COLORADO DEPARTMENT OF AGRICULTURE

AGRICULTURAL CHEMICALS AND GROUNDWATER PROTECTION

Groundwater Monitoring Report
San Luis Valley

The Agricultural Chemicals and Groundwater Protection Act (C.R.S. 25-8-205.5) took effect on July 1, 1990, and established the Groundwater Protection Program (Program). The goal of the Program is to reduce negative impacts to groundwater and the environment by improving management of fertilizer and pesticide (agrichemicals) and to assure that groundwater remains safe for domestic and livestock consumption by preventing contamination. A key component of the Program is to collect current, scientifically valid data for the assessment of groundwater quality.

This report discusses monitoring history in the San Luis Valley (SLV), sample collection and analysis information for the 2009 field season, and statistics and maps detailing laboratory results. Information pertaining to sampling frequency and purpose, sampling network development, location and character of the San Luis Valley, and long-term history of the Program, is available in greater detail from the following 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 first became involved with water quality monitoring in the SLV in 1993 when 93 domestic wells were sampled for analysis the nitrate ion in nitrogen fertilizer and pesticides. Seventeen wells contained nitrate-nitrogen (NO_3-N) above the United States Environmental Protection Agency's (EPA) drinking water standard of 10.0 milligrams per liter (mg L^{-1}) or parts-per-million (ppm). There were 29 wells that tested below the detection limit of 0.5 ppm. Wells exceeding the standard were generally found in the area between and around the towns of Monte Vista and Center – the center of the SLV. The Program discovered three wells with a detectable pesticide concentration with one of those – a single detection of Lindane – being above its established EPA Standard of 0.20 micrograms per liter (µg L^{-1}) or parts-per-billion (ppb).

The Program worked alongside the United States Geologic Survey's North America Water Quality Assessment project (USGS NAWQA), in 2000, to obtain split samples from a network of 35 monitoring wells. NO_3-N concentrations were above the EPA standard in 10 of the 33 wells sampled and only two wells were below the detection limit of 0.05 ppm. The maximum NO_3-N concentration was 61.01 ppm. The majority of wells with elevated nitrate were again in the center of the SLV. Detections of metolachlor and metribuzin occurred in nine and five wells, respectively, in this sampling event, but not at any levels exceeding EPA standards.

In 2001, the Program received an inquiry from some SLV residents voicing concerns of a high occurrence of cancer in an area between Monte Vista and Center. The Program then conducted a special sampling of eight domestic wells in response to their concerns. Only one well contained NO_3-N over the EPA standard while the remainder of the wells contained much lower concentrations; no pesticides were detected in any of the samples. The presence of a widespread, inordinate concentration of nitrate or pesticide was not discovered in the area sampled.

The USGS NAWQA program returned to sample their network of 35 wells in 2007 and the Program again obtained split samples. Only four of 35 wells were below the detection limit of 0.05 ppm NO_3-N while eight wells were over the EPA standard with a maximum concentration of 32.9 ppm. The well location with the maximum in 2000 is in the same location as the maximum in 2007. However, due to a decrease in the aquifer level it is not possible to conclude that the change in concentration is due to changes in land or agrichemical management. Eight sampled wells that did not

