Agricultural Chemicals and Groundwater Protection

Front Range Urban – 2010 Groundwater Monitoring Report

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 Front Range Urban (FRU) monitoring well network, sample collection and analysis information for the 2010 field season, as well as statistics and maps detailing laboratory results. Any information pertaining to sampling frequency and purpose, sampling network development, laboratory methodology and protocol, Front Range Urban location and character, and long–term history of the Program, is available in greater detail from these documents found on the Program webpage (http://www.colorado.gov/ag/gw):

- Agricultural Chemicals & Groundwater Protection in Colorado 1990–2006
- Program Monitoring Strategy 2007–2017
- Agricultural Chemicals & Groundwater Protection Program SOP Manual
- Groundwater Quality Database
- Colorado Dept. of Agriculture Groundwater Laboratory Analytical SOPs

Groundwater Quality Monitoring History

Initial investigations by the Program in Colorado were concentrated primarily in areas of irrigated agriculture; however, use of agrichemicals occurs within the urban landscape as well, so groundwater sampling in this environment was initiated in 1996. A collection of 77 wells were sampled and analyzed for basic water quality constituents, nitrate, and a suite of 46 different pesticide compounds. Most of the wells were privately owned and permitted as domestic wells but nine monitoring use wells located in some incorporated communities of agriculturally–intense Weld County were sampled as well. Because of the difficulties of finding established wells within an urbanized (developed) landscape, many wells were located on the fringe of or even outside the urban environment. **Figure 1a** shows the distribution of samples in 1996 and demonstrates the lack of uniform distribution throughout the Front Range urban corridor. There was adequate representation of Fort Collins, Greeley, and Boulder County although many of Boulder County sites were outside the urban landscape.

Nitrate analysis indicates that groundwater collected in those areas mentioned above, does not show as high a level of impact as is found in agricultural land use areas also sampled in and prior to 1996. Approximately 9% of samples exceeded the U.S. Environmental Protection Administration (EPA) drinking water standard of 10.0 milligrams–per–liter (mg L^{-1}) or parts–per–million (ppm). The detected concentration of nitrate–nitrogen in 53 wells (69%) was in the range of 0.5 to 9.9 ppm, and 17 wells were below the detection limit of 0.5 ppm. Data from wells in the Fort Collins urban landscape showed a median nitrate–nitrogen concentration of 2.4 ppm. In general, a nitrate–nitrogen concentration less than 2.5 ppm is considered by many experts to be naturally occurring and is not a result of anthropogenic influence.

Pesticide data for 1996 revealed detections of four pesticide compounds: atrazine, deethyl atrazine (DEA), prometon, and bromacil. Atrazine was detected in nine wells with concentrations ranging from 0.16 to 0.88 micrograms–per–liter (µg L^{-1}) or parts–per–billion (ppb). A common degradation product of atrazine, DEA, was found in 11 wells and within a similar range of concentration. Nine of these eleven wells also accounted for one

