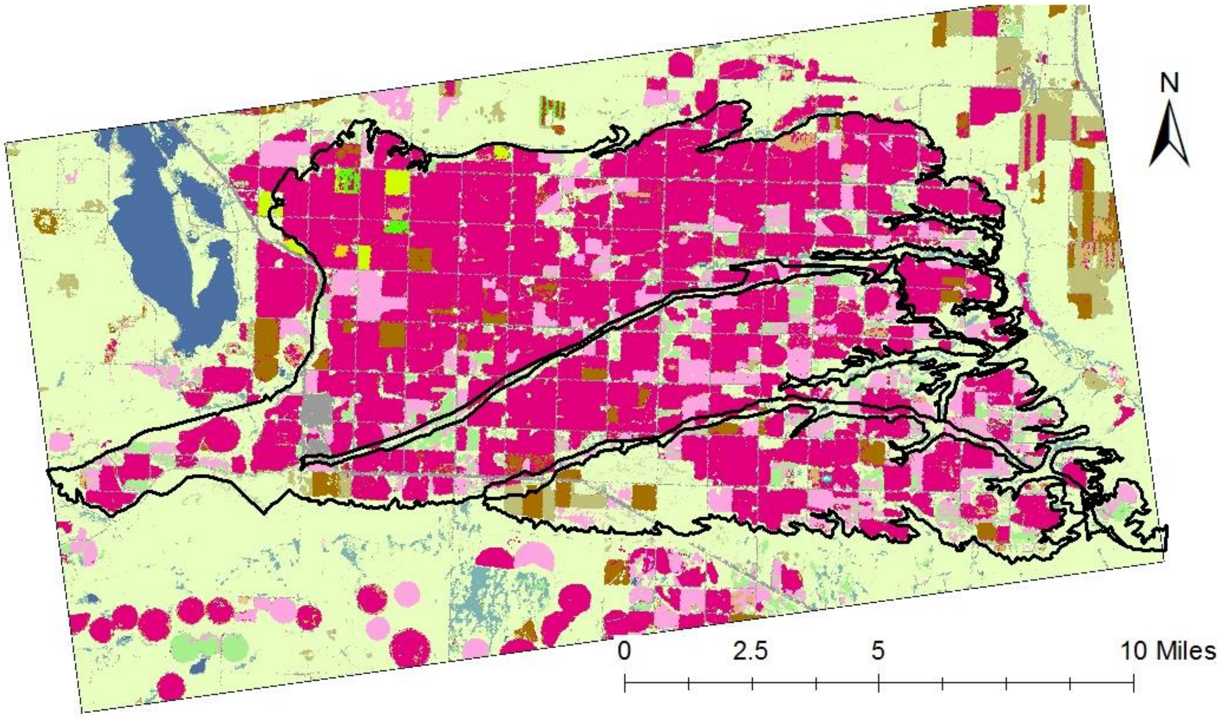

Figure 10: 2013 Crop Data Layer.

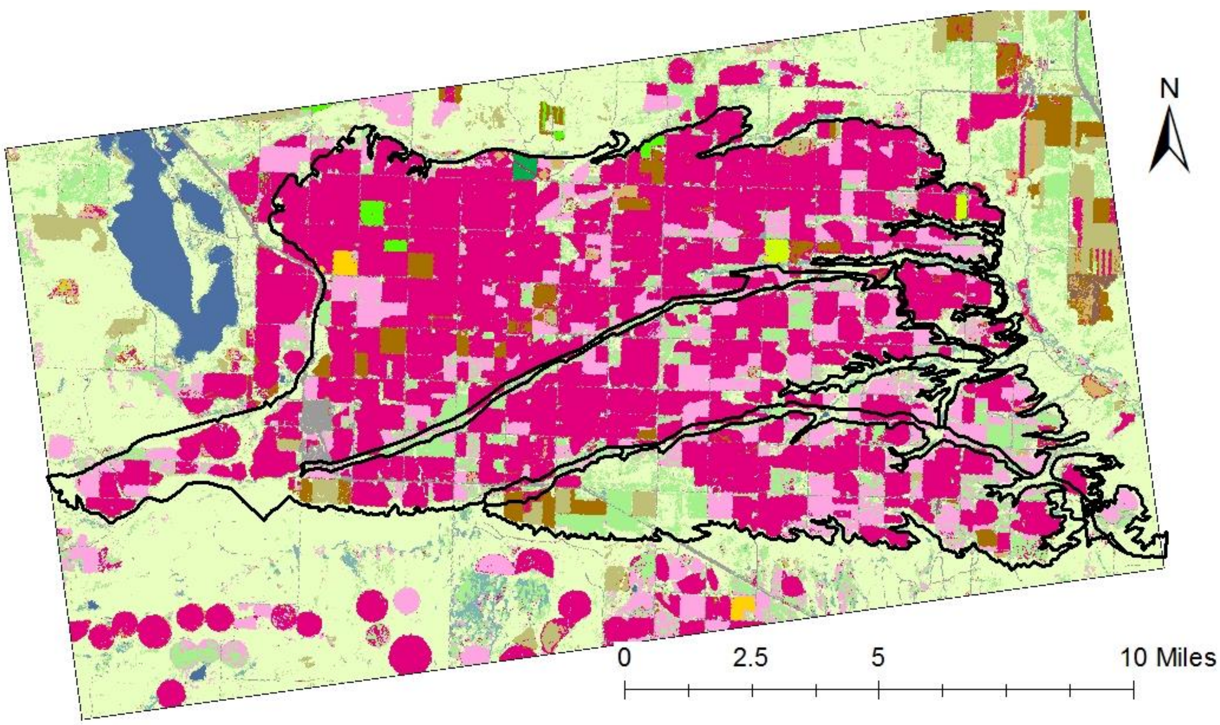

Figure 11: 2014 Crop Data Layer.

