Agricultural Chemicals and Groundwater Protection

Groundwater Monitoring Report
Weld County Long-Term

The Agricultural Chemicals & Groundwater Protection Program is responsible for conducting monitoring to detect the presence of commercial fertilizer constituents and pesticide compounds (agrichemicals) in groundwater throughout Colorado. This program has been established to provide current, scientifically valid, groundwater quality data to the Commissioner of Agriculture and the general public.

This report discusses monitoring history in the Weld County Long-Term well networks, sample collection and analysis information for the 2009 field season, and statistics and maps detailing laboratory results. Any information pertaining to sampling frequency and purpose, sampling network development, Weld County location and character, and long-term history of the Program, is available in greater detail from these documents found on the Program webpage (http://tinyurl.com/CDAGroundwater):

- Agricultural Chemicals & Groundwater Protection in Colorado 1990-2006
- Long-Term Groundwater Monitoring Strategy and Plan: May 2007
- Agricultural Chemicals & Groundwater Protection Program SOP Manual

Groundwater Quality Monitoring History

The Program's monitoring efforts in all of Colorado began with the 1992 and 1993 surveying of groundwater quality in the South Platte River Basin. Of the 96 wells sampled along the South Platte River from just north of Denver-metropolitan to Julesburg, 90 wells contained measurable nitrate-nitrogen (NO_3-N) concentrations with 33 wells measuring above the United State Environmental Protection Agency (EPA) drinking water standard of 10 milligrams per liter (mg L^{-1}) or parts per million (ppm). These results demonstrated that nitrate contamination was impacting some portions of the South Platte watershed. One particular area in Weld County stretching from just north of Brighton to Greeley, was found to have several wells >20 ppm NO_3-N with an average value above the EPA standard. The detection of pesticides in wells within this area, especially a detection of lindane exceeding the EPA standard of 0.2 micrograms per liter (µg L^{-1}) or parts per billion (ppb), further warranted the need to intensify sampling efforts.

In 1995 and 1996, a long-term monitoring effort was established in the South Platte aquifer from Brighton to Greeley in an attempt to better identify the extent of contamination and to provide a means for determining long-term contamination trends. The initial sampling design was a well-dispersed, integrated network of 20 monitoring wells sampling near the top of the water table, and 10 domestic and 60 irrigation wells collecting water from deeper portions of the aquifer. Some of the monitoring wells were originally installed by the United State Geologic Survey in 1993 and have since then been acquired by Central Colorado Water Conservancy District (Central). By establishing cooperation with Central in 1995, the Program has been able to collect samples from these wells on an annual basis. Results from the first two years of sampling showed median NO_3-N <10 ppm for domestic wells, 20 ppm for monitoring wells and slightly less than 20 ppm for irrigation wells. While both the monitoring and irrigation well networks had a similar number of wells over the EPA standard, the monitoring network had > 50% of its wells over 20 ppm compared to 38% in the irrigation network.

The pesticides atrazine, prometon, DCPA, metolachlor, and bromacil were all detected in multiple wells in the study area. Ten atrazine detections in the 19 monitoring wells sampled in 1996 ranged 0.16-0.55 ppb. Deethylatrazine (DEA), an atrazine degradate, was found in 13 monitoring wells at concentrations ranging 0.18-0.94 ppb. Detections of prometon and metolachlor were also reported with one metolachlor detection reaching 30.0 ppb. The EPA Lifetime Health Advisory Level for metolachlor is 70 ppb, so this was a significant detection at the time.

Subsequent annual sampling events, in Weld County, continue to show consistently high nitrate concentrations in the monitoring and irrigation well networks. Several monitoring wells have shown significant variability from year to year but the network as a whole does not appear to be trending in any one direction. Fifteen different pesticide compounds have been detected since 1995 in the monitoring wells, but atrazine, DEA, metolachlor, and prometon have accounted for 77% or more of all yearly detections.