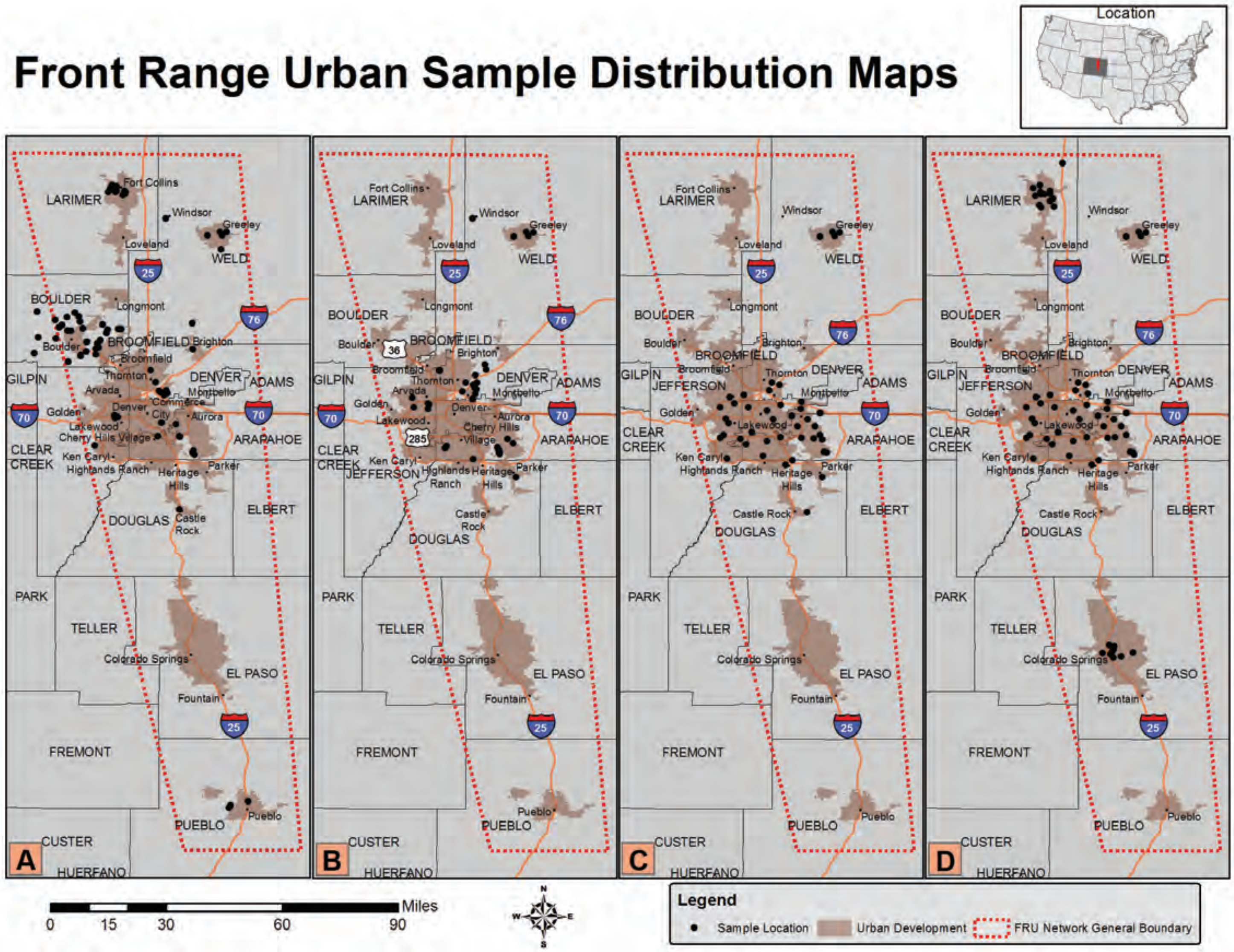

Figure 1. Maps of sample spatial variability in the Front Range Urban sampling events of 1996 (A), 2005 (B), 2007 (C), and 2008 (D).

of the atrazine detections. The most detected pesticide compound was Prometon with 24 detections ranging in concentration from 0.23 to 1.6 ppb. This large number of detections in groundwater suggested significant use of prometon in the urban landscape. Prometon is a non–selective herbicide used primarily for total vegetation control along roadsides, railways, and industrial areas, which tend to be highly concentrated compared to rural and agricultural land–use areas.

Sampling efforts in the Front Range Urban (FRU) corridor resumed in 2005 with a greater emphasis on establishing a long–term network of monitoring wells instead of continued sampling of domestic use wells. Domestic wells are more uncommon inside urban landscapes because most residents rely upon municipal supplies following development. A large number of existing monitoring wells were present in the Denver–metropolitan (D-M) area but many were associated with monitoring and reclamation activities associated with leaking underground storage tanks containing various organic compounds. Wells of this nature are avoided to prevent interference with agrichemical sampling. Cooperation from existing well owners allowed for a sampling of 40 monitoring wells in 2005 as seen in **Figure 1b**.

The majority of wells sampled contained measurable nitrate but only five contained concentrations above the EPA standard. Average nitrate–nitrogen was 7.5 ppm and the median concentration was 3.7 ppm. Eight wells were below the detection limit of 0.12 ppm. The maximum concentration detected was 91 ppm in a monitoring well in northwest D-M. It is unclear why the nitrate concentration was so high in this well, but this result is not characteristic of Front Range Urban groundwater quality with respect to nitrate as both the average and median nitrate concentrations were ten times less.

MCPP, also known as mecoprop, was the only pesticide detected in 2005. MCPP is stable to hydrolysis (breakdown by water from large molecules to smaller ones), photodegrades (breakdown by UV radiation) slowly with a half–life of 83 days under artificial light, and is very mobile in soil textures ranging from sand to silty clay loam. Hydrolysis rates are highest in warm water and lessen with temperature decreases as depth below the root zone increases. Therefore, MCPP discovered in groundwater is likely to persist for a long time. The three detections were found in fairly close proximity to one another, and down–gradient from a waste water treatment facility. MCPP is a common general herbicide found in weed killer and "weed–and–feed" products purchased at a multitude of consumer retailers for use on turf. The fact that all monitoring wells with MCPP detections were below the discharge of a waste water treatment facility could indicate that contamination was due to disposal in the residential wastewater stream and subsequent inadequate degradation in the waste water treatment facility. However, there were five monitoring wells sampled in transect below the treatment facility discharge and three contained measurable levels of MCPP so it is also possible that pesticide use and/or land use management around the three individual wells contributed to the contamination. Only three detections of one pesticide compound were discovered, and the 2005 sampling of FRU water quality, did not provide evidence of extensive contamination with pesticide compounds.

The 2007 sampling effort for the FRU network was focused on achieving more adequate coverage of the urban landscape from Fort Collins to Pueblo. The distribution of monitoring wells sampled during the 2005 was inadequate, and further network delineation was required. Investigation into existing monitoring wells and subsequent cooperation of various entities led to a well–distributed sampling of most of the D-M and a few samples in Greeley and Pueblo. **Figure 1c** shows the distribution of samples in 2007. Median nitrate–nitrogen concentrations were 2.86 and 4.69 with sample counts of 38 and 4 for D-M and Greeley, respectively. **Table 1** shows the results for Front Range Urban network as a whole (Total Network) which includes one sample collected in Castle Rock and two samples from Pueblo, in addition to the results for D-M and Greeley wells. All four wells containing nitrate over the EPA standard were located in D-M with the maximum concentration of 31.6 ppm coming from a well in northwest D-M. This well was several miles south of the well that returned 91 ppm during the 2005 sampling effort. Due to laboratory complications no pesticide results were available for samples collected in 2007.

In the winter of 2007 the Program installed new monitoring wells in Fort Collins and southern Colorado Springs in order to increase coverage of the Front Range Urban monitoring network. Due to the addition of new wells and the lack of pesticide results from 2007, the Program sampled the network again in 2008. The planned frequency of sampling this network is once every three years. A total of 67 wells were sampled and 39 of those – primarily in D-M and Greeley – were compared against 2007 results. **Figure 1d** shows the current distribution of samples in the Front Range Urban network. Twelve wells exceeded the EPA nitrate standard with a maximum concentration of 30.8 ppm found in one of the Colorado Springs wells. The network–wide median was 4.2 ppm. Only five wells were below the detection limit of 0.05 ppm, which indicates that 75% of sampled wells in 2008 contained detectable nitrate below the EPA drinking water standard. **Table 2** shows statistics for 2008 nitrate results. Colorado Springs had the highest percentage of wells above the EPA standard with 36%. Comparatively only 13 and 8% of wells in D-M and Fort Collins, respectively, contained nitrate above the EPA standard.