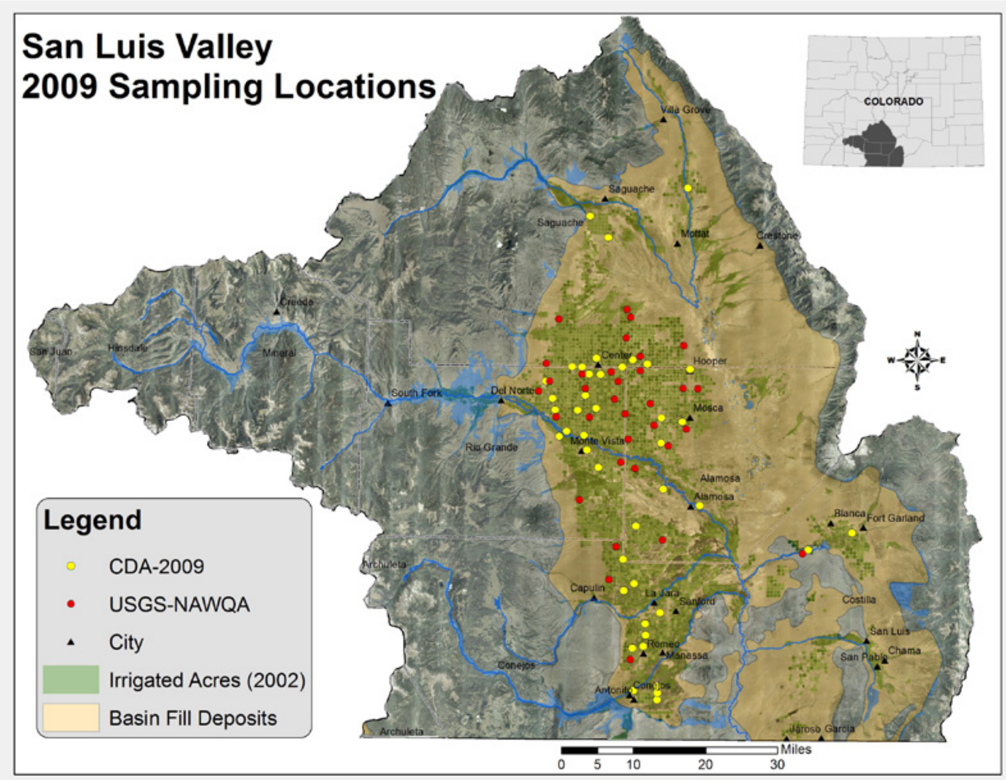

Figure 1. Map depicting locations of CDA 2009 domestic well samples and their placement in comparison to locations of USGS-NAWQA monitoring wells.

change in depth did not show any significant difference in nitrate from 2000 to 2007. Metribuzin and metolachlor again were detected in 2007, but in far fewer instances and lower concentrations which again is likely a result of 22 wells being installed to greater depths. Of the five wells with one or more detected pesticides in 2007, only one well had a repeat detection of metolachlor in 2000. The concentration was unchanged even though well depth had increased 13 ft.

2009 Sampling and Lab Analysis Notes

With recurring evidence of agrichemical contamination in SLV groundwater, the Program finds it a priority to sample once every two years. Unfortunately, the USGS NAWQA program currently only samples once every 10-12 years so utilization of their network was not possible in 2009. Instead, the Program conducted a domestic well sampling event in cooperation with the San Luis Valley Ecosystem Council (SLVEC). The Program sampled a well-distributed collection of 43 domestic wells for analysis of nitrate and a suite of 90 pesticide compounds. Sampled wells were selected in similar locations as USGS NAWQA well locations, and provide insight into areas of the SLV not previously studied for groundwater quality by the Program **(Figure 1)**.

In nearly all instances, domestic wells were purged utilizing a flow-cell and multi-parameter meter to ensure adequate purging. Wells with no ability to connect the flow cell, or with excessively high flow rates or pressure, were purged for a length of time to ensure adequate flushing of the well casing and associated plumbing. Where possible, samples were filtered with a disposable glass-fiber, 1.0 micron filter. Sample wells are assumed to be established in the unconfined aquifer of the SLV as according to either owner records or well records on the

San Luis Valley Nitrate Comparison Between Domestic and Monitoring Wells					
	Well Depth		Nitrate-nitrogen		
Statistic	Domestic Wells	Monitoring Wells	2000	2007	2009
# of Wells	43	33	33	33	43
Average	78	32	8.8	6.7	3.4
Standard Deviation	42	12	12.9	9.5	4.9
Minimum	20	15	BDL	BDL	BDL
1st Quartile (25%)	53	22	0.3	0.1	0.5
Median (50%)	80	31	3.1	0.8	1.7
3rd Quartile (75%)	100	36	15.2	10.6	3.3
Maximum	260	75	61.0	32.9	23.5
# ≥ 10.0 ppm	NA	NA	10	8	3

Table 1. Comparison of well depth and nitrate-nitrogen concentrations between domestic wells sampled in 2009 and monitoring wells sampled in 2000 and 2007 in the San Luis Valley of south-central Colorado. Well depth is feet below land surface. Nitrate-nitrogen units are mg/L or ppm. BDL is below detection limit.