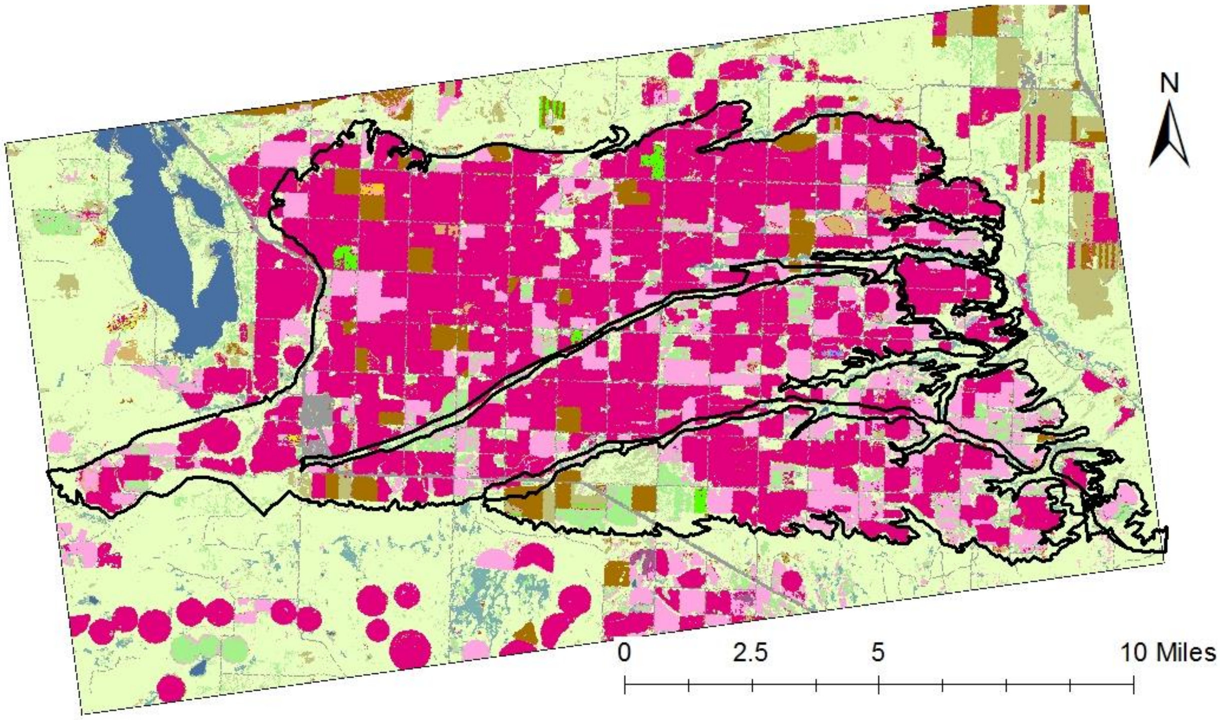

Figure 12: 2015 Crop Data Layer.

*Abbreviated Crop Data Layer Land Cover Categories

Agriculture

Non-agriculture

*Full list of Land Cover Categories in in Appendix B.

Irrigation

The Greenfield Irrigation District is fed by 3 reservoirs and approximately 295 miles of canals and lateral ditches. The reservoirs combined store almost 170,000 acre feet of water, most of it in the Gibson Reservoir (105,000 acre feet) and the rest in the Pishkun Reservoir (32,050 acre feet) and the Willow Creek Reservoir (32,300 acre feet).

Irrigation patterns on the Bench have changed over the last decades. In 1980, Walther (1981) determined that flood irrigation was practiced on 90% of ~81,000 irrigated acres while pivot and sprinkler irrigation was practiced on only 10%. By 2002 Miller et al. (2002) estimated that flood irrigation had fallen to 55-60% of the irrigated acres and pivot and sprinkler irrigation had risen to 40-45%. As of 2014, based on irrigated land areas reported to the Montana Department of Revenue (Figure 13), irrigation acreage on the Greenfield Bench is 50% flood, 38% pivot, and 12% sprinkler.

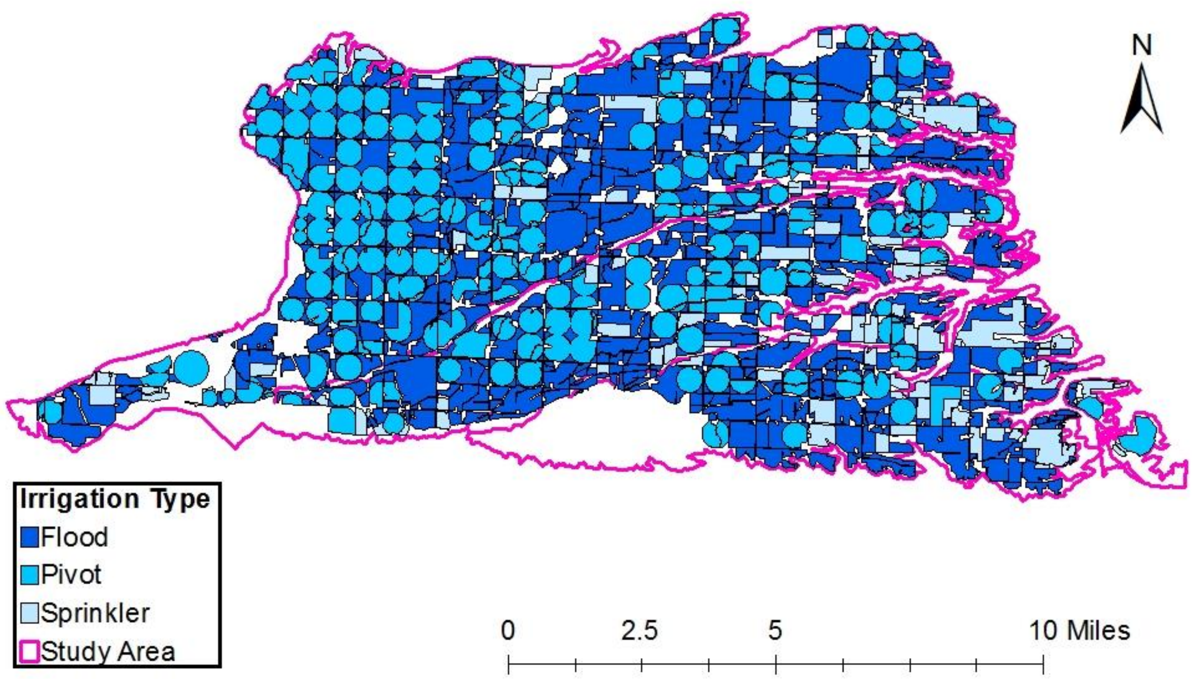

Figure 13: Irrigation on Greenfield Bench.

Methods

Groundwater samples are collected according to GWPP standard operating procedures (SOPs). For each sample collected for analysis, the static water level (for monitoring wells only) is measured, the well casing is purged, and field parameters are measured. Field parameters include water temperature, pH, conductivity, dissolved oxygen, and TDS, measured with an YSI 556 MPS. Nitrate and nitrite concentrations are also measured in the field with Hach Aquacheck test strips (Cat. 27454-25). If nitrate concentration exceeds 2 ppm or if nitrite was detected at any concentration a lab analysis is also performed. Laboratory analyses for both pesticides and nitrate/nitrite are conducted by the MDA Analytical Laboratory Bureau using established chromatographic methods. Most pesticides are analyzed using solid phase extraction and liquid chromatography/mass spectrometry/mass spectrometry method (SPE/LC/MS/MS), except glufosinate/ glyphosate/ AMPA, which are analyzed using a specific chromatography method for those analytes. Groundwater samples are analyzed for ~100 pesticide analytes. There is a small year to year change as old analytes which have not been detected are removed and new analytes are added to address new products (active ingredients) or changes in pesticide labels that allow for expanded uses. Table 1 has a complete list of the detected analytes and their respective reporting limit for each year that detections occurred.

Detections are standardized using two methods to compensate for the low concentrations typical of these samples (typically <1% of the respective analytes water quality standard) and because the reporting limit (the lowest limit at which a sample can be accurately quantified) has decreased over time as analytical methods have improved. First, detections are reported as detection frequency, which is calculated as:

$$Analyte\ Detection\ Frequency\ (\%) = \frac{n_{detections}}{n_{analzyed}} \times 100$$

where $n_{detections}$ is the number of positive detections for a specific analyte and $n_{analyzed}$ is the number of times a water, sample was analyzed for that analyte.