These three networks in Weld County have undergone some changes over time mostly due to loss of wells to ownership changes or state mandated irrigation well shutdowns, but also through some additions made to the monitoring well network. As of 2008 the sampling networks are as follows: a 10 well domestic use network, a 24 well quality monitoring network, and a 36 well irrigation use network. Figure 1 shows the layout of the three networks which lie nearly exclusively in areas of high vulnerability to groundwater contamination. All wells are sampled annually, whereas prior to 2007 domestic wells were only sampled every third year. Monitoring wells are analyzed for pesticides, nitrate, and nitrite; irrigation and domestic wells only for nitrate and nitrite.

2009 Sampling and Lab Analysis Notes

Sampling for the monitoring well network took place from June 18th through June 30th. All 24 monitoring wells in the network were sampled as planned, but unfortunately, one landowner is no longer willing to cooperate with the Program, which will result in the removal of two wells from the network after the 2010 sampling season. All irrigation and domestic wells were sampled together from July 14th to July 23rd. All wells were sampled by Karl Mauch, the Program's Groundwater Monitoring Specialist.

Monitoring well samples were sent to Montana Department of Agriculture Analytical Laboratory in Bozeman, MT, where they were screened for 90 different pesticides at very low detection limits. All sample sites, in all three networks, also had a sample collected for nitrate and nitrite analysis which was conducted by the Program's Groundwater Laboratory in Denver, CO. A list of all compounds analyzed for and their reporting limits is found in **Table 3** at the end of this report.

2009 Nitrate Results

Nitrate-nitrogen concentrations were found to be over the EPA standard of 10.0 ppm in wells of all three networks in 2009. The box and whisker plots in Figure 2 compare NO_3-N data from 2008 to that from 2009 for the three different well networks. The median nitrate concentration is highest for the monitoring network while the irrigation and domestic network medians are lower. For the most part, with the exception of some outlier values (asterisk symbols in Figure 2) in 2009, the nitrate concentration responses are very similar between years. The outliers in 2009 are nitrate concentrations that were much higher than the majority of the sampled domestic or monitoring wells.

Table 1 demonstrates the greater magnitude and variability of NO_3-N concentrations in monitoring wells compared to the other networks. The higher concentrations seen in monitoring wells compared to domestic and irrigation wells is a pattern seen in other areas monitored by the Program, and has been seen in Weld County since sampling began in 1995. Water from the near the top of the aquifer (collected from monitoring wells) represents water that has most recently filtered through the soil and geologic material above. Data from this water is essentially the report card on how land use or chemical use practices on the surface are impacting groundwater quality. Information obtained from these wells allows managers and users of the land to better understand what practices are impacting groundwater quality the most, and hopefully, with enough foresight to prevent shallow

