# Agricultural Chemicals and Groundwater Protection

# Groundwater Monitoring Report

## Western Slope – Tri-River Area

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 the monitoring history of the Western Slope Tri-River Area, 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, location and character of the Western Slope Tri-River Area, 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 for agrichemicals on the Western Slope in 1998. Eighty-one samples were collected from domestic and livestock wells throughout the entire Western Slope from Craig in the north to Durango in the south. Only one well, near Craig, contained nitrate-nitrogen ($NO_3$-N) over the EPA drinking water standard of 10.0 milligrams per liter ($mg\ L^{-1}$) or parts-per-million (ppm). Nearly 40% of the samples were below the detection limit of 0.5 ppm, 51 samples contained $NO_3$-N between 0.5-9.9 ppm, and only four samples were $\geq$ 5.0 ppm. Malathion was the only pesticide detected and was only found in one well.

In 1999, the Program sampled 10 monitoring wells in the Clifton-Grand Junction area of the Grand Valley. Two of the 10 wells had $NO_3$-N greater than 10.0 ppm with a maximum of 15.0 ppm. Seven wells were below the detection limit of 0.10 ppm. No pesticide compounds were detected. These samples are all within a localized area and do not likely provide an adequate representation of overall groundwater quality in the Grand Valley. Even though no evidence has surfaced with respect to significant contamination with agrichemicals in these previous sampling events of Western Slope groundwater, the expansive size of the survey area and the abundance of irrigated agricultural and oil and gas (O&G) land use warrants continued sampling efforts.

### 2009 Sampling and Lab Analysis Notes

Re-evaluation of the Western Slope area in 2009 led the Program to split the expansive Western Slope into three more manageable sub-areas: Northwest, Tri-River, and Southwest. Each area has different characteristics with respect to water consumption, land use/land cover, and varying levels of vulnerability to contamination from agrichemicals. By surveying these smaller areas, effort can be applied to getting sample density in irrigated agriculture and O&G intense areas. The Program decided groundwater in the Tri-River Area was the most vulnerable and had the highest potential contamination due to the large amount of irrigated agriculture in the Uncompahgre and Grand Valleys, and the high density of O&G activity in areas with shallow groundwater. Areas with high O&G activity were chosen for sampling because it is desirable for the drilling pad areas to be kept clear of vegetation which requires the use of herbicide and/or soil sterilants. An area with a large number of these pads may be an appreciable non-point source of pesticide contamination to the groundwater, especially in areas of shallow groundwater and permeable soils.