The second method used to standardize detections is to compare the concentration detected to the respective water quality standards determined by DEQ and published in Circular DEQ-7, Montana Numeric Water Quality Standards (DEQ, 2012). Section 80-15-212 of the MCA requires that a specific management plan be developed and implemented if a detected analyte is 50% or greater of the standard or interim numerical standard, using the calculation method below:

$$Percent\ of\ Water\ Quality\ Standard\ (\%) = \frac{[C]_{measured}}{[C]_{water\ quality\ standard}} \times 100$$

where $[C]_{measured}$ is the analytically measured concentration of the analyte of concern and $[C]_{water\ quality\ standard}$ is the Montana Numeric Water Quality Standard for that analyte.

<table>
<tr><th rowspan="2">Analyte</th><th colspan="24">Reporting Limit (ppb)</th></tr>
<tr><th>1992</th><th>1993</th><th>1994</th><th>1995</th><th>1996</th><th>1997</th><th>1998</th><th>1999</th><th>2000</th><th>2001</th><th>2002</th><th>2003</th><th>2004</th><th>2005</th><th>2006</th><th>2007</th><th>2008</th><th>2009</th><th>2010</th><th>2011</th><th>2012</th><th>2013</th><th>2014</th><th>2015</th></tr>
<tr><td>2,4-D</td><td colspan="2"></td><td colspan="5">X</td><td colspan="7">0.28</td><td colspan="9">0.0045</td><td>0.009</td></tr>
<tr><td>Aminopyralid</td><td colspan="17"></td><td colspan="3">0.053</td><td colspan="3">0.015</td><td>0.03</td></tr>
<tr><td>Atrazine</td><td colspan="14"></td><td colspan="9">0.0022</td><td></td></tr>
<tr><td>Azoxystrobin</td><td colspan="14"></td><td colspan="4">0.0011</td><td colspan="3"></td><td>0.003</td><td colspan="2"></td></tr>
<tr><td>Bentazon</td><td colspan="14"></td><td colspan="7">0.0011</td><td colspan="3"></td></tr>
<tr><td>Bromacil</td><td colspan="10"></td><td colspan="2">3</td><td colspan="2">2.5</td><td colspan="6">0.0074</td><td colspan="3">0.0041</td><td></td></tr>
<tr><td>Bromoxynil</td><td colspan="19"></td><td colspan="4">0.006</td><td></td></tr>
<tr><td>Carbaryl</td><td colspan="17"></td><td>0.04</td><td colspan="6"></td></tr>
<tr><td>Chlorsulfuron</td><td colspan="14"></td><td colspan="5">0.0056</td><td colspan="5"></td></tr>
<tr><td>Clopyralid</td><td colspan="4"></td><td colspan="8">1</td><td colspan="2">0.5</td><td>0.007</td><td colspan="8">0.022</td><td>0.088</td></tr>
<tr><td>Clothianidin</td><td colspan="23"></td><td>0.016</td></tr>
<tr><td>Deethyl atrazine</td><td colspan="14"></td><td colspan="10">0.0017</td></tr>
<tr><td>Dicamba</td><td></td><td colspan="8">x</td><td colspan="6"></td><td>0.051</td><td colspan="8"></td></tr>
<tr><td>Diuron</td><td colspan="14"></td><td colspan="6">0.01</td><td colspan="3">0.0053</td><td></td></tr>
<tr><td>Flucarbazone</td><td colspan="19"></td><td colspan="4">0.0012</td><td></td></tr>
<tr><td>Fluroxypyr</td><td colspan="20"></td><td colspan="3">0.016</td><td></td></tr>
<tr><td>Glutaric Acid</td><td colspan="9"></td><td>X</td><td colspan="4">0.05</td><td colspan="10"></td></tr>
<tr><td>Hexazinone</td><td colspan="14"></td><td colspan="6">0.0059</td><td colspan="2">0.0015</td><td colspan="2"></td></tr>
<tr><td>Hydroxy atrazine</td><td colspan="17"></td><td>0.006</td><td colspan="6"></td></tr>
<tr><td>Imazamethabenz methyl acid metabolite</td><td colspan="4">X</td><td colspan="10">0.2</td><td colspan="6">0.0552</td><td colspan="4">0.0025</td></tr>
<tr><td>Imazamethabenz methyl ester</td><td colspan="4">X</td><td colspan="10">0.2</td><td colspan="10">0.001</td></tr>
<tr><td>Imazamox</td><td colspan="14"></td><td colspan="6">0.012</td><td colspan="4">0.0057</td></tr>
<tr><td>Imazapyr</td><td colspan="14"></td><td colspan="5">0.011</td><td colspan="5">0.0035</td></tr>
<tr><td>Imidacloprid</td><td colspan="14"></td><td colspan="10">0.0018</td></tr>
<tr><td>Malathion</td><td colspan="6"></td><td>0.4</td><td colspan="7"></td><td colspan="2">0.028</td><td colspan="8"></td></tr>
<tr><td>MCPA</td><td colspan="6"></td><td>1</td><td colspan="4"></td><td>1</td><td colspan="6"></td><td>0.002</td><td></td><td>0.002</td><td colspan="2"></td><td>0.005</td></tr>
<tr><td>MCPP</td><td colspan="15"></td><td>0.002</td><td colspan="4"></td><td>0.002</td><td colspan="3"></td></tr>
<tr><td>Metalaxyl</td><td colspan="14"></td><td>0.012</td><td colspan="2"></td><td colspan="2">0.012</td><td></td><td colspan="4">0.0035</td></tr>
<tr><td>Metsulfuron methyl</td><td colspan="18"></td><td>0.026</td><td colspan="2"></td><td colspan="2">0.01</td><td></td></tr>
<tr><td>Nitrate as Nitrogen *ppm</td><td colspan="19">1</td><td colspan="5">0.1</td></tr>
</table>

Table 1: Reporting limits for detected analytes by year.

Analyte	Reporting Limit (ppb)																							
	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
NOA 407854															0.0052									
NOA 447204															0.01									0.02
Picloram					0.4			0.4							0.14			0.14						
Prometon					0.3										0.0051						0.001			
Propiconazole																	0.01		0.01					
Pyrasulfotole																		0.023			0.0093		0.007	0.02
Pyroxsulam																			0.027		0.013		0.007	0.013
Simazine															0.0026			0.0026						
Sulfentrazone																					0.035			
Sulfometuron methyl																		0.01				0.0025		
Tebuthiuron															0.0011									
Thifensulfuron																			0.026		0.011		0.006	0.022
Tralkoxydim	X							X			0.05				0.0051									
Tralkoxydim acid											0.05				0.005									
Triasulfuron															0.026						0.0055			
Triclopyr																			0.011					0.022
Triticonazole															0.032						0.016			

Table 1 continued: Reporting limits for detected analytes by year.