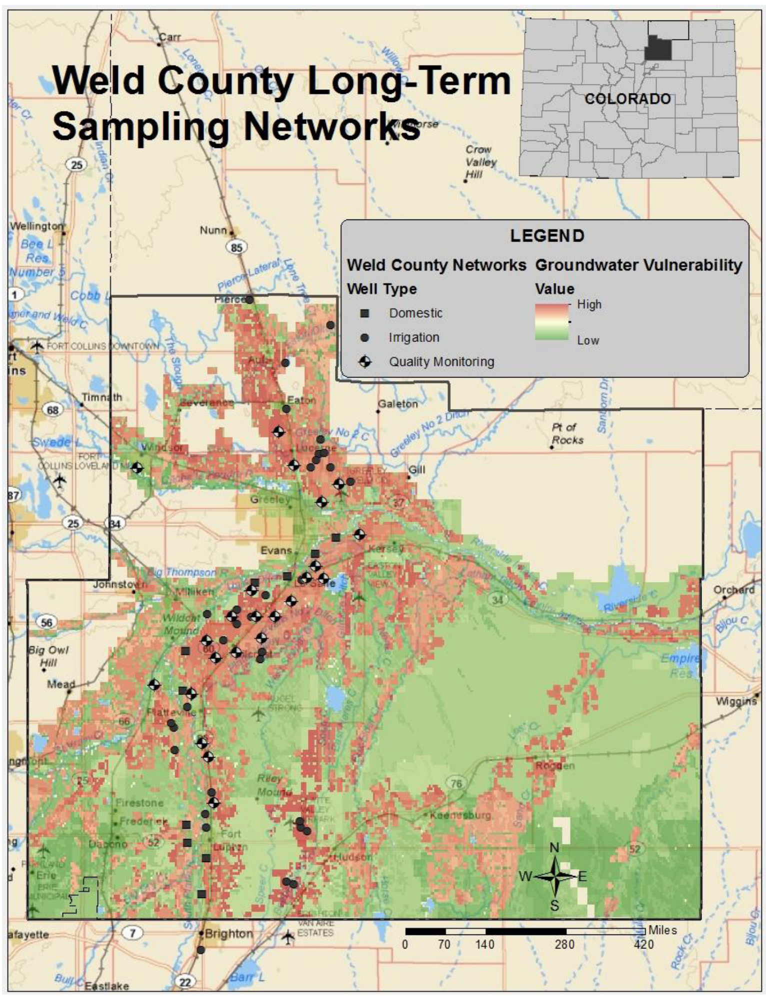

Figure 1. Distribution of domestic, irrigation, and quality monitoring wells in the Weld County Long-Term Sampling Networks. Well placement within areas that are vulnerable to groundwater contamination is important for collecting representative data.

2009 Nitrate-nitrogen Statistics			
	Monitoring	Irrigation	Domestic
Minimum	1.4	BDL	1.5
Q1 (25%)	13.2	7.8	6.3
Median	21.1	12.6	10.6
Average	26.9	14.9	14.4
Q3 (75%)	34.4	24.1	17.7
Maximum	104.2	39.2	44.9
STD	23.5	10.0	13.0
>10.0 ppm	19	20	6
N	24	36	10

Table 1. Nitrate-nitrogen statistics for samples collected from Weld County long-term sampling networks in 2009. BDL is below detection limit. Units are mg L^{-1} or ppm.

contamination from progressing into deeper portions of the aquifer where more domestic and irrigation wells are installed.

Some of the difference in nitrate between well types is because of where samples are collected in relation to each other on the surface, but well depth and pumping rate differences also have some affect. Sometimes domestic wells are installed at shallower depths than monitoring wells but for the most part, domestic and irrigation wells require deeper installation in order to achieve adequate supply for the well during pumping. This is especially true for irrigation wells that pump anywhere from hundreds to thousands of gallons per minute. While there are instances of significant differences in magnitude of nitrate concentrations between the well networks in Weld County, the important discovery is that nitrate over the EPA standard is being discovered of the sampling area, regardless of the well type sampled. As can be seen in Figure 3, the area between Platteville and Greeley has the greatest collection of such wells, but there is also a cluster of wells north of Greeley exhibiting this response. While nitrate in these two areas has always tended to be elevated, nitrate concentrations in the Weld County well networks have shown quite a bit of variability since 1995. Figure 4 shows the variability in annual median nitrate that has occurred in the well networks as a whole, but a good amount of variability occurs in individual wells too. Especially in monitoring wells since they tend to be first in line, first in response with regards to contaminants leaching through the soil profile.

One monitoring well in particular has seen NO_3-N range from a low of 43 ppm in 1997 to a high of 111 ppm in 2003. The 2008 and 2009 NO_3-N concentrations for this well were 64 and 104 ppm, respectively. The location of this well in an area where septic system leach fields, confined animal feeding operations, and irrigated cropland provide ample sources of nitrate that can leach into groundwater. The irrigated cropland in such areas has more potential for nitrate leaching if feedlot manure is applied as soil-amendment above agronomic rates. If irrigation water is applied in amounts greater than crop evapotranspiration then the extra water can push unused nutrients from the manure through the soil profile and into the groundwater. An irrigation well sampled within the same area as the monitoring well mentioned above consistently shows nitrate concentrations nearly double the irrigation network median, and a domestic well in the area has seen NO_3-N range from a low of 12.9 ppm in 2004 to a high of 26.4 ppm in 2009. While it is not understood how each of these wells represent the groundwater individually, it is obvious that nitrate contamination in the area is affecting more than just the top of the water table.