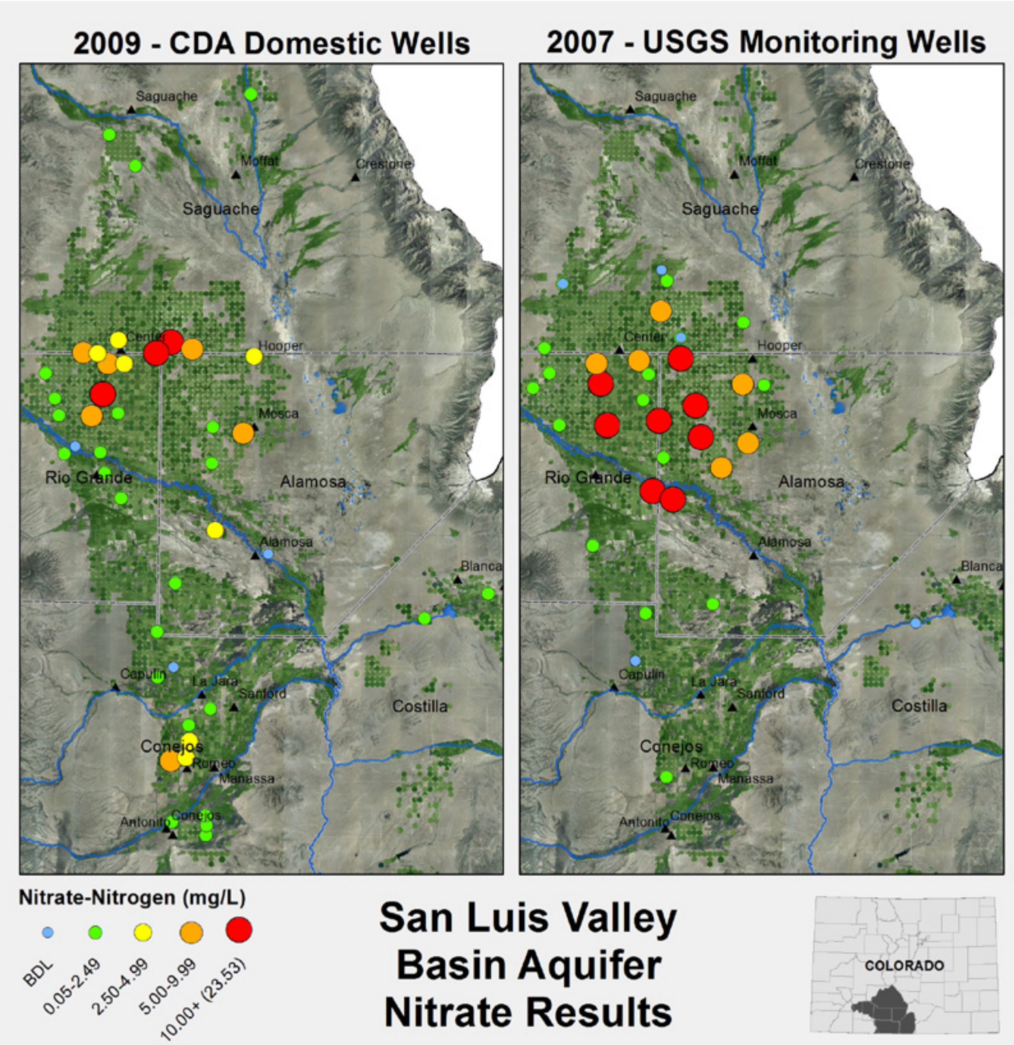

Figure 2. Nitrate-nitrogen results for 2009 domestic well groundwater samples compared to 2007 monitoring well groundwater samples. BDL stands for below detection limit. Nitrate value in parenthesis is maximum detected concentration in the 2009 domestic well network.

Colorado State Engineer's well records database. All wells were sampled by Karl Mauch, the Program's Groundwater Monitoring Specialist.

Due to instrument issues at the Program's laboratory, domestic water well samples were sent to the Montana Department of Agriculture Analytical Laboratory in Bozeman, MT for pesticide analysis. Using methodology similar in nature to those used at the Colorado Department of Agriculture, this laboratory screened the samples for 90 different pesticide compounds at very low detection limits. Two historically detected pesticides, metribuzin and lindane, were not part of Montana's pesticide screen so the Program's laboratory set up a method to analyze a split sample for these two analytes. This was devised in order to screen for all previously detected pesticides. Samples were hand-delivered to the Program's laboratory for determination of nitrate, nitrite, metribuzin, and lindane. A list of all compounds analyzed for and their respective reporting limits is available in Table 3 at the end of this report **Table 3** at the end of this report.