Results and Discussion

Groundwater samples collected from the Greenfield Bench study area tested positive for 49 pesticide analytes from 1992 through 2015, with 18 of those pesticide analytes having a detection frequency over 10% (Figure 14). Analyte detection frequency ranged from <1%, indicating a single detection during the entire study period, to over 90%. Analyte detections typically change from year to year for several reasons, such as agricultural management practices like crop rotations, pesticide rotations to prevent resistance, and new pesticide product registrations. One way to compensate for pesticide use variations is to look at classes of pesticides (Figure 15). A class of pesticides is a group of pesticides that have a similar chemical structure and mode of action; they are used for the same reasons. Appendix C has a list detailing analytes in each pesticide class. This approach yields the following general conclusions:

- During this study 20 different pesticide classes and fertilizer (as nitrate) were detected (Figure 15), with 8 of those classes represent ~77% of the detections.
- The most commonly detected pesticide class, as number of detections, was imidazolinone with 1032 detections in 1588 samples or 65%.
- The pesticide class with the highest detection frequency was the pyrazole class with 258 detections out of 320 samples or 81%.

With the dominance of the malt barley production in the region (Figures 4 through 12) combined with the presence of shallow aquifer used for drinking water, it is not surprising that pesticides or their metabolites commonly used in barley and other small grain production were detected in groundwater samples on the Greenfield Bench. While these detections frequently occur, it is important to note that the detected concentrations of pesticides or their metabolites are extremely low, always in the ppb (part per billion) or ppt (part per trillion) level. In general:

- Pesticide analyte median detected concentrations are <1% of the respective analytes standard. The action threshold for MDA to initiate an SMP is 50% (Table 2).
- Median detected nitrate concentration was 50% of the Montana Human Heath Standard for nitrate as nitrogen groundwater. However, this calculation excluded samples with no detection and samples tested in the field to have a nitrate concentration < 2 ppm. We also cannot rule out non-fertilizer sources of nitrate such as septic systems and animal manure.

The following sections provide more information on analytes detected at a frequency greater than 10%, along with concentration summaries.

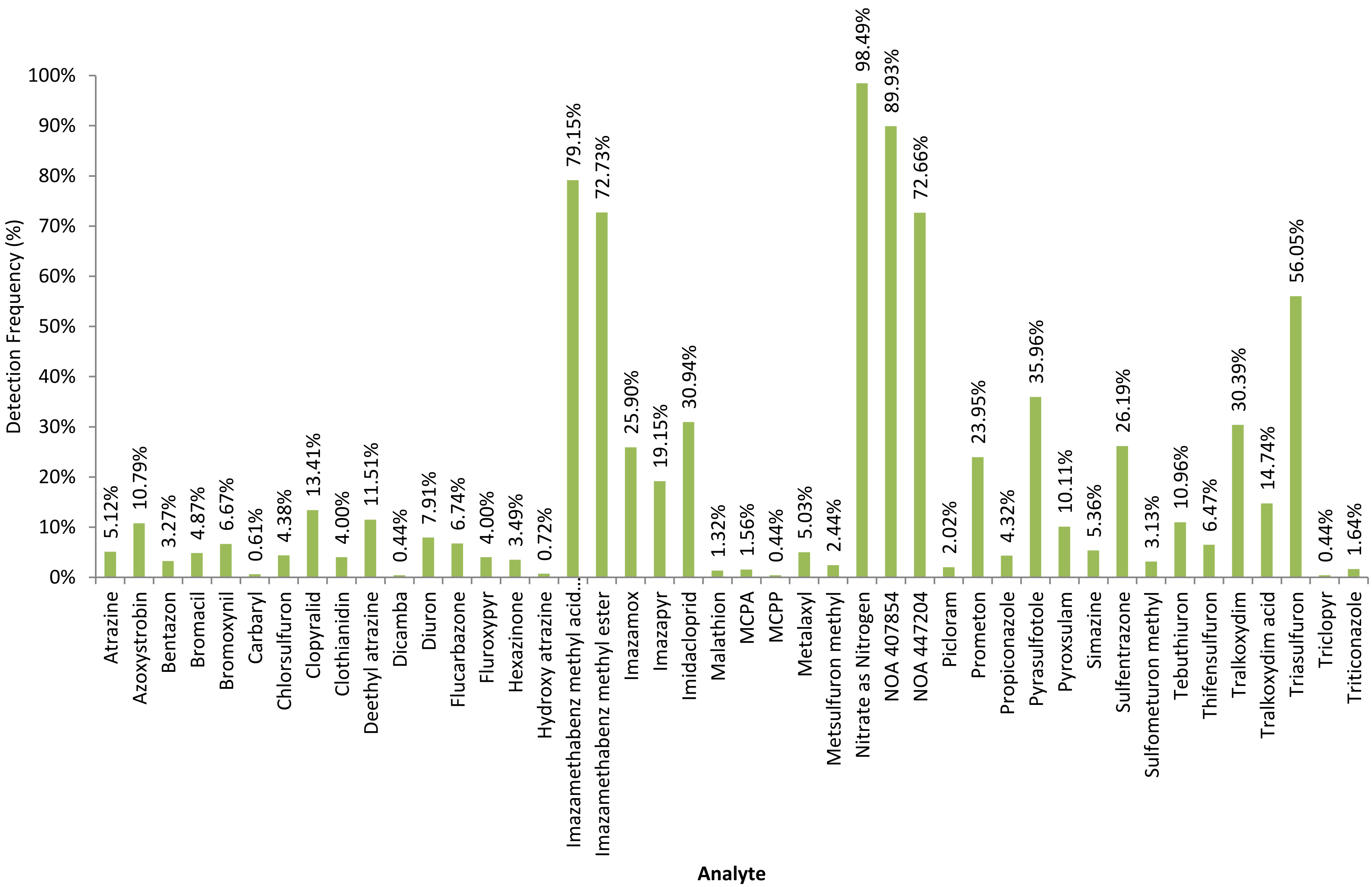

Figure 14: Detection Frequency for analytes on the Greenfield Bench. Calculated as the percent of samples that had detectable concentrations of a given pesticide.