Comparing the 2007 and 2008 results for 39 wells in D-M and Greeley shows some fluctuation in nitrate concentrations in selected wells. The largest decrease of 9.8 ppm was in the well in northwest D-M that contained the maximum concentration of 31.6 ppm in 2007. The largest increase of 6.2 ppm was in a well that contained less than two ppm in 2007. Overall, results from these wells show relatively low nitrate concentrations with

2007 Nitrate-nitrogen Results			
	Total Network	Denver-Metro	Greeley
Sample Count	44	38	4
Average	4.71	4.42	4.94
Standard Deviation	5.50	5.61	2.19
Minimum	BDL	BDL	2.70
Q1 (25%)	1.04	0.93	3.49
Median	3.21	2.86	4.69
Q3 (75%)	6.28	6.10	6.14
Maximum	31.64	31.64	7.68

Table 1. Nitrate–nitrogen statistics for samples collected from Front Range Urban monitoring wells in 2007. 'BDL' is below detection limit. Units are mg L^{-1} or ppm.

2008 Nitrate-nitrogen Results					
	Total Network	Denver-Metro	Greeley	Ft. Collins	CO Springs
Sample Count	67	37	4	13	11
Average	5.68	4.72	5.64	4.33	9.78
Standard Deviation	6.19	4.60	3.77	5.94	10.04
Minimum	BDL	BDL	0.87	0.07	BDL
Q1 (25%)	0.95	0.98	3.49	0.61	2.39
Median	3.74	3.65	6.48	2.55	8.24
Q3 (75%)	8.42	7.07	8.63	3.89	12.20
Maximum	30.76	21.83	8.73	19.48	30.76

Table 2. Nitrate–nitrogen statistics for samples collected from Front Range Urban monitoring wells in 2008. 'BDL' is below detection limit. Units are mg L^{-1} or ppm.

2008 Results by Land Use Class							
	GC	OS Park	GC Res	Com Ind	Res Com	Res	All
# Wells	5	6	7	5	12	31	67
Nitrate-Nitrogen (mg L^{-1})							
Average	0.9	1.7	2.4	5.5	6.2	7.6	5.7
Q1 (25%)	0.5	0.7	0.5	BDL	2.4	2.6	1.0
Median	0.7	0.9	1.7	4.9	4.8	5.9	3.7
Q3 (75%)	1.0	3.0	4.2	8.7	8.7	10.1	8.4
Maximum	2.1	3.9	6.1	14.1	21.8	30.8	30.8
% Wells BDL	0%	0%	14%	40%	8%	3%	7%
% Wells ≥10.0	0%	0%	0%	20%	17%	26%	18%
Dissolved Oxygen (mg L^{-1})							
Average	2.5	1.8	2.2	2.3	3.8	2.8	2.8
Q1 (25%)	1.5	1.3	0.9	0.8	2.1	0.9	1.0
Median	1.7	1.6	1.1	1.6	3.9	2.4	2.1
Q3 (75%)	1.7	2.0	3.2	3.0	5.2	4.3	4.3
Maximum	6.8	3.4	5.3	5.8	7.1	7.2	7.2
Static Water Level (ft bgs)							
Average	11.8	9.4	15.0	16.0	20.6	17.2	16.4
Q1 (25%)	9.8	7.4	8.3	9.6	10.6	10.6	9.6
Median	11.9	8.8	12.7	16.0	15.7	13.2	12.9
Q3 (75%)	13.3	11.6	17.2	20.1	29.6	20.3	19.2
Maximum	15.1	12.8	36.1	27.2	57.7	57.2	57.7

Table 3. Statistics for nitrate–nitrogen, dissolved oxygen, and static water level for Front Range Urban monitoring wells sampled in 2008. GC is golf course; OS/Park is Open Space–Parkland; GC/Res is Golf Course–Residential; Com/Ind is Commercial–Industrial; Res/Com is Residential–Commercial; Res is Residential. 'ft bgs' is feet below ground surface. 'BDL' is below detection limit.

Dissolved Oxygen Influence			
NO_3-N	# Wells	# Oxic	# Anoxic
BDL	5	0	5
0.05<2.5	20	5	15
2.5<10.0	30	17	13
≥ 10.0	12	12	0

Table 4. Nitrate–nitrogen results in comparison to dissolved oxygen state of groundwater for samples collected in the Front Range Urban network in 2008. Units for NO_3–N are mg L^{-1}. 'BDL' is below detection limit. Oxic is <2.0 mg L^{-1} dissolved oxygen. Anoxic is >2.0 mg L^{-1} dissolved oxygen.

little fluctuation compared to shallow monitoring wells in irrigated agriculture landscapes.

Within the urban landscape land–use classifications were delineated for Front Range Urban monitoring wells sampled in 2008. Land–use classifications were determined by evaluating aerial imagery around every well location, and classifying the land–use believed to be within 500 meters and up–gradient of the well into one of the following classes: Park/Open Space, Golf Course, Golf Course/Residential, Residential, Residential/Commercial, Commercial, Commercial/Industrial, or Industrial. Groundwater flow direction was estimated from topography. USGS studies focused on correlating land–use activity to groundwater quality utilize a similar strategy. **Table 3** shows nitrate–nitrogen results for the various land–uses in the urban landscape. The influence that residential development has on nitrate concentrations in groundwater is obvious when comparing the results. It is worth noting the low impact golf courses are having on groundwater quality (with respect to nitrate) in the areas sampled. Further interpretation of groundwater age and the length of time each course has been established is necessary in order to accurately proclaim that golf course management, in general, does not lend much to groundwater contamination with nitrate; however, given the extensive amount of grass turf (a nitrogen and water thirsty plant) on a golf course and their general location within areas with shallow water tables (as seen by static water levels), fertility management at golf courses involved in this study appears adequate for keeping excess nitrate out of groundwater. Comparatively, residential areas accounted for the highest percentage of wells above the EPA standard (26%) and two of the highest nitrate concentrations if the residential–commercial land use is included. This result could be due to several possibilities which could include over–application of nitrogen fertilizer, misapplication to impermeable surfaces that may wash nutrients into surface water supplies interconnected with shallow groundwater, or other sources of nitrate are available for leaching. While the number of wells acquired for each designated land–use class is not equal, the greatest number of samples was collected in residential or residential–commercial areas, which are the primary land–use classes in Front Range Urban cities.