2009 Nitrate Results

Nitrate-nitrogen was detected in 40 of 43 domestic wells with a minimum of 0.05 ppm and a maximum of 23.53 ppm. The median concentration was just under 2.0 ppm as seen in **Table 1**. Only three wells had concentrations over the EPA standard of 10.0 ppm. Figure 2 compares the locations and the nitrate results of the 2009 domestic wells with the USGS NAWQA monitoring well locations. Any well exceeding the EPA standard is symbolized in red, while concentrations above what is commonly believed to be a natural background concentration of 2.5 ppm are symbolized in yellow and orange.

Consistent with previous studies, locations of the highest nitrate concentrations clustered in the center of the SLV. While there are some gaps in sample locations within the area between Center and Mosca, the 2009 sampling effort overlaps reasonably with the 2007 monitoring well sampling event. Compared to the USGS NAWQA network, sample density was higher in the southern reach of the SLV. While no wells exceeded the EPA standard for NO3-N in this area, there were a few wells with elevated concentrations just north and west of Romeo. Due to this discovery, it may be valuable to install more monitoring wells in order to fully understand the extent of nitrate contamination in this portion of the SLV.

Table 1 presents some important differences between the USGS NAWQA network and the wells sampled in 2009. The USGS NAWQA monitoring well network has a median well depth of 31 ft and a maximum depth of 75 ft. The domestic wells selected in 2009 have a much wider range of 20 ft to 260 ft deep. Excluding the three domestic wells installed at 160 ft or greater, which in the SLV are more likely to be installed in the confined aquifer instead of the unconfined aquifer, the median depth for the domestic well network is still more than double the median USGS well depth. Removing the three nitrate values corresponding to these wells does not greatly change overall statistics for the domestic well network.

It is important to consider the differences in well depth when comparing water quality results between the two networks, but it is likely that differences in well types

San Luis Valley 2009 Pesticide Detections					
Pesticide	**# Detects**	**Minimum**	**Median**	**Average**	**Maximum**
Azoxystrobin	1	0.0009			0.0009
Chlorosulfuron	1	0.0400			0.0400
Imazamethabenz acid	3	0.0070	0.0190	0.0177	0.0270
Imazamox	1	0.0200			0.0200
Imazapyr	1	0.0110			0.0110
Imazathapyr	1	0.0100			0.0100
Imidacloprid	4	0.0040	0.0085	0.0098	0.0180
MCPP	1	0.0030			0.0030
Metolachlor (ESA)	18	0.0025	0.0330	0.3889	2.2000
Metolachlor (OA)	6	0.0370	0.2350	0.4623	1.4000
Simazine	1	0.0040			0.0040

Table 2. Pesticide compound detections in domestic well groundwater samples collected in the San Luis Valley of south-central Colorado in 2009. Concentrations are in micrograms per liter (µg L-1) or parts-per-billion (ppb).

and sampling methods may also be playing a role in the results. Due to these differences it is difficult to ascertain any presence of statistical trend or concentration changes from the 2009 domestic well data and previous USGS data. Nonetheless, the data allows us to make a few conclusions. First, it is apparent from the overall lower statistics that domestic wells in the SLV are less contaminated from nitrate than monitoring wells. While depth is probably a factor, the lack of a statistically significant correlation between depth and concentration suggests that other factors influence the level of nitrate contamination. And secondly, while the domestic wells with elevated nitrate contamination in the northern part of the SLV are in close proximity to monitoring wells that also had elevated levels of nitrate, the 2009 domestic well results show evidence of nitrate contamination in the southern reach of the SLV where the monitoring well network is sparse.

Nitrate-nitrogen data for these two networks shows that nitrate concentrations are both higher and more variable near the top of the water table where monitoring wells commonly sample, and that these concentrations occasionally exceed the EPA standard. Additionally, the domestic wells, which are deeper in the aquifer, show less variable, all-around lower nitrate concentrations, but still potential for nitrate to exceed the EPA standard. Both of these responses are seen in other areas of the state where monitoring wells and domestic wells are sampled. This demonstrates that while retention time and soil thickness is greater for deeper installed wells, which allows a greater chance for nitrate to attenuate, some conditions exist that allow for nitrate to leach to and impact deeper depths in the aquifer.