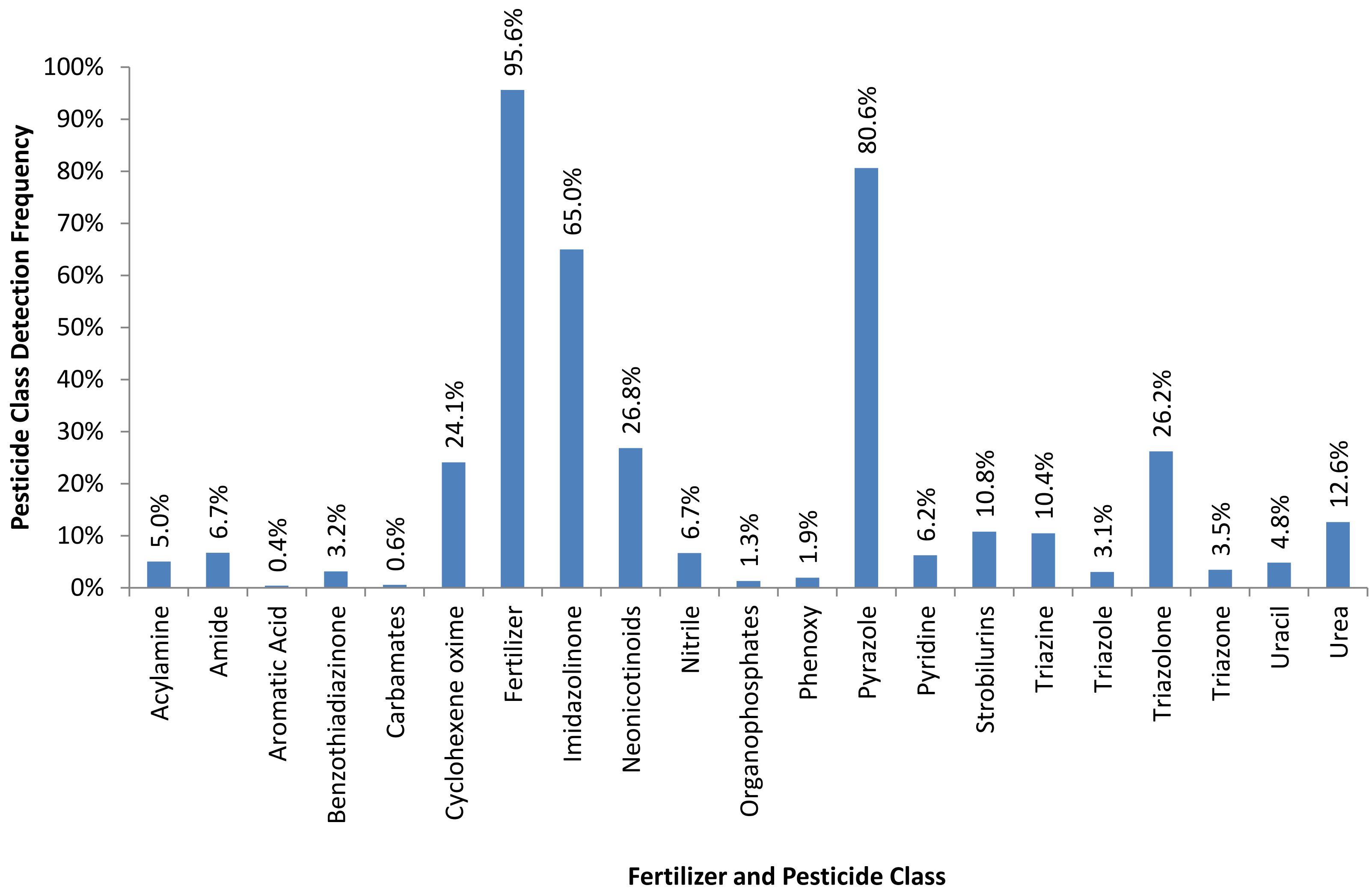

Figure 15: Fertilizer and Pesticide Class detection frequency during the Greenfield Bench Study. Fertilizer was measured as nitrate and may include non-fertilizer nitrogen sources such as septic systems and animal waste.

Analyte	Median Detected Concentration (ppb)	Sum Parent + metabolites (ppb)	DEQ-7 Human Health Standard for Groundwater (ppb)	Percent Drinking water standard
2,4-D	0.007		70	0.0100%
Aminopyralid	0.02		4000	0.0005%
Atrazine	0.0022	0.0103	3	0.3433%
Deethyl atrazine	0.0017			
Hydroxy atrazine	0.0064			
Azoxystrobin	0.0011		1000	0.0001%
Bentazon	0.0011		200	0.0006%
Bromacil	2.2		90	2.4444%
Bromoxynil	0.0063		3.4	0.1853%
Carbaryl	0.04		700	0.0057%
Chlorsulfuron	0.0056		1750	0.0003%
Clopyralid	0.2		1000	0.0200%
Clothianidin	0.016		700	0.0023%
Dicamba	0.2305		200	0.1153%
Diuron	0.016		10	0.1600%
Flucarbazone	0.0012		3000	0.0000%
Fluroxypyr	0.016		7000	0.0002%
Hexazinone	0.05		400	0.0125%
Imazamethabenz methyl acid metabolite	0.58	1.095	400	0.2738%
Imazamethabenz methyl ester	0.515			
Imazamox	0.0125		20000	0.0001%
Imazapyr	0.011		21000	0.0001%
Imidacloprid	0.0018		400	0.0005%
Malathion	0.12		100	0.1200%
MCPA	0.12		4	3.0000%
MCPP	0.0022		300	0.0007%
Metalaxyl	0.0035		600	0.0006%
Metsulfuron methyl	0.018		2000	0.0009%
Nitrate as Nitrogen	5.0		10	50.0%
NOA 407854	0.15	0.168	2000	0.0084%
NOA 447204	0.018			
Picloram	0.14		500	0.0280%
Prometon	0.0052		100	0.0052%
Propiconazole	0.011		700	0.0016%
Pyrasulfotole	0.0535		70	0.0764%
Pyroxsulam	0.015		7000	0.0002%

Table 2: Median detected concentration, groundwater standard, and percent standard.

Analyte	Median Detected Concentration (ppb)	Sum Parent + metabolites (ppb)	Groundwater Drinking Water Standard (ppb)	Percent Drinking water standard
Simazine	0.0026		4	0.0650%
Sulfentrazone	0.035		700	0.0050%
Sulfometuron methyl	0.004		2000	0.0002%
Tebuthiuron	0.012		500	0.0024%
Thifensulfuron	0.011		910	0.0012%
Tralkoxydim	0.081	0.1365	20	0.6825%
Tralkoxydim acid	0.0555			
Triasulfuron	0.036		70	0.0514%
Triclopyr	0.0285		400	0.0071%
Triticonazole	0.024		1000	0.0024%

Table 2 continued: Median detected concentration, groundwater standard, and percent standard.

Nitrate:
Nitrate was detected in 95.6% of the samples collected. Nitrate detected in groundwater can have several human caused sources such as fertilizers, septic tank drain field runoff, and livestock waste as well as natural sources like decomposing organic matter, atmospheric deposition, and underlying geologic formations. The Montana Human Heath Standard for nitrate (as nitrogen) in groundwater is 10 ppm (10,000 ppb). Based on the median of detected concentrations (Table 2), the typical detection is 50% of the groundwater standard.

Table 2: Detected Triasulfuron Concentration Summary (ppb)	
$n_{detected}$	326
Min*	1.0*
Q1	3.8
Median	5.0
Q3	6.5
Max	20

While the median nitrate detection was 5.0 ppm, there was significant variability between the locations ranging from <2 ppm to over 10 ppm (Figure 16). The minimum value in Table 2 excludes the no detections that were not also analyzed by the Analytical Lab. Only one site had a median nitrate concentration greater than 10 ppm. In response, the land owners at that location have installed a reverse osmosis system to lower nitrate concentrations in water used for drinking and cooking.