While dissolved oxygen (DO) concentration is only one of several factors determining nitrification–denitrification rates of nitrogen species in groundwater, the results seen in **Table 4** demonstrate that DO content itself can be very influential. DO concentration above 2.0 mg L^{-1} in groundwater results in an oxic environment which facilitates aerobic biological processes while DO below 2.0 mg L^{-1} results in an anoxic environment which facilitates anaerobic processes like denitrification. All Front Range Urban wells with nitrate above the EPA standard are oxic in nature. The opposite is true of the five wells below the detection limit. The naturally occurring concentration of nitrate–nitrogen is considered to be less than 2.5 ppm while greater concentrations indicate potential impact from various anthropogenic activities. Seventy–five percent of wells with nitrate–nitrogen concentrations within the naturally occurring range are in groundwater of anoxic nature. Percentages of both redox conditions are nearly equal for the nitrate–nitrogen concentrations in the range of 2.5–9.9 ppm. These differences suggest that if hydrologic conditions of groundwater are appropriate for natural attenuation of nitrate, and the influx of nitrate to groundwater is low, measured contamination should be minimal and likely within the naturally occurring concentration range. As inputs increase in areas and hydrologic conditions do not facilitate denitrification, then measured concentrations will likely be above naturally occurring concentrations. These results also suggest that wells exceeding the EPA standard of 10.0 ppm nitrate–nitrogen are likely a result of both high N inputs and high DO, which likely create a cumulative negative impact on groundwater quality. No obvious pattern between nitrate concentration and depth to groundwater was discernable from the data.

Of the 100+ pesticide compounds screened for in 2008 only three compounds had detectable concentrations. Two detections of bromacil at 1.196 and 8.636 ppb, a detection of endosulfan–alpha at 0.042 ppb, and a detection of prometon at 0.093 ppb were all discovered in wells in the Denver–metropolitan. Prometon and bromacil have been detected historically in the Front Range urban landscape. The detection of endosulfan–alpha (a form of endosulfan) was the first ever by the Program and was somewhat surprising as it has not been sold in the United States since 1982, but has been used to make other chemicals. The endosulfan–alpha detection and one of the bromacil detections were discovered in commercial–industrial land–use while the other bromacil detection and the prometon detection were found in the residential land–use. Overall, the number of pesticide detections discovered in the Front Range Urban landscape is lower than areas of irrigated agriculture in Colorado.