While NO_3-N concentrations in some irrigation and domestic wells have and continue to exceed the EPA standard, individual wells and the domestic and irrigation networks as a whole, have seen a lot less variability than that seen in the shallower monitoring wells. It is plausible that a dilution affect is present in

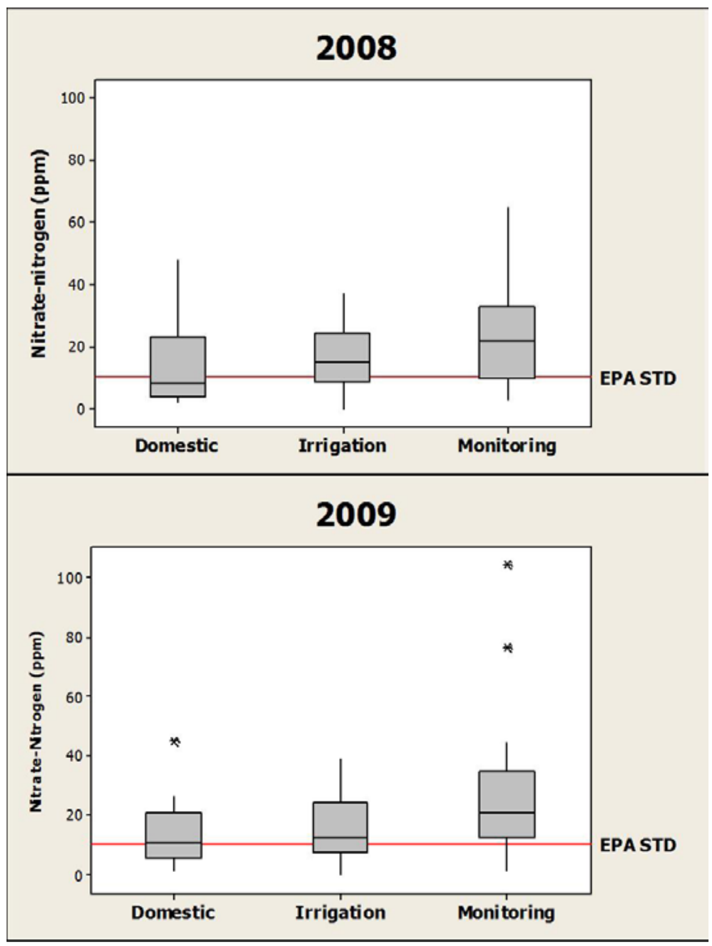

Figure 2. Box-whisker plots of nitrate-nitrogen results for groundwater samples collected from the domestic, irrigation, and monitoring well networks in Weld County, Colorado in 2008 and 2009. EPA Standard for nitrate in drinking water is 10.0 ppm or mg/L.