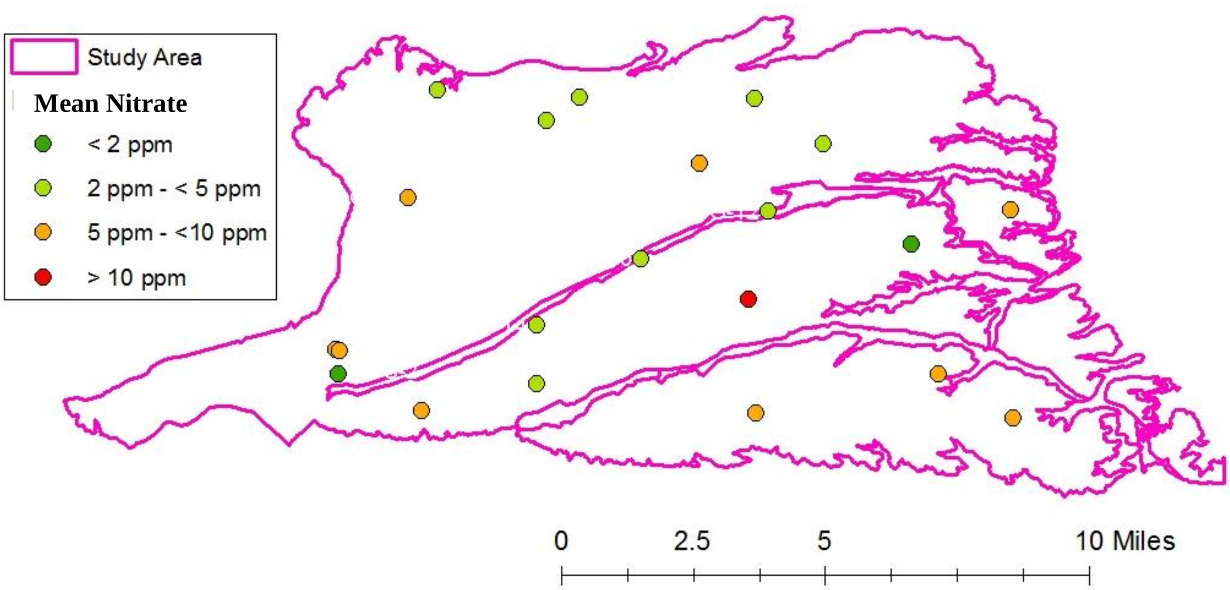

Figure 16: Median nitrate concentrations for each sampling site in the Greenfield Bench study area.

It is not possible to accurately identify the sources of nitrate in the groundwater of a rural area such as the Greenfield Bench. There are a few small towns, but housing units are generally widely distributed across the landscape. Fertilizer use on lawns and farms, an abundance of livestock, residential septic systems, and natural sources all contribute to the nitrate levels that are present.

Most nitrate detections are at levels considered background, even though many of them do exceed 2 ppm. The distribution of nitrate concentrations in the Greenfield Bench groundwater changed very little between a 1981 study by Walter and the MDA dataset (1992-2015; see Figure 17a), suggesting that the current situation is relatively stable.

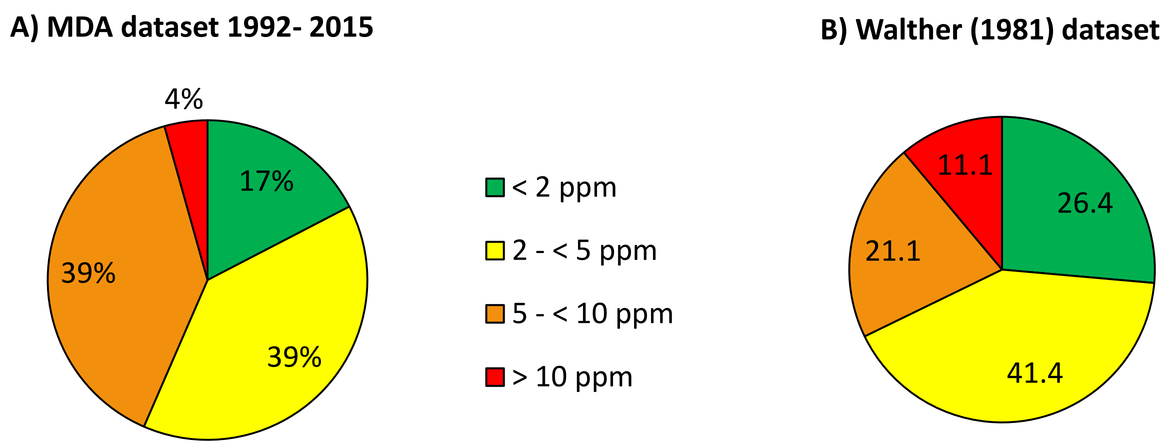

Figure 17: Distributions of nitrate concentrations for MDA and Walther (1981).

Pinoxaden metabolites:

NOA 407854 and NOA 447204 (Table 4) are metabolites of Pinoxaden, an herbicide used for post-emergence control of annual grass weeds in cereal crops like winter and spring barley, winter wheat, and rye. Neither compound is very persistent in soil. Both, however, are highly leachable and persistent in water. The Montana Human Heath Standard for Pinoxaden and metabolites combined in groundwater is 2000 ppb. The median detected concentrations of NOA 407854 and NOA 447204 combined were 0.0084% of the groundwater standard.

Table 4: Detected Concentration Summary (ppb)		
	NOA 407854	NOA 447204
$n_{detected}$	125	101
Min	0.0052	0.01
Q1	0.075	0.01
Median	0.15	0.018
Q3	0.25	0.04
Max	0.77	0.22

Imazamethabenz methyl:

Imazamethabenz methyl ester is a selective, systemic herbicide, commonly labeled for crop use in wheat, barley, and sunflowers. It is highly soluble in water, leachable in soil, and persistent in both soil and groundwater. The primary metabolite, imazamethabenz methyl acid, is also persistent in both soil and groundwater. Both compounds are regularly detected on the Greenfield Bench, albeit at extremely low levels (Table 3). The Montana Human Heath Standard for the parent compound and its metabolite combined in groundwater is 400 ppb. The median detected concentration of imazamethabenz methyl ester and imazamethabenz methyl acid is 0.27% of the groundwater standard.

Table 3: Detected Concentration Summary (ppb)		
	Imazamethabenz methyl ester	Imazamethabenz methyl acid metabolite
$n_{detected}$	464	505
Min	0.0017	0.0031
Q1	0.2	0.195
Median	0.515	0.58
Q3	1.2	1.45
Max	8.1	7.5

Triasulfuron:

Triasulfuron is selective herbicide used in cereal crops like wheat, oats, and barley. It is highly soluble, leachable, and persistent in soils and water. The Montana Human Heath Standard for triasulfuron in groundwater is 70 ppb. The median detected concentration is 0.051% of the groundwater standard (Table 5).

Table 5: Detected Triasulfuron Concentration Summary (ppb)	
$n_{detected}$	88
Min	0.0043
Q1	0.026
Median	0.036
Q3	0.09325
Max	0.89

Pyrasulfotole:

Pyrasulfotole is a selective herbicide registered for use on cereal grains, and is most commonly used in wheat and barley. Pyrasulfotole is more persistent in water than in soil, highly leachable from soils into groundwater, and very mobile in surface water runoff. The Montana Human Heath Standard for Pyrasulfotole in groundwater is 70 ppb. The median detected concentrations 0.076% of the groundwater standard (Table 6).