2009 Pesticide Results

Pesticide analysis presented an assortment of detected compounds throughout the sample network. **Table 2** shows types of pesticide compounds discovered and their minimum and maximum concentrations. No pesticide compound was detected at a level exceeding an established EPA drinking water standard. The greatest number of detections and highest concentrations were of the metolachlor breakdown products, metolachlor ethane sulfonic acid (ESA) and metolachlor oxanilic acid (OA), both of which are known by research to show up in concentrations several factors higher in areas where the parent compound, metolachlor, is used. Nearly all detections of the metolachlor breakdown products were located in the Closed Basin part of the SLV aquifer system, except for one detect northwest of La Jara **(Figure 3)**. These detections closely follow the historic records of metolachlor detections from monitoring wells in the center of the SLV and suggest that there is vulnerability of the aquifer to this frequently used compound in this portion of the SLV. Unfortunately, due to complications in the laboratory, the other historically detected pesticides, metribuzin and lindane, had minimum reporting limits greater than 14 ppb in 2009. All detections of these compounds in previous sampling events were < 0.3 ppb, so the 2009 results did little to shed light on the persistence of these compounds in the SLV.

Several other herbicide compounds were detected including MCPP (mecoprop), chlorosulfuron, imazathapyr, imazamox, and simazine. Most were single detections at concentrations < 0.05 ppb. Beyond the multiple detections of metolachlor breakdown products, two other pesticide compounds, imidacloprid and imazamethabenz acid, had three and four detections, respectively, and never together in the same well. In total, 38 pesticide detections were