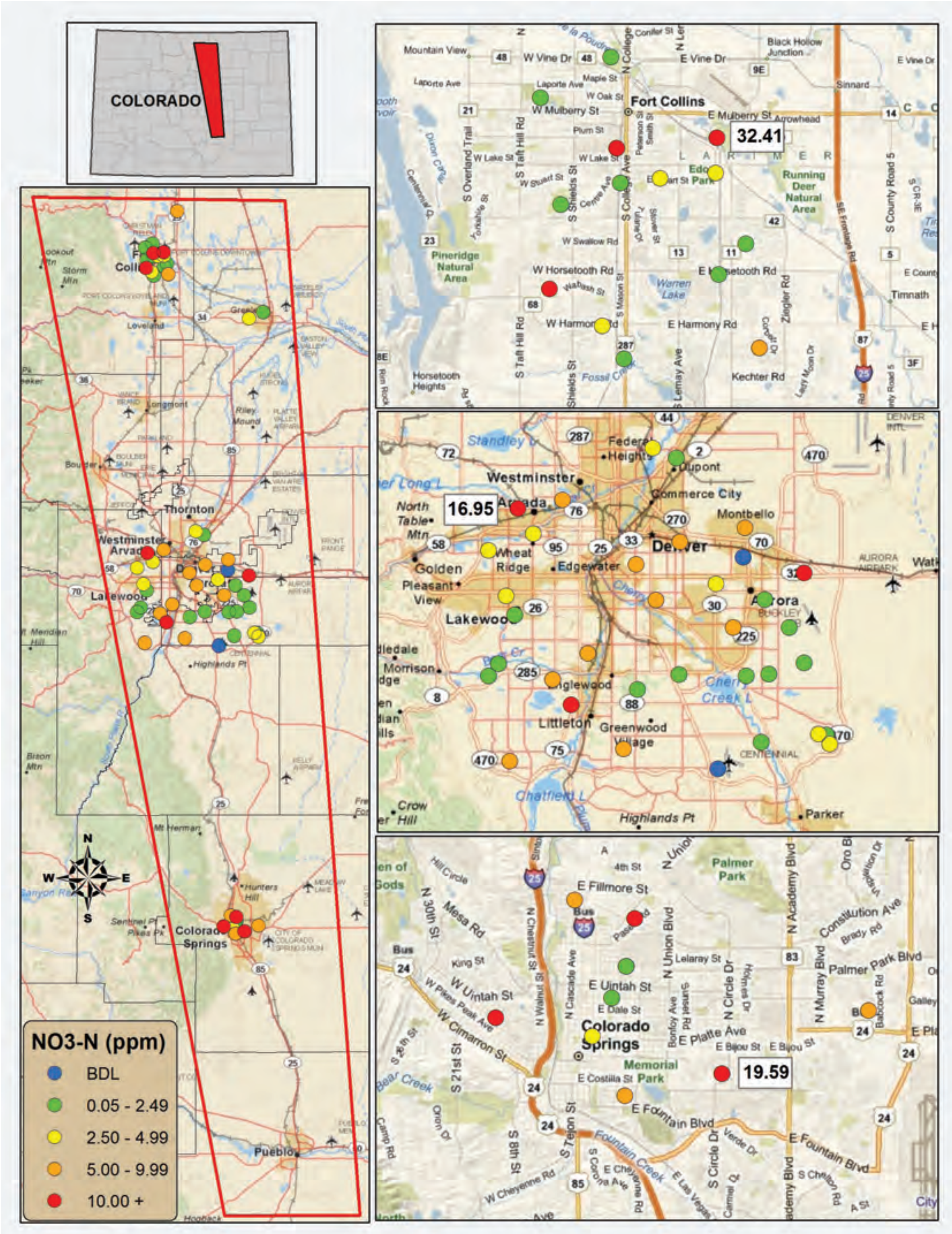

Figure 2. Nitrate–nitrogen results for 2010 samples collected from monitoring wells in the Front Range Urban network (red outline). 'BDL' is below detection limit.

2010 Sampling and Lab Analysis Notes

Sampling of the Front Range Urban monitoring wells in 2010 took place from April 29th – June 6th. Distribution of sample sites is very similar to the 2008 distribution seen in Figure 1d. Three wells sampled in 2008 were not able to be sampled in 2010 due to damage or vandalism that compromised well integrity. Samples were sent to the Program's Groundwater Laboratory in Denver, CO, where they were screened for 102 different pesticide compounds at very low detection limits and also analyzed for nitrate and nitrite concentrations. In 2010, an opportunity to have an additional sample analyzed qualitatively for more than 600 pesticide compounds was pursued and seven samples were sent to the Center for Environmental Mass Spectrometry (CEMS) at the University of Colorado in Boulder, CO. A list of all quantitatively determined analytes screened for and their reporting limits is found in Table 8 at the end of this report. For clarification, qualitative analysis shows the presence or absence of a compound, while quantitative analysis provides the concentration of a detected compound.

2010 Nitrate Results

The general statistics for nitrate–nitrogen concentrations discovered in 2010 were very comparable to prior years. The median of 3.6 ppm is only a tenth lower than the median nitrate–nitrogen concentration in 2008, and the average dropped from 5.7 to 5.1 ppm. This is likely a result of a few things: the three wells not sampled in 2010 did not have 2008 nitrate–nitrogen concentrations that would have influenced the central tendency of the data (i.e. not above EPA standard); groundwater underlying the Front Range Urban landscape (where sampled) is not extensively impacted by nitrate contamination; and concentrations discovered from one sampling event to another are fairly consistent. **Figure 2** shows the distribution of 2010 nitrate results. Although nitrate was relatively consistent within the whole network, one well in Fort Collins saw nitrate–nitrogen go from 19.5 to 32.4 ppm and nitrite–nitrogen from below detection to 2.28 ppm. Nitrite is an intermediate step of ammonia or ammonium converting to nitrite by aerobic bacteria, and has rarely ever been detected by the Program. Remember from earlier that dissolved oxygen concentration in water must be greater than 2.0 ppm in order to be considered oxic and thereby supportive of aerobic biological processes. This particular well

2010 Results by Land Use Class	GC	OS Park	GC Res	Com Ind	Res Com	Res	All
# Wells	5	6	6	5	10	30	63
Nitrate-Nitrogen (mg L^{-1})							
Average	0.7	1.9	2.9	4.6	5.4	6.7	5.1
Q1 (25%)	0.2	0.5	0.6	2.1	1.8	2.5	0.9
Median	0.5	1.0	2.7	2.4	4.0	5.5	3.6
Q3 (75%)	0.6	2.2	4.2	8.3	8.2	8.6	7.4
Maximum	2.2	6.1	7.6	10.3	17.0	32.4	32.4
% Wells BDL	0%	0%	17%	20%	0%	3%	5%
% Wells ≥ 10.0	0%	0%	0%	20%	10%	23%	14%
Dissolved Oxygen (mg L^{-1})							
Average	0.7	0.8	1.8	2.1	3.5	1.9	2.0
Q1 (25%)	0.4	0.3	0.2	0.6	2.1	0.2	0.3
Median	0.6	0.4	0.3	1.6	3.5	0.6	0.8
Q3 (75%)	0.8	1.4	3.3	2.1	4.9	3.1	3.5
Maximum	1.6	1.7	5.5	5.6	7.2	8.1	8.1
Static Water Level (ft bgs)							
Average	9.2	7.8	14.0	15.2	16.0	16.0	14.5
Q1 (25%)	8.7	6.6	6.9	8.8	7.3	8.6	7.4
Median	9.7	7.4	11.8	15.8	12.3	12.7	11.3
Q3 (75%)	11.3	9.6	15.0	17.1	26.8	19.5	18.0
Maximum	13.9	11.6	33.9	27.1	31.4	55.7	55.7

Table 5. Statistics for nitrate-nitrogen, dissolved oxygen, and static water level for Front Range Urban monitoring wells sampled in 2010. GC is golf course; OS/Park is Open Space-Parkland; GC/Res is Golf Course-Residential; Com/Ind is Commercial-Industrial; Res/Com is Residential-Commercial; Res is Residential. 'ft bgs' is feet below ground surface. 'BDL' is below detection limit.

had a DO concentration of 0.5 ppm which may explain the higher than normal nitrite concentration but is not consistent with DO levels in other wells with high nitrate concentrations.

In comparing nitrate results by land use class, as was done initially in 2008, there does not appear to be any patterns other than those previously seen. Golf courses (GC) and open space – parkland (OS–Park) areas had the lowest overall nitrate–nitrogen concentrations with medians of 0.5 and 1.0 ppm respectively. Sample locations lying in residential areas had the highest median of 8.6 ppm, but results seen in residential–commercial and commercial–industrial areas are not significantly different from residential, with medians of 8.2 and 8.3 ppm, respectively. While there were some wells exceeding the EPA standard, the nitrate concentrations encountered in the Front Range Urban landscape in 2010 continues to suggest that nitrate contamination is not an extensive problem as compared to concentrations encountered in other areas of the state.