Table 6: Detected Pyrasulfotole Concentration Summary (ppb)	
$n_{detected}$	32
Min	0.01
Q1	0.023
Median	0.0535
Q3	0.155
Max	0.99

Imidacloprid:

Imidacloprid is a synthetic, broadly-labeled neonicotinoid insecticide. It is very soluble and leachable, and tends to be stable and relatively persistent in most environments. The Montana Human Heath Standard for imidacloprid in groundwater is 400 ppb. The median detected concentration is 0.00045% of the groundwater standard (Table 7).

Table 7: Detected Imidacloprid Concentration Summary (ppb)	
$n_{detected}$	43
Min	0.0018
Q1	0.0018
Median	0.0018
Q3	0.0042
Max	0.13

Tralkoxydim:

Tralkoxydim is foliar applied oxime herbicide used for grass weed control in cereals including wheat, rye, triticale, and barley. While tralkoxydim and its primary metabolite tralkoxydim acid have a low solubility and leaching potential, they are both persistent in both soil and water. The Montana Human Heath Standard for tralkoxydim and its metabolites (combined) in groundwater is 20 ppb. The median detected concentration is 0.68% of the groundwater standard (Table 8).

Table 8: Detected Concentration Summary (ppb)		
	Tralkoxydim	Tralkoxydim Acid
$n_{detected}$	141	46
Min	0.0051	0.005
Q1	0.0525	0.0071
Median	0.081	0.0555
Q3	0.13	0.09475
Max	0.28	0.2

Sulfentrazone:

Sulfentrazone is a broadly labeled systemic herbicide used for control of sedges, broad-leaved weeds, and cool-season grasses in turf. It is somewhat persistent in soil, and is labeled for use as a pre-emergent herbicide for some crops. Sulfentrazone is highly soluble and mobile, giving it a high potential to leach to groundwater. It is somewhat persistent in surface waters, but breaks down in sunlight. Currently there is no Montana Human Heath Standard for sulfentrazone in groundwater established by MT DEQ; the human health standard set by the U.S. Environmental Protection Agency (EPA) is 667 ppb. The median detected concentration is 0.005% of the groundwater standard (Table 9).

Table 9: Detected Sulfentrazone Concentration Summary (ppb)	
$n_{detected}$	11
Min	0.035
Q1	0.035
Median	0.035
Q3	0.087
Max	0.22

Imazamox:

Imazamox is a post-emergence herbicide used to control broad-leaved plants. Imazamox is labeled for use in some small grains, lentils, sunflowers, canola, and alfalfa, for non-crop applications including rights-of-way, industrial areas, and in some aquatic environments. It is highly soluble, leachable, and tends to be persistent in most soil and water environments. The Montana Human Heath Standard for imazamox in groundwater is 20,000 ppb. The median detected concentration is 0.00006% of the groundwater standard (Table 10).

Table 10: Detected Imazamox Concentration Summary (ppb)	
$n_{detected}$	36
Min	0.0057
Q1	0.00695
Median	0.0125
Q3	0.03475
Max	0.081

Prometon:

Prometon is a non-selective herbicide used on non-crop land such as industrial sites and rights-of-way. Prometon is soluble, leachable, and persistent in soils and water. The Montana Human Heath Standard for prometon in groundwater is 100 ppb. The median detected concentration is 0.0052% of the groundwater standard (Table 11).

Table 11: Detected Prometon Concentration Summary (ppb)	
$n_{detected}$	103
Min	0.001
Q1	0.0051
Median	0.0052
Q3	0.026
Max	0.52

Imazapyr:

Imazapyr is a non-selective herbicide that is registered for use in a variety of non-crop application sites. Imazapyr is soluble, highly leachable, and persistent in water. It degrades at a moderately fast rate in most soils. The Montana Human Heath Standard for imazaypr in groundwater is 21,000 ppb. The median detected concentration is 0.00002% of the groundwater standard (Table 12).

Table 12: Detected Imazapyr Concentration Summary (ppb)	
$n_{detected}$	27
Min	0.0035
Q1	0.0052
Median	0.011
Q3	0.013
Max	0.085

Clopyralid:

Clopyralid is a pyridine compound and functions as a selective systemic herbicide. It is labeled for non-crop uses, including fallow land, roadsides, rights-of-way, pasture, rangeland, and CRP. It has a high solubility and is highly leachable to groundwater. The Montana Human Heath Standard for clopyralid in groundwater is 1,000 ppb. The median detected concentration is 0.0046% of the groundwater standard (Table 13).

Table 13: Detected Imazapyr Concentration Summary (ppb)	
$n_{detected}$	61
Min	0.0066
Q1	0.046
Median	0.2
Q3	1.0
Max	2.9

Atrazine:

Atrazine is a selective systemic herbicide primarily used on corn, sorghum, and ornamental turf. Its metabolites include deethyl atrazine and hydroxy atrazine. All formulations are Restricted Use Pesticides due to groundwater-protection concerns. Atrazine and its metabolites tend to be persistent in the environment and have moderate to high leachability in soils. The Montana Human Heath Standard for atrazine and its metabolites in groundwater is 3 ppb (combined). The median detected concentration is 0.34% of the groundwater standard (Table 14).

Table 14: Detected Concentration Summary (ppb)			
	Atrazine	Deethyl Atrazine	Hydroxy atrazine
$n_{detected}$	22	16	1
Min	0.0022	0.0017	0.0064
Q1	0.0022	0.0017	
Median	0.0022	0.0017	
Q3	0.0022	0.0017	
Max	0.0028	0.0017	

Tebuthiuron:

Tebuthiuron is a systemic low selectivity herbicide that is used on non-crop sites, especially rights-of-way and industrial sites. Tebuthiuron is persistent in soil and water, very water soluble, and can be leached readily through soil. The Montana Human Heath Standard for tebuthiuron and its metabolites in groundwater is 500 ppb (combined). The median detected concentration is 0.0024% of the groundwater standard (Table 15).

Table 15: Detected Tebuthiuron Concentration Summary (ppb)	
$n_{detected}$	47
Min	0.0011
Q1	0.0011
Median	0.0012
Q3	0.047
Max	0.31

Azoxystrobin:

Azoxystrobin is a post-emergence broad spectrum fungicide used on ornamental turf and a wide variety of crops. It has a low solubility, is moderately persistent in soils, and very persistent in water. The Montana Human Heath Standard for azoxystrobin in groundwater is 1000 ppb combined. The median detected concentration is 0.0001% of the groundwater standard (Table 16).

Table 16: Detected Azoxystrobin Concentration Summary (ppb)	
$n_{detected}$	15
Min	0.0011
Q1	0.0011
Median	0.0012
Q3	0.0022
Max	0.0045

Pyroxsulam:

Pyroxsulam is a post-emergence herbicide used for the control of annual grasses and broad-leaved weeds in cereals like wheat, rye, and barley. Pyroxsulam is not persistent in soil but is very soluble and persistent in water. The Montana Human Heath Standard for pyroxsulam in groundwater is 7000 ppb. The median detected concentration is 0.0002% of the groundwater standard (Table 17).