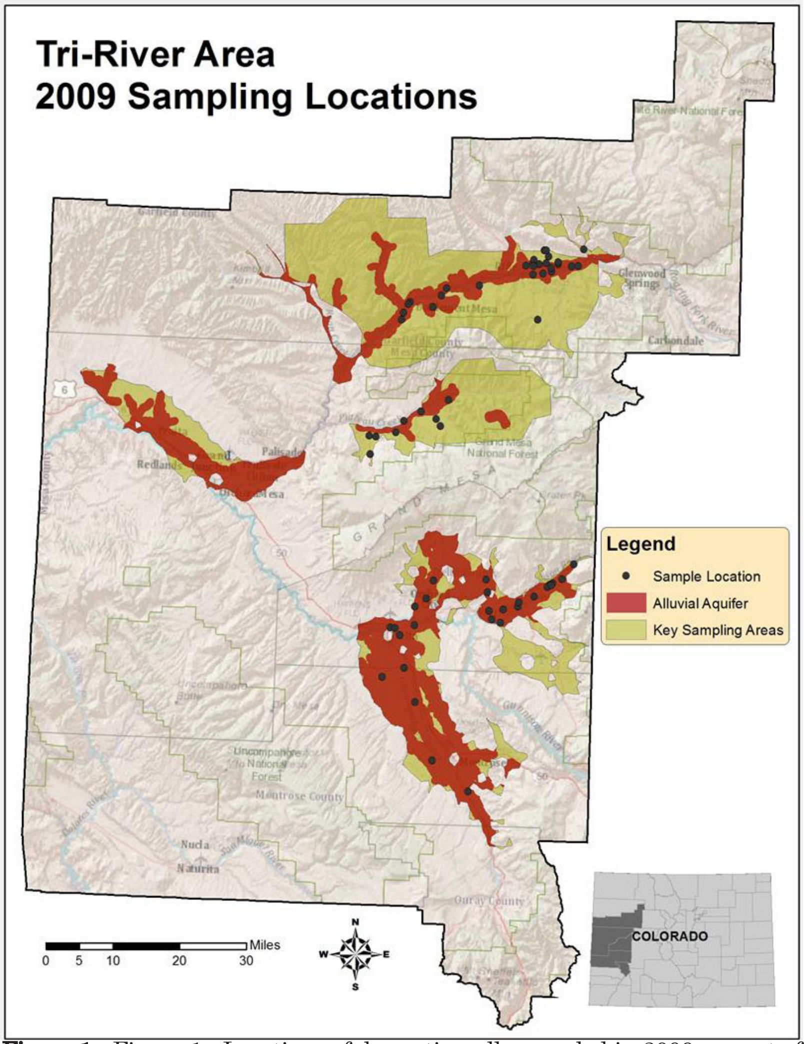


**Figure 1.** Figure 1. Locations of domestic wells sampled in 2009 as part of groundwater quality monitoring in the Western Slope Tri-River Area. Effort was made to locate all samples within a key sampling area and within an alluvial aquifer.

Where appropriate and when granted access, domestic wells sampled in 1998 were included in the 2009 sampling efforts. Due to restructuring of the study areas and missing contact information, only four wells were able to be included from the 1998 well set in the Tri-River sampling. Other wells from 1998 may be included in future sampling efforts in the Northwest and Southwest areas. Sampling of existing monitoring wells is always the preference of the Program, but low abundance of cooperative partners owning such wells greatly limited the Program's access in the Tri-River Area. Two domestic purpose wells that were drilled but had not yet had a pump installed, were sampled with a bladder pump similar to monitoring well sampling protocol. The remaining 61 wells are actively used domestic or livestock use wells. Figure 1 shows the distribution of sample locations within key areas of the Tri-River Area. Key areas are delineations based on presence of irrigated agriculture and/or high density O&G land uses and soils with high leaching potential.

In nearly all instances, domestic wells were purged utilizing a flow-cell and multi-parameter meter to ensure adequate purging, except for the two wells that did not have pumps installed, which were sampled as monitoring wells. Wells with no ability to connect the flow cell, or with excessively high flow rates or pressure, were purged long enough to thoroughly flush the well casing and associated plumbing. Sampled wells were assumed to be established in the alluvial aquifer systems within the Colorado or Gunnison River Basins according to either owner records or well records on the Colorado State Engineer's well records database. All wells were sampled by Karl Mauch, the Program's Groundwater Monitoring Specialist during the months of September and October.

Domestic water well samples were sent to the Montana Department of Agriculture Analytical Laboratory in Bozeman, MT for pesticide analysis. Methodology at this laboratory screened samples for 90 different pesticides at very low detection limits. Samples were also delivered to the Program's Groundwater Laboratory for determination of nitrate and nitrite, and to Colorado State University's Soil, Plant, and Water Testing Laboratory for analysis of other basic inorganic nutrients and dissolved metals. A list of all compounds analyzed for and their respective limit of detection can be found in Table 3 at the end of this report.

## 2009 Nitrate Results

Of the 63 samples collected, only two contained $NO_3$-N above the EPA standard of 10.0 ppm. Both of these wells contained > 100 ppm $NO_3$-N and excessively high levels of other dissolved salts like sulfate, calcium, and sodium. The high nitrate detection near Parachute, CO (Figure 2a) is peculiar given the surrounding land use activities. The other $NO_3$-N detection of 167 ppm was from a well in the Uncompahgre Valley, between the towns of Delta and Olathe (Figure 2c) that is a drilled domestic use well without a pump installed. The owners of this well had it previously tested in 2003 by an environmental consulting firm for bacteria and inorganic analysis. Since 2003, $NO_3$-N concentration increased six-fold from 26.3 to 167.5 ppm. It is difficult to assume that nitrate may be coming from geologic material since all other dissolved nutrients had such significant decreases. It is more likely a point source contamination is affecting groundwater at this site, but unfortunately additional samples in the immediate vicinity were not collected during sampling. This well is certainly an anomaly compared to other wells sampled in the Uncompahgre Valley.