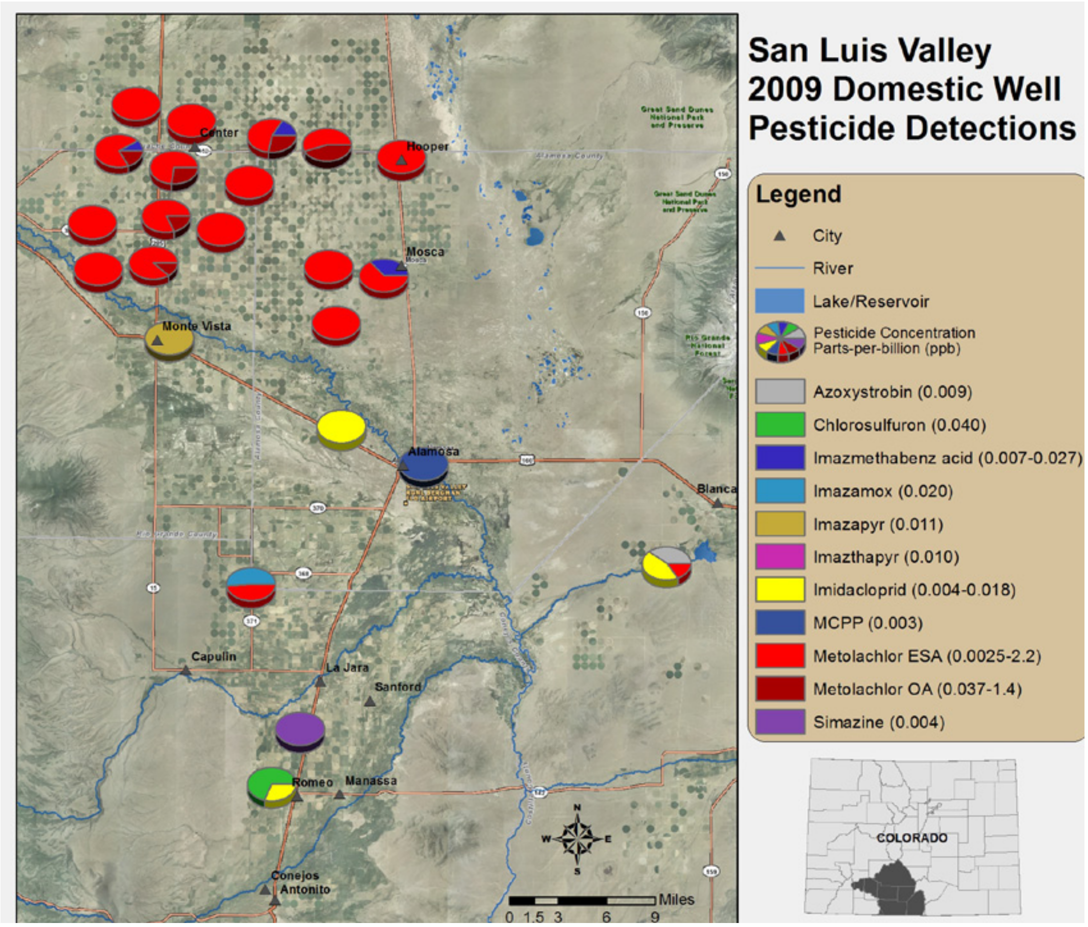

Figure 3. Pesticide detections from domestic well groundwater samples collected in the San Luis Valley in 2009. Pie charts indicate approximate location of domestic well containing pesticide(s). Values in parenthesis after pesticide name in legend indicate range of concentrations detected.

found in 23 wells at concentrations ranging from 0.003 - 2.2 ppb. The detection of multiple pesticide compounds from domestic wells in the southern reach of the SLV stresses the need to increase monitoring efforts near the top of the water table in that area.

Summary

In 2009, the CDA collaborated with the SLVEC to sample domestic wells in the San Luis Valley. Sample results agreed with previous monitoring in that the shallow, unconfined aquifer is vulnerable to contamination from nitrate and pesticides, especially in the center portion of the SLV. Use of domestic wells, installed at depths not aimed at sampling the top of the water table like in the USGS NAWQA monitoring well network, creates a conflict in comparing the two datasets. While the median nitrate concentration from the 2009 sampling effort is lower when compared to previous USGS NAWQA reports, the reason for the difference is not clearly defined and may be a combination of factors. Factors that include well depth, well type sampled, increased contaminant degradation and/or improved management of land or agrichemicals. The presence of agrichemicals in domestic wells located in historically contaminated areas, as well as new areas not intensely studied before, provides further definition to the extent of contamination in the SLV. Future efforts by the Program will include establishing a long-term, dedicated monitoring well network that focuses on the central SLV where contamination has been most prevalent. The network should stretch into the southern SLV where elevated nitrate and pesticides were discovered in domestic wells, and may include monitoring wells drilled into the confined aquifer of the SLV.

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 San Luis Valley - Sampling Year 2009

Analyte	Tradename[1]	Use	Reporting Limit
Nitrate as nitrogen (mg L^{-1})			0.05
Nitrite as nitrogen (mg L^{-1})			0.05
Acetochlor	Harness	Herbicide	0.1400
Acetochlor (ESA)	Metabolite	Herbicide	0.0100
Alachlor	Lasso	Herbicide	0.1100
Alachlor (ESA)	Metabolite	Herbicide	0.0110
Alachlor(OA)	Metabolite	Herbicide	0.0042
Aldicarb	Temik	Insecticide	0.0028
Aldicarb sulfone	Metabolite	Insecticide	0.0011
Aldicarb sulfoxide	Metabolite	Insecticide	0.0560
Aminopyralid	Milestone	Herbicide	0.0530
Atrazine	Aatrex	Herbicide	0.0022
Azinphos methyl	Guthion	Insecticide	0.0370
Azinphos methyl (OA)	Metabolite	Insecticide	0.0310
Azoxystrobin	Amistar	Fungicide	0.0011
Bentazon	Basagran	Herbicide	0.0011
Bromacil	Hyvar X	Herbicide	0.0074
Carbaryl	Sevin	Insecticide	0.0400
Carbofuran	Furadan	Insecticide	0.0052
Chlorpyrifos	Lorsban	Insecticide	0.0310
Chlorsulfuron	Glean	Herbicide	0.0056
Clodinafop acid	Topik	Herbicide	0.0130
Clopyralid	Lontrel	Herbicide	0.0220
Cyproconazole	Alto	Fungicide	0.0051
2,4-D	Weed B Gone	Herbicide	0.0045
2,4-DB	Butyrac	Herbicide	0.0910
Deethyl atrazine	Metabolite	Herbicide	0.0017
Deisopropyl atrazine	Metabolite	Herbicide	0.0100
Dicamba	Banvel D	Herbicide	0.0510
Difenoconazole	Dividend	Fungicide	0.0200
Dimethenamid	Frontier	Herbicide	0.0100
Dimethenamid (OA)	Metabolite	Herbicide	0.0038
Dimethoate	Cygon	Insecticide	0.0011
Diuron	Karmex	Herbicide	0.0100
Epoxyconazole	Epic	Fungicide	0.0280
Ethion	Nialate	Insecticide	0.3900
Ethofumesate	Solera	Herbicide	0.0250
Ethoprop	Mocap	Insecticide	0.0120
Fenbuconazole	Enable	Fungicide	0.0053
Flucarbazone	Everest	Herbicide	0.0012
Flucarbazone sulfonamide	Metabolite	Herbicide	0.0010
Flufenacet (OA)	Metabolite	Herbicide	0.0053
Flumetsulam	Broadstrike	Herbicide	0.0630
Glutamic acid	L-Glutamic acid	Growth Reg	0.0074
Hydroxy Atrazine	Metabolite	Herbicide	0.0064
Halosulfuron methyl	Permit	Herbicide	0.0100
Hexazinone	Velpar	Herbicide	0.0059
Imazalil	Deccozil	Fungicide	0.0100