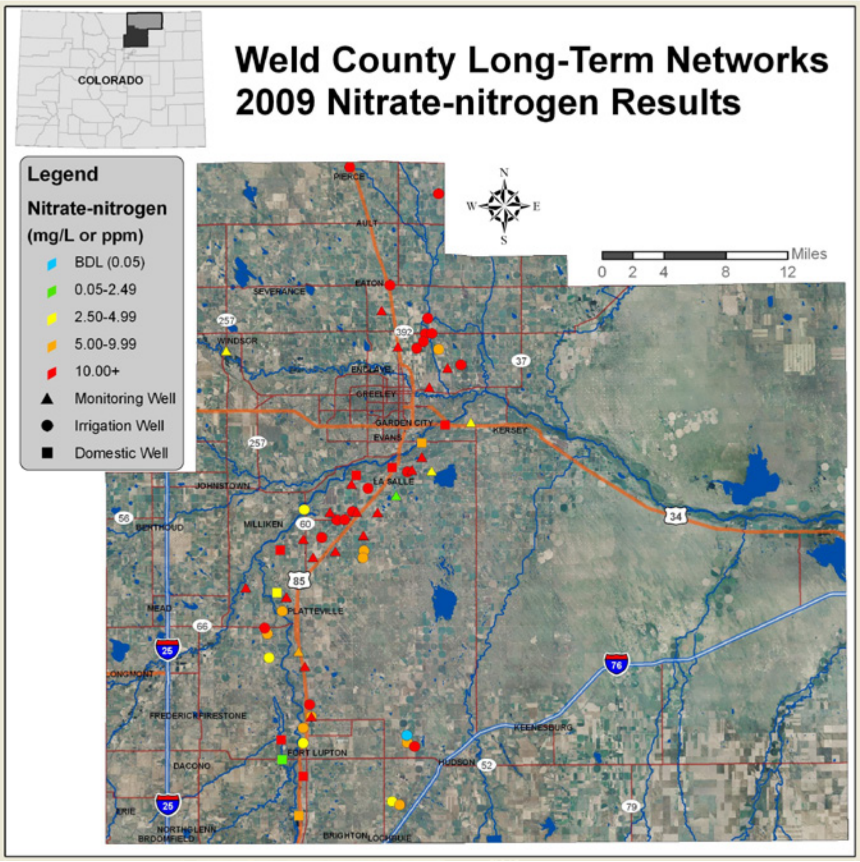

Figure 3. Nitrate-nitrogen results for groundwater samples collected from Weld County Long-Term monitoring, irrigation, and domestic well networks in 2009. Units are mg/L or ppm. EPA Drinking Water Standard is 10.0 mg/L.

domestic and irrigation wells. This means that samples from these wells are not as reliable as monitoring wells when it comes to knowing exactly what the concentration of a contaminant is at a particular depth in the groundwater. Monitoring wells, sampled with low-flow bladder pumps, pump at less than 0.1 gpm, and greatly minimize the effect of dilution because they are sampling a very discreet area with very little disturbance of the aquifer formation. These discreet samples provide groundwater quality samples representative of exact areas of the aquifer, versus domestic and irrigation wells that represent more average conditions throughout the aquifer because of longer screened intervals and higher pumping rates.

The time series of monitoring well annual median nitrate concentration, while highly variable, has not provided any evidence of a significant trend from 1995 to 2009. The irrigation network on the other hand, with the addition of the 2009 data, now shows a statistically significant downward trend response (Mann-Kendall, $P < 0.05$). The domestic well network was only sampled once every three years prior to 2007, and was fairly stable in median NO_3-N; however, 2009 data was the first time median NO_3-N exceeded 10 ppm.

2009 Pesticide Results

Monitoring well samples were analyzed for 90 pesticide compounds at concentration levels in the lower micrograms per liter (µg L^{-1}) or parts per billion (ppb). The addition of new analytes and lower detection limits (compared to previous methods) greatly increased the number of compounds detected in Weld County alluvial groundwater in 2009 compared to historical findings. A total of 27 different pesticide compounds were detected in samples collected from the 24 wells. Thirteen of the compounds detected were on the analysis screen for the first time. Each well sample had eight or more detectable pesticide compounds in it. One well had 16 different pesticide compounds detected. Concentrations of the 272 total pesticide detections ranged from a minimum 0.0014 ppb tebuthiuron detection, to a maximum 16.0 ppb metolachlor ESA (a metolachlor degradate) detection. **Table 2** shows all pesticides detected, the number of wells detecting each pesticide, and the range of concentrations discovered.

While the number of total pesticide detections and the number of different pesticide compounds found may seem alarming, it is important to note that 56% (153) of all detections were of various constituents of atrazine, metolachlor, and prometon. As mentioned earlier these compounds have consistently been detected in Weld County over time but concentrations