Table 17: Detected Pyroxsulam Concentration Summary (ppb)	
$n_{detected}$	9
Min	0.011
Q1	0.013
Median	0.015
Q3	0.027
Max	0.028

Conclusions

There have been numerous detections of agricultural chemicals on the Greenfield Bench dating back to the early 1990s, but none of these detections exceed the 50% of the respective numerical groundwater standard or suggest an increasing trend in detected concentration that would require the development of an SMP. While the bench-wide median detected nitrate concentration does meet the 50% threshold, an SMP is not believed necessary because;

1. The calculations omit field detections of nitrate that were < 2ppm, which would have lowered the overall median.
2. The sources of nitrates in the Greenfield Bench groundwater cannot be identified as originating from agricultural chemical use. Nitrate sources other than agricultural fertilizer use are at least just as, and probably more likely, to be the primary contributors to localized (individual well) detected nitrate concentrations.

Based on this interpretation of these data, MDA's GWPP program will discontinue sampling on the Greenfield Bench except for the permanent monitoring well F-1.

References

Deluca, T., Larson, J., Torma, L. and Algard, G. 1989. A Survey of Pesticide Residues in Groundwater in Montana. Helena, MT. Montana Department of Agriculture, Technical Report 89-1, 15pp.

Ingman, G. L., Weber, E. E., and Bahls, L. L. 1984. The Effects of Muddy Creek on the Biology of the Lower Sun River. Helena, MT. Montana Department of Health and Environmental Sciences, 74pp.

Knapton, J. R., Jones, W. E., and Sutphin, J. W. 1988. Reconnaissance Investigation of Water Quality, Bottom Sediment, and Biota Associated with Irrigation Drainage in the Sun River Area, West-Central Montana, 1986-87. U. S. Geological Survey, Water-Resources Investigation Report 87-4244, 78pp.

Lambing, J. H., Nimick, D. A., and Palawski, D. U. 1994. Physical, Chemical, and Biological Data for Detailed Study of the Sun River Irrigation Project, Freezeout Lake Wildlife Management Area, and Benton Lake National Wildlife Refuge, West-Central Montana, 1990-92, with Selected Data for 1987-89. U. S. Geological Survey, Open-File Report 94-120,171pp.

Miller, K., D.S. Rise, C. McDonald. 2002. Ground-water and surface-water quality, herbicide transport , and irrigation practices: Greenfield Bench Aquifer, Teton County, Montana. Montana Bureau Mines and Geology. Open-file Report 463, 67.

Montana DEQ, Planning Prevention and Assistance Division, Water Quality Planning Bureau, Water Quality Standards Section. 2012. DEQ-7 Montana Numeric Water Quality Standards. Helena, MT: Montana Dept. of Environmental Quality.

Osborne, T. J., Noble, R. A., Zaluski, M. H., and Schmidt, F. A. 1983. Evaluation of the Ground Water Contribution to Muddy Creek from the Greenfield Irrigation District. Montana Bureau of Mines and Geology, Open-File Report 113, 141pp.

USDA National Agricultural Statistics Service Cropland Data Layer. 2016. Published crop-specific data layer [Online]. Available at https://nassgeodata.gmu.edu/CropScape/ (accessed February 22, 2016. USDA-NASS, Washington, DC.

Walther, K. C. 1981. Nitrate in Wells of the Greenfield Irrigation District, Fairfield, Montana. Helena, MT. Montana Department of Health and Environmental Sciences, Water Quality Bureau Report 81-1, 23pp.

Walther, K. C. 1982. Nutrients in Muddy Creek and Wastewater Drains of the Greenfield Irrigation District. Helena, MT. Montana Department of Health and Environmental Sciences, Water Quality Bureau Report 82-1, 25p.

Appendix A – GWIC Well log summary

MDA Site ID	MBMG Number	Well Use	Total Depth (ft)
F-1	122338	Monitoring	34.7
FUS-10	76605	Public Water Supply	40
G-1	166836	Domestic	30
G-2	140907	Domestic	40
G-3	123421	Domestic	40
G-4	166839	null	45
G-5	142043	Domestic	26
G-6	75586	Domestic	36
G-7	76510	Stock	30
G-8	166837	Domestic	18.2
G-9	76555	Domestic	27
G-10	76565	Public Water Supply	16
G-11	149990	Domestic	22
G-12	-	null	50
G-13	166840	Domestic	14.8
G-14	135323	Domestic	28
G-15	166838	Public Water Supply	23
G-16	-	Domestic	63
G-17	-	Public Water Supply	-
PWS-1	75567	Public Water Supply	40
PWS-2	76705	Public Water Supply	22

Appendix B: Full list of Land Cover Categories from USDA National Agricultural Statistics Service Cropland Data Layer (2016).

Appendix C: Pesticide Classes

Pesticide Class	Analyte	Parent or Metabolite	Parent	Herbicide, Fungicide, Insecticide
Acylamine	Metalaxyl	Parent		Fungicide
Amide	Flucarbazone	Parent		Herbicide
Aromatic Acid	Dicamba	Parent		Herbicide
Benzothiadiazinone	Bentazon	Parent		Herbicide
Carbamates	Carbaryl	Parent		Insecticide
Cyclohexene oxime	Tralkoxydim	Parent		Herbicide
	Tralkoxydim acid	Metabolite	Tralkoxydim	
Imidazolinone	Imazamethabenz methyl acid metabolite	Metabolite	Imazamethabenz methyl ester	
	Imazamethabenz methyl ester	Parent		Herbicide
	Imazamox	Parent		Herbicide
	Imazapyr	Parent		Herbicide
Neonicotinoids	Clothianidin	Parent		Insecticide
	Imidacloprid	Parent		Insecticide
Nitrile	Bromoxynil	Parent		Herbicide
Organophosphates	Malathion	Parent		Insecticide
Phenoxy	2,4-D	Parent		Herbicide
	MCPA	Parent		Herbicide
	MCPP	Parent		Herbicide
Pyrazole	NOA 407854	Metabolite	Pinoxaden	
	NOA 447204	Metabolite	Pinoxaden	
	Pyrasulfotole	Parent		Herbicide
Pyridine	Clopyralid	Parent		Herbicide
	Aminopyralid	Parent		Herbicide
	Fluroxypyr	Parent		Herbicide
	Picloram	Parent		Herbicide
	Pyroxsulam	Parent		Herbicide
	Triclopyr	Parent		Herbicide
Strobilurins	Azoxystrobin	Parent		Fungicide

Pesticide Class	Analyte	Parent or Metabolite	Parent	Herbicide, Fungicide, Insecticide
Triazine	Atrazine	Parent		Herbicide
	Deethyl atrazine	Metabolite	Atrazine	
	Hydroxy atrazine	Metabolite	Atrazine	
	Prometon	Parent		Herbicide
	Simazine	Parent		Herbicide
Triazole	Propiconazole	Parent		Fungicide
	Triticonazole	Parent		Fungicide
Triazolone	Sulfentrazone	Parent		Herbicide
Triazone	Hexazinone	Parent		Herbicide
Uracil	Bromacil	Parent		Herbicide
Urea	Chlorsulfuron	Parent		Herbicide
	Diuron	Parent		Herbicide
	Metsulfuron methyl	Parent		Herbicide
	Sulfometuron methyl	Parent		Herbicide
	Tebuthiuron	Parent		Herbicide
	Thifensulfuron	Parent		Herbicide
	Triasulfuron	Parent		Herbicide