Analyte	Tradename	Use	Reporting Limit
Imazamethabenz acid	Assert	Herbicide	0.0052
Imazamethabenz ester	Assert	Herbicide	0.0010
Imazamox	Raptor	Herbicide	0.0120
Imazapic	Plateau	Herbicide	0.0110
Imazapyr	Arsenal	Herbicide	0.0110
Imazethapyr	Pursuit	Herbicide	0.0100
Imidacloprid	Admire	Insecticide	0.0018
Isoxaflutole	Balance	Herbicide	0.1300
Lindane	Gammexane	Insecticide	14.200
Linuron	Afalon	Herbicide	0.0110
Malathion	Malathion	Insecticide	0.0280
MCPA	MCPA	Herbicide	0.0023
MCPP	Kilprop	Herbicide	0.0022
Metalaxyl	Allegiance	Fungicide	0.0120
Methomyl	Lannate	Insecticide	0.0016
Metolachlor	Bicep	Herbicide	0.0120
Metolachlor (ESA)	Metabolite	Herbicide	0.0025
Metolachlor (OA)	Metabolite	Herbicide	0.0210
Metribuzin	Lexone	Herbicide	14.900
Metsulfuron methyl	Ally	Herbicide	0.0260
Nicosulfuron	Accent	Herbicide	0.0110
NOA 407854	Metabolite	Herbicide	0.0052
NOA 447204	Metabolite	Herbicide	0.0100
Picloram	Tordon K	Herbicide	0.1400
Prometon	Pramitol	Herbicide	0.0051
Propachlor	Ramrod	Herbicide	0.0028
Propachlor (OA)	Metabolite	Herbicide	0.0094
Propiconazole	Banner	Fungicide	0.0100
Prosulfuron	Peak	Herbicide	0.0050
Pyrasulfatole	Pyrasulfatole	Herbicide	0.0230
Pyroxsulam	XDE-742	Herbicide	0.0270
Simazine	Primatol S	Herbicide	0.0026
Sulfometuron methyl	Oust	Herbicide	0.0100
Sulfosulfuron	Certainty	Herbicide	0.0054
Tebuconazole	Elite	Fungicide	0.0100
Tebuthiuron	Graslan	Herbicide	0.0011
Tembotrione	Tembotrione	Herbicide	0.2200
Tetraconazole	Eminent	Fungicide	0.0062
Thifensulfuron	Harmony	Herbicide	0.0260
Tralkoxydim	Achieve	Herbicide	0.0051
Tralkoxydim acid	Achieve	Herbicide	0.0050
Triadimefon	Amiral	Fungicide	0.0057
Triadimenol	Baytan	Fungicide	0.0260
Triallate	Avadex BW	Herbicide	0.3000
Triasulfuron	Amber	Herbicide	0.0260
Triclopyr	Garlon	Herbicide	0.0110
Triticonazole	Charter	Fungicide	0.0320

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