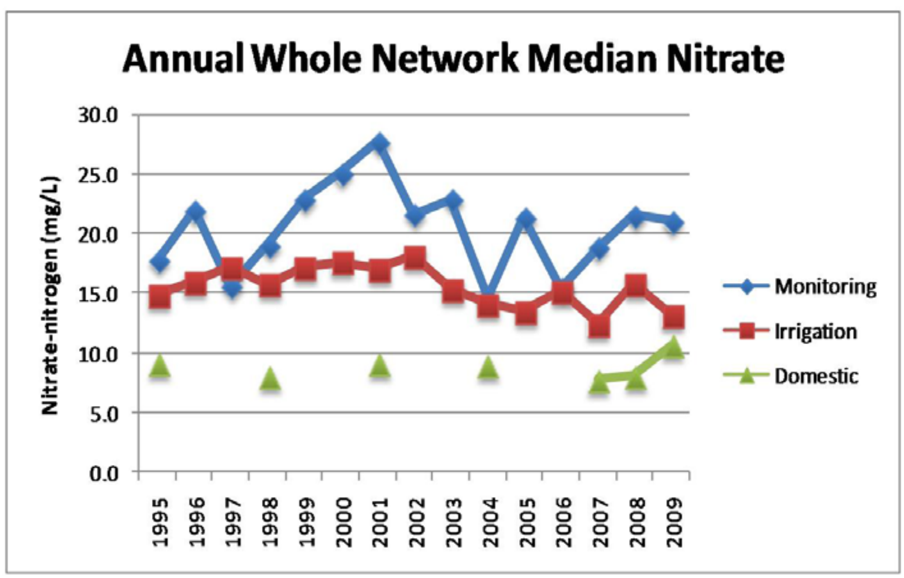

Figure 4. Graph of median nitrate-nitrogen concentrations calculated annually on a whole network basis. Monitoring, irrigation, and domestic well networks are used for monitoring groundwater quality in the South Platte alluvial aquifer system in Weld County, Colorado.

Weld County 2009 Pesticide Detections					
Pesticide	**# Detects**	**Minimum**	**Median**	**Average**	**Maximum**
Acetochlor ESA	1	0.1000			0.1000
Alachlor ESA	22	0.0130	0.0590	0.1510	0.9300
Alachlor OA	6	0.0037	0.0070	0.0110	0.0240
Aldicarb sulfone	2	0.0020	0.0027	0.0027	0.0030
Atrazine	24	0.0025	0.0190	0.0380	0.2000
Azoxystrobin	1	0.0110			0.0110
Bentazon	3	0.0017	0.0020	0.0020	0.0026
Bromacil	1	0.0080			0.0080
Deethyl atrazine	24	0.0047	0.0470	0.1150	0.7900
Deisopropyl atrazine	11	0.0160	0.0570	0.0840	0.2900
Dimethenamid OA	4	0.0043	0.0120	0.0400	0.1300
Diuron	3	0.0200	0.0200	0.0230	0.0300
Hexazinone	7	0.0075	0.0130	0.0300	0.0650
Hydroxy atrazine	17	0.0081	0.0230	0.0370	0.1200
Imazamox	2	0.0210	0.0310	0.0310	0.0400
Imazapyr	23	0.0140	0.0610	0.0530	0.3300
Imidacloprid	12	0.0032	0.0140	0.0230	0.0850
Linuron	1	0.1500			0.1500
Metalaxyl	1	0.0360			0.0360
Metolachlor	7	0.0210	0.0980	0.0860	0.1600
Metolachlor ESA	24	0.0580	1.2000	2.4970	16.0000
Metolachlor OA	22	0.0300	0.3200	0.9270	7.2000
Nicosulfuron	2	0.0830	0.1270	0.1270	0.1700
Prometon	24	0.0079	0.0200	0.0230	0.0540
Simazine	7	0.0030	0.0040	0.0050	0.0120
Tebuthiuron	20	0.0014	0.0040	0.0070	0.0360
Tetraconazole	1	0.0170			0.0170

Table 2. Pesticides detected in Weld County Long-Term monitoring well samples in 2009. Concentrations are in micrograms per liter or parts-per-billion.

have been decreasing. Of these particular 153 detections only 18 of them were over 1.0 ppb, with metolachlor ESA and metolachlor OA representing all of those detections. Metolachlor ESA and OA products are known to exist in groundwater at much higher concentrations than the parent product, metolachlor. Remember, metolachlor was detected at 30 ppb in 1996, so this compound has proven to significantly impact groundwater quality. Another 35 detections of various pesticide breakdown products means that 69% of all detections in 2009 were of breakdown products indicating that degradation pathways are active.

The highest atrazine concentration was 0.20 ppb from a well that also contained the highest desethyl atrazine (DEA) concentration of 0.79 ppb. This particular well is at a site where two wells are installed side by side, at different depths. The above results are from the deep well which has a screened interval running 22-32 ft below the ground surface, while the shallow well screened interval runs 11.6-21.6 ft below the ground surface. Depth to groundwater at the site is about 17 ft. The concentrations of atrazine and DEA were much lower in the shallow well at 0.035 and 0.094 ppb, respectively. This is an inverse response to nitrate levels detected in these two wells in 2008 and 2009. In 2008, nitrate detected in the shallow well was 4X the concentration of that in the deep well and even though the nitrate concentration decreased in both wells in 2009, the shallow well once again had nearly 3X the nitrate concentration of the deep well. The responses from these wells are interesting and show the different behavior and impact individual contaminants can have in groundwater.