Dissolved oxygen concentrations seen in Table 5 show the low nitrate concentrations in GC and OS–Park areas are at least partly a result of groundwater's anoxic conditions in these areas. Table 6 compliments these results in showing that of wells with no detection of nitrate or with levels of nitrate below naturally occurring concentrations (<2.5 ppm), nearly all were sampled of groundwater in an anoxic redox state. As was seen in 2008, wells with concentrations between 2.5 and 9.9 are once again equally distributed between oxic and anoxic states while 66% of the wells with nitrate above the EPA standard were found in oxic groundwater. All three wells of anoxic state with nitrate–nitrogen above the EPA standard of 10.0 ppm were in the residential land use. Furthermore the concentrations discovered in these wells in 2010 ranged from 1.3 to 12.9 ppm higher than in 2008 but dissolved oxygen concentrations dropped to <1.0 ppm when they ranged from 1.9 to 4.6 ppm in 2008. This relationship is backwards from what is normally seen and suggests that nitrogen inputs in these areas are exceeding the natural attenuating properties of the soil and groundwater, thereby resulting in accumulation of the nitrate ion.

The 2010 data confirmed the well–established relationship between depth to groundwater and vulnerability to nitrate contamination. Eighty–seven percent of sample sites were in areas where groundwater was less than 25 ft below ground surface (bgs), while seven and one wells were in the 25–49 and

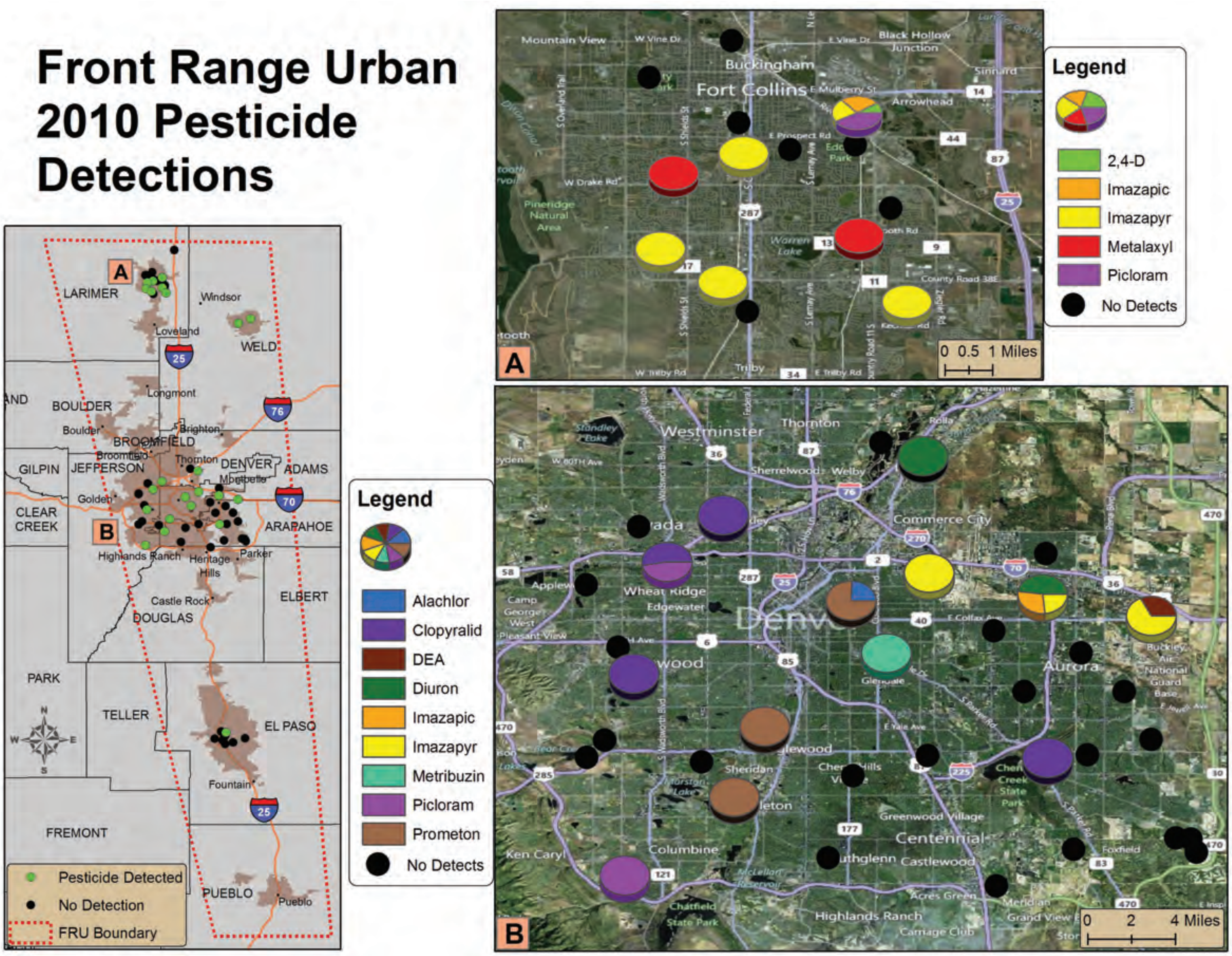

Figure 3. Pesticide detection results for samples collected from monitoring wells of the Front Range Urban network in 2010.

50+ ft depth to water classes, respectively. All nine of the wells exceeding the EPA standard were in the <25 ft bgs category. Nitrate–nitrogen concentrations were 2.5 to 9.9 ppm for wells between 25 and 49 ft bgs, and one well over 50 ft bgs contained a low concentration of 0.8 ppm. The relationship between depth to groundwater and DO described above will continue to be investigated by the Program as it interprets results in monitoring networks. Key data elements that will be beneficial to interpretations are nitrogen inputs, irrigation inputs, and groundwater age.