Another domestic well sampled by the Program in September was coincidentally sampled by the United States Geologic Survey in April. Nitrate-nitrogen concentrations from these two sampling events were very similar at 0.18 and 0.20 ppm in April and September, respectively, and more typical of other wells sampled by the Program in the Tri-River Area. Aside from the two wells with greater than 100 ppm $NO_3$-N , the remaining 61 wells all contained less than 10.0 ppm. Eighty-five percent of sampled wells contained less than 2.5 ppm $NO_3$-N , with 11 of those below the detection limit of 0.05 ppm. These results are similar to the 1998 results which demonstrate that widespread nitrate contamination does not appear to be a concern in Colorado's Western Slope Tri-River Area. Evaluation of the inorganic constituent data demonstrates the presence of high concentrations of basic water quality parameters like conductivity, sodium, chloride, sulfate, and magnesium. This suggests that domestic well owners in the Tri-River Area likely have more reason to be concerned with hardness and high salt concentrations, than they do with nitrate contamination in the areas sampled.

As mentioned earlier only four locations, previously sampled in 1998, were able to be sampled in 2009. Individual $NO_3$-N results for these four wells were all within 0.5 ppm from 1998 to 2009 with a range from below detection to 3.34 ppm. While these results do not suggest any significant exceeding of primary drinking water standards beyond the two wells with high nitrate, samples collected from the Tri-River Area do show evidence of the hard, moderately saline water characteristic of groundwater found within much of the lower-Colorado River and its tributaries.

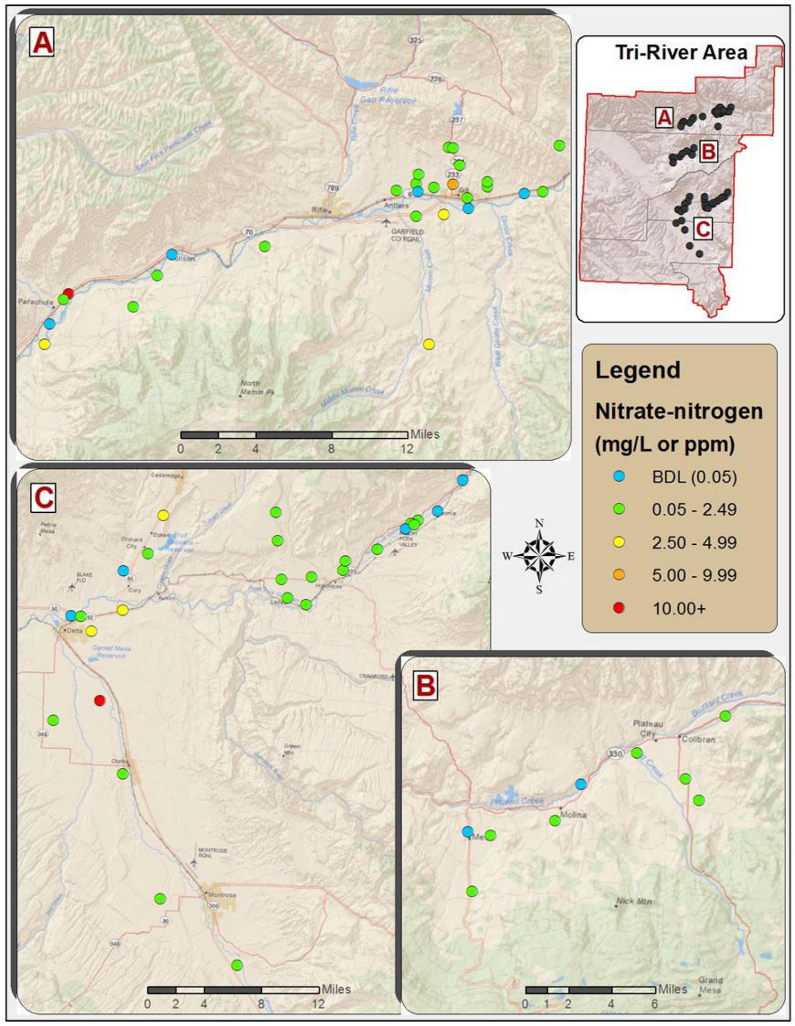


**Figure 2.** Nitrate concentrations for domestic wells sampled in 2009. Samples were collected from three key areas (A, B, and C) of the Tri-River Area on Colorado's Western Slope.