Besides the atrazine, metolachlor, and prometon compounds mentioned above, there were also 28, 23, and 20 detections of alachlor breakdown products (alachlor ESA and alachlor OA), imazapyr, and tebuthiuron, respectively. Tebuthiuron was initially detected in 9 of 23 sampled wells in 2008, and those 9 wells all reported significantly lower concentrations in 2009. Tebuthiuron in the deep well of the site mentioned earlier was 0.768 ppb in 2008 and only 0.011 ppb in 2009. The shallow well concentration decreased from 0.198 ppb in 2008 to 0.036 ppb in 2009.

Summary

This recent data from the 2009 sampling effort shows that groundwater quality in the South Platte Basin alluvial aquifer is continuing to be compromised by nitrate leaching. Several sources for nitrate exist within the sampling network area which runs from Pierce in the north to Brighton in the south, including irrigated crop production, confined animal feeding operations, rural and urban septic systems, and urban fertilizer use. It is not known which factor may be contributing more than another but with some areas showing NO_3-N contamination 10 fold higher than the EPA standard, it is apparent that additional improvements in the management of nitrate sources will be necessary to improve water quality to levels below the EPA standard.

Pesticides and their breakdown products are also continuing to impact groundwater quality in study area. While a high number of compounds were discovered, concentrations were very low. The high number of detections of breakdown products suggests that degradation of parent compounds is active and is helping to keep pesticide concentrations well below established drinking water maximum contaminant levels. Even though atrazine, prometon, and metolachlor detections were numerous in 2009, concentrations of these compounds compared to historical values are much lower.

For questions or comments on this report, or the Program in general, please contact Rob Wawrzynski (303-239-5704, rob.wawrzynski@ag.state.co.us) or Karl Mauch (303-239-5713, karl.mauch@ag.state.co.us).

Table 3. Reporting limits of analytes tested for in 2009 by the laboratories of the Montana Department of Agriculture and the Colorado Department of Agriculture. Concentrations are in micrograms per liter (µg L^{-1}) or parts-per-billion (ppb) unless otherwise noted.