2010 Pesticide Results

The increased number of pesticide detections from four in 2008 to 31 in 2010 is mostly explained by the Program's laboratory lowering their method detection limits and increased familiarity and efficiency with newly adopted analytical methodologies. Eleven different compounds were discovered in concentrations ranging from a low of 0.14 to a high of 3.77 ppb. The most often detected compound was imazapyr with nine detections ranging in concentration from 0.14 to 0.87 ppb as seen in Table 7. Imazapyr is used for pre– and post–emergent control of annual and perennial grasses and broadleaf weeds, brush, vines, and many deciduous trees. Some products containing imazapyr allow application in riparian areas or to emerged aquatics. Several detections within the urban environment are consistent with its pattern of use and chemical–physical properties identified in the United States Department of Agriculture – Natural Resource Conservation Service's Windows Pesticide Screening Tool (Win–PST) pesticide database (http://www.wsi.nrcs.usda.gov/products/W2Q/pest/winpest31.html) that give it a high leaching potential risk. Imazapyr is considered to be of low toxicity to humans and animals.

Another pesticide with multiple detections is metalaxyl, a fungicide used on ornamentals and turf. Its discovery in the urban landscape can be explained by the high percentage of residential land use which is usually associated with turf maintenance. Imazapic is similar in use to imazapyr and was discovered in one well each in Fort Collins and Denver–metro as seen in **Figure 3**. Denver–metro also accounted for all four of the clopyralid detections discovered in the Front Range Urban network. Clopyralid was initially used as a broadleaf weed controller in turf, but recycling or composting of turf clippings on which it was applied was discovered to result in contaminated compost material that affected plant growth. Subsequently that use was removed from the label and now clopyralid is used primarily in non–crop industrial areas or commercial right–of–ways. The high density of such areas within the urban environment makes it understandable why clopyralid is detected more often in the urban landscape than in the agricultural or rural landscape. Prometon is another pesticide with a similar detection pattern. Having been detected in previous Front Range Urban samplings it is not surprising that three detections of prometon were discovered in 2010.

Dissolved Oxygen Influence			
NO_3-N	# Wells	# Oxic	# Anoxic
BDL	3	0	3
0.05<2.5	23	4	19
2.5<10.0	28	12	16
≥ 10.0	9	6	3

Table 6. Nitrate-nitrogen results in comparison to dissolved oxygen state of groundwater for samples collected in the Front Range Urban network in 2010. Units for NO_3-N is mg L^{-1}. 'BDL' is below detection limit. Oxic is <2.0 mg L^{-1} dissolved oxygen. Anoxic is >2.0 mg L^{-1} dissolved oxygen.

Summary

Monitoring of Urban Front Range groundwater has not resulted in discovery of extensive contamination with agrichemicals. Nitrate results from 2010 continue to show that groundwater quality is not being highly impacted by the urban land use when compared to impacts associated with irrigated agriculture land use. Within the urban landscape it is obvious that the residential land use and its associated need for turf management, is a key source of nitrate being discovered above naturally occurring concentrations. In many situations, dissolved oxygen concentrations and depth to groundwater help explain nitrate concentrations and variability in those concentrations over a time period; however, results from 2010 suggest that there are most likely other factors that determine the rate of denitrification in a particular area and more research is needed in order to better interpret changes in nitrate concentrations.

Both the number of detections and the number of types of pesticide compounds increased from 2008 to 2010. While some of this is likely a reflection of changes in method detection limits or implementation of new methods at the Program's laboratory, it also may be

Front Range Urban 2010 Pesticide Detections					
Pesticide	# Detects	Minimum	Median	Mean	Maximum
2,4-D	1	0.37			0.37
Alachlor	1	0.54			0.54
Clopyralid	4	0.81	0.83	0.83	0.85
Desethyl atrazine*	2	0.13			0.17
Diuron	2	0.30			0.52
Imazapic	2	0.31			1.35
Imazapyr	9	0.14	0.25	0.30	0.87
Metalaxyl	3	0.20	0.21	0.21	0.23
Metribuzin	1	3.77			3.77
Picloram	3	0.65	0.74	1.12	1.96
Prometon	3	0.40	0.41	0.84	1.71

Table 7. Pesticide compounds detected in samples collected from the Front Range Urban monitoring network in 2010. '*' indicates pesticide degradation product. Concentration units are in parts-per-billion (ppb) or micrograms-per-liter (ug L^{-1}).

an indication that pesticide management practices in the past, or more recently, are impacting groundwater quality. There were no detected pesticide concentrations above established EPA drinking water standards; however, it is important to note that only a few of the pesticide compounds screened for actually have defined standards. The pesticide compounds imazapyr and clopyralid were the most commonly detected, but several other compounds with known leaching capabilities were discovered within the network.

Future sampling of the Front Range Urban network will likely take place in 2013 and may attempt to establish more monitoring wells in areas of the network currently lacking coverage like Boulder, Longmont, Loveland, and Pueblo.

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 8. Reporting limits of analytes tested for in 2010 by the Biochemistry Laboratory of the Colorado Department of Agriculture. Concentrations are in micrograms per liter (µg L^{-1}) for fungicide, herbicide, nematicide and insecticide analyte types. Concentrations for inorganic analytes are in milligrams per liter (mg L^{-1}).