Reporting Limits for Analytes Tested in Weld County - Sampling Year 2009

Analyte	Tradename[1]	Use	Reporting Limit	Analyte	Tradename	Use	Reporting Limit
Nitrate as nitrogen (mg L^{-1})			0.05	Imazalil	Deccozil	Fungicide	0.0100
Nitrite as nitrogen (mg L^{-1})			0.05	Imazamethabenz acid	Assert	Herbicide	0.0052
Acetochlor	Harness	Herbicide	0.1400	Imazamethabenz ester	Assert	Herbicide	0.0010
Acetochlor (ESA)	Metabolite	Herbicide	0.0100	Imazamox	Raptor	Herbicide	0.0120
Alachlor	Lasso	Herbicide	0.1100	Imazapic	Plateau	Herbicide	0.0110
Alachlor (ESA)	Metabolite	Herbicide	0.0110	Imazapyr	Arsenal	Herbicide	0.0110
Alachlor(OA)	Metabolite	Herbicide	0.0042	Imazethapyr	Pursuit	Herbicide	0.0100
Aldicarb	Temik	Insecticide	0.0028	Imidacloprid	Admire	Insecticide	0.0018
Aldicarb sulfone	Metabolite	Insecticide	0.0011	Isoxaflutole	Balance	Herbicide	0.1300
Aldicarb sulfoxide	Metabolite	Insecticide	0.0560	Linuron	Afalon	Herbicide	0.0110
Aminopyralid	Milestone	Herbicide	0.0530	Malathion	Malathion	Insecticide	0.0280
Atrazine	Aatrex	Herbicide	0.0022	MCPA	MCPA	Herbicide	0.0023
Azinphos methyl	Guthion	Insecticide	0.0370	MCPP	Kilprop	Herbicide	0.0022
Azinphos methyl (OA)	Metabolite	Insecticide	0.0310	Metalaxyl	Allegiance	Fungicide	0.0120
Azoxystrobin	Amistar	Fungicide	0.0011	Methomyl	Lannate	Insecticide	0.0016
Bentazon	Basagran	Herbicide	0.0011	Metolachlor	Bicep	Herbicide	0.0120
Bromacil	Hyvar X	Herbicide	0.0074	Metolachlor (ESA)	Metabolite	Herbicide	0.0025
Carbaryl	Sevin	Insecticide	0.0400	Metolachlor (OA)	Metabolite	Herbicide	0.0210
Carbofuran	Furadan	Insecticide	0.0052	Metsulfuron methyl	Ally	Herbicide	0.0260
Chlorpyrifos	Lorsban	Insecticide	0.0310	Nicosulfuron	Accent	Herbicide	0.0110
Chlorsulfuron	Glean	Herbicide	0.0056	NOA 407854	Metabolite	Herbicide	0.0052
Clodinafop acid	Topik	Herbicide	0.0130	NOA 447204	Metabolite	Herbicide	0.0100
Clopyralid	Lontrel	Herbicide	0.0220	Picloram	Tordon K	Herbicide	0.1400
Cyproconazole	Alto	Fungicide	0.0051	Prometon	Pramitol	Herbicide	0.0051
2,4-D	Weed B Gone	Herbicide	0.0045	Propachlor	Ramrod	Herbicide	0.0028
2,4-DB	Butyrac	Herbicide	0.0910	Propachlor (OA)	Metabolite	Herbicide	0.0094
Deethyl atrazine	Metabolite	Herbicide	0.0017	Propiconazole	Banner	Fungicide	0.0100
Deisopropyl atrazine	Metabolite	Herbicide	0.0100	Prosulfuron	Peak	Herbicide	0.0050
Dicamba	Banvel D	Herbicide	0.0510	Pyrasulfatole	Pyrasulfatole	Herbicide	0.0230
Difenoconazole	Dividend	Fungicide	0.0200	Pyroxsulam	XDE-742	Herbicide	0.0270
Dimethenamid	Frontier	Herbicide	0.0100	Simazine	Primatol S	Herbicide	0.0026
Dimethenamid (OA)	Metabolite	Herbicide	0.0038	Sulfometuron methyl	Oust	Herbicide	0.0100
Dimethoate	Cygon	Insecticide	0.0011	Sulfosulfuron	Certainty	Herbicide	0.0054
Diuron	Karmex	Herbicide	0.0100	Tebuconazole	Elite	Fungicide	0.0100
Epoxyconazole	Epic	Fungicide	0.0280	Tebuthiuron	Graslan	Herbicide	0.0011
Ethion	Nialate	Insecticide	0.3900	Tembotrione	Tembotrione	Herbicide	0.2200
Ethofumesate	Solera	Herbicide	0.0250	Tetraconazole	Eminent	Fungicide	0.0062
Ethoprop	Mocap	Insecticide	0.0120	Thifensulfuron	Harmony	Herbicide	0.0260
Fenbuconazole	Enable	Fungicide	0.0053	Tralkoxydim	Achieve	Herbicide	0.0051
Flucarbazone	Everest	Herbicide	0.0012	Tralkoxydim acid	Achieve	Herbicide	0.0050
Flucarbazone sulfonamide	Metabolite	Herbicide	0.0010	Triadimefon	Amiral	Fungicide	0.0057
Flufenacet (OA)	Metabolite	Herbicide	0.0053	Triadimenol	Baytan	Fungicide	0.0260
Flumetsulam	Broadstrike	Herbicide	0.0630	Triallate	Avadex BW	Herbicide	0.3000
Glutamic acid	L-Glutamic acid	Growth Reg	0.0074	Triasulfuron	Amber	Herbicide	0.0260
Hydroxy Atrazine	Metabolite	Herbicide	0.0064	Triclopyr	Garlon	Herbicide	0.0110
Halosulfuron methyl	Permit	Herbicide	0.0100	Triticonazole	Charter	Fungicide	0.0320
Hexazinone	Velpar	Herbicide	0.0059				

1 - Tradenames used are strictly examples of products containing a particular analyte and does not suggest analysis of a specific product.