Reporting Limits for Analytes Tested - Sampling Year 2010

Analyte	Tradename[1]	Use	Reporting Limit	Analyte	Tradename	Use	Reporting Limit
Nitrate as nitrogen (mg L^{-1})			0.05	3-Hydroxy carbofuran	Metabolite	Insecticide	0.25
Nitrite as nitrogen (mg L^{-1})			0.05	Halofenozide	Mach 2	Insecticide	0.10
Acetochlor	Harness	Herbicide	0.20	Halosulfuron methyl	Permit	Herbicide	0.10
Acetochlor (ESA)	Metabolite[2]	Herbicide	0.10	Hexazinone	Velpar	Herbicide	0.20
Acetochlor (OA)	Metabolite	Herbicide	0.25	Hydroxy Atrazine	Metabolite	Herbicide	0.10
Acifluorfen	Storm	Herbicide	0.10	Imazamethabenz methyl ester	Assert	Herbicide	0.10
Alachlor	Lasso	Herbicide	0.20	Imazamox	Raptor	Herbicide	0.10
Alachlor (ESA)	Metabolite	Herbicide	0.10	Imazapic	Plateau	Herbicide	0.10
Alachlor(OA)	Metabolite	Herbicide	0.10	Imazapyr	Arsenal	Herbicide	0.10
Aldicarb	Temik	Insecticide	0.50	Imazethapyr	Pursuit	Herbicide	0.10
Aldicarb sulfone	Metabolite	Insecticide	0.25	Imidacloprid	Admire	Insecticide	0.25
Aldicarb sulfoxide	Metabolite	Insecticide	0.10	Isoxaflutole	Balance	Herbicide	0.10
Aminopyralid	Milestone	Herbicide	0.50	Kresoxim methyl	Cygnus	Fungicide	0.25
Atrazine	Aatrex	Herbicide	0.10	Lindane	Gammexane	Insecticide	0.20
Azoxystrobin	Amistar	Fungicide	0.10	Linuron	Afalon	Herbicide	0.20
Bentazon	Basagran	Herbicide	0.50	Malathion	Malathion	Insecticide	0.20
Bromacil	Hyvar X	Herbicide	0.10	MCPA	MCPA	Herbicide	0.10
Carbofuran	Furadan	Insecticide	0.20	MCPP	Kilprop	Herbicide	0.10
Chlorantraniliprole	Durivo	Insecticide	0.10	Metalaxyl	Allegiance	Fungicide	0.20
Chlorimuron ethyl	Classic	Herbicide	0.25	Metconazole	Caramba	Fungicide	0.10
Chlorothalonil	Bravo	Fungicide	0.20	Methomyl	Lannate	Insecticide	0.10
Chlorsulfuron	Glean	Herbicide	0.10	Metolachlor	Bicep	Herbicide	0.20
Clopyralid	Lontrel	Herbicide	0.50	Metolachlor (ESA)	Metabolite	Herbicide	0.25
Cyanazine	Bladex	Herbicide	0.20	Metolachlor (OA)	Metabolite	Herbicide	0.25
Cyproconazole	Alto	Fungicide	0.10	Metribuzin	Lexone	Herbicide	0.20
Cyromazine	Larvadex	Insecticide	0.25	Metsulfuron methyl ester	Ally	Herbicide	0.10
2,4-D	Weed B Gone	Herbicide	0.10	Nicosulfuron	Accent	Herbicide	0.10
2,4-DB	Butyrac	Herbicide	0.50	Norflurazon	Solicam	Herbicide	0.20
DCPA	Dacthal	Herbicide	0.20	Picloram	Tordon K	Herbicide	0.50
Deethyl atrazine	Metabolite	Herbicide	0.10	Prometon	Pramitol	Herbicide	0.20
Deisopropyl atrazine	Metabolite	Herbicide	0.25	Propazine	Milo-Pro	Herbicide	0.20
Dicamba	Banvel D	Herbicide	0.50	Propoxur	Baygon	Insecticide	0.10
Dichlobenil	Casoron	Herbicide	0.20	Prosulfuron	Peak	Herbicide	0.25
Dichlorprop	Patron	Herbicide	0.10	Pyrimethanil	Distinguish	Fungicide	0.10
Diflufenzopyr	Distinct	Herbicide	0.10	Quinclorac	Drive	Herbicide	0.10
Dimethenamid	Frontier	Herbicide	0.10	Simazine	Primatol S	Herbicide	0.20
Dimethenamid (ESA)	Metabolite	Herbicide	0.25	Sulfentrazone	Spartan	Herbicide	0.50
Dimethenamid (OA)	Metabolite	Herbicide	0.50	Sulfometuron methyl ester	Oust	Herbicide	0.10
Dimethoate	Cygon	Insecticide	0.10	Sulfosulfuron	Certainty	Herbicide	0.10
Dinotefuran	Safari	Insecticide	0.20	Tebuconazole	Elite	Fungicide	0.10
disulfoton	Disyston	Insecticide	0.20	Tebufenozide	Confirm	Insecticide	0.10
disulfoton sulfone	Metabolite	Insecticide	0.20	Tebuthiuron	Graslan	Herbicide	0.10
disulfoton sulfoxide	Metabolite	Insecticide	0.20	Thiamethoxam	Cruiser	Insecticide	0.25
Diuron	Karmex	Herbicide	0.25	Triadimefon	Amiral	Fungicide	0.10
Ethofumesate	Solera	Herbicide	0.25	Triallate	Avadex BW	Herbicide	0.25
Ethoprop	Mocap	Insecticide	0.20	Triasulfuron	Amber	Herbicide	0.10
Fenamiphos	Nemacur	Nematicide	0.20	Trichlorfon	Dylox	Insecticide	0.20
Fenamiphos sulfone	Metabolite	Nematicide	0.20	Triclopyr	Garlon	Herbicide	0.50
Flufenacet	Axiom	Herbicide	0.10	Triticonazole	Charter	Fungicide	0.10
Flumetsulam	Broadstrike	Herbicide	0.10	Vinclozolin	Curalan	Fungicide	0.20

1 - Tradenames used are strictly examples of products containing a particular analyte and does not suggest analysis of a specific product.
2 - 'Metabolite' is a degradation product of a parent pesticide.