## 2009 Pesticide Results

Pesticide analysis showed detections of a variety of parent and metabolite compounds. Table 2 shows the pesticide products detected and their associated statistics. Half of the 35 total detections were of metabolite products from acetochlor, alachlor, and metolachlor. Only four detections were greater than 0.1 micrograms per liter ($\mu g\ L^{-1}$) or parts per billion (ppb), all of which were of alachlor ethane sulfonic acid (ESA). Products of degradation have been seen to exist in higher concentrations than the parent for a variety of pesticide compounds.

Figure 3 shows the distribution of wells with pesticide detections in the Tri-River Area. All of the above mentioned acetochlor, alachlor, and metolachlor degradate products were discovered in the Uncompahgre and North Fork Valleys. Alachlor degradates were only found in the Uncompahgre Valley which is an area that contains a greater variety of agricultural crops including corn, vegetables, and orchards compared to predominant cultivation of grass and alfalfa hay in the Silt-area. The type of crops being produced in a particular area usually dictates the types of chemicals used. Alachlor is primarily used for grass and broadleaf weed control in corn. Multiple detections of the non-selective herbicide imazapyr were found in the Silt-area and the Uncompahgre Valley. These compounds are used by certified applicators for weed control on O&G pads, in addition to agricultural uses. Chlorsulfuron, a selective grass and broadleaf control agent, was detected in four wells. The only pesticide detection in the Plateau Creek Valley was of a very small deethyl atrazine (atrazine degradate) detection of 0.002 ppb.

All of the pesticide compounds detected either have a groundwater advisory on their label and/or have intermediate to high leaching potential (Bauder et al., 2010). This means that they have properties such as low soil adsorption, high solubility, and/or are persistent in the environment. These properties, combined with leaching due to irrigation can make groundwater contamination more likely. However, the concentrations at which they were found are so small that significant contamination from over-application or point source discharge is not apparent. The fact

| Tri-River Area 2009 Inorganic Analysis Summary | | | | | | |
|---|---|---|---|---|---|---|
| **Variable** | **Unit** | **# Detects** | **Minimum** | **Median** | **Average** | **Maximum** |
| **Lab Determined Inorganic** | | | | | | |
| Aluminum (Al) | mg/L | 36 | 0.01 | 0.23 | 1.84 | 59.35 |
| Barium (Ba) | mg/L | 36 | 0.01 | 0.01 | 0.02 | 0.06 |
| Bicarbonate ($HCO_3$) | mg/L | 63 | 168 | 268 | 287 | 832 |
| Boron (B) | mg/L | 48 | 0.01 | 0.03 | 0.07 | 0.98 |
| Cadmium (Cd) | mg/L | 8 | 0.01 | 0.01 | 0.011 | 0.02 |
| Calcium (Ca) | mg/L | 63 | 0.1 | 45.7 | 63.3 | 231.4 |
| Carbonate ($CO_3$) | mg/L | 0 | | No Detections | | |
| Chloride (Cl) | mg/L | 63 | 1.9 | 12.08 | 33.12 | 236 |
| Chromium (Cr) | mg/L | 22 | 0.01 | 0.02 | 0.02 | 0.04 |
| Copper (Cu) | mg/L | 9 | 0.01 | 0.02 | 0.02 | 0.04 |
| Iron (Fe) | mg/L | 10 | 0.01 | 0.01 | 0.31 | 2.89 |
| Lead (Pb) | mg/L | 0 | | No Detections | | |
| Magnesium (Mg) | mg/L | 63 | 0.68 | 40.9 | 48.8 | 112 |
| Manganese (Mn) | mg/L | 36 | 0.01 | 0.03 | 0.19 | 1.35 |
| Molybdenum (Mo) | mg/L | 8 | 0.04 | 0.07 | 0.07 | 0.11 |
| Nickel (Ni) | mg/L | 18 | 0.01 | 0.01 | 0.03 | 0.22 |
| Nitrate-Nitrogen ($NO_3$-N) | mg/L | 53 | 0.03 | 0.62 | 6.31 | 167 |
| Nitrite-Nitrogen ($NO_2$-N) | mg/L | 8 | 0.07 | 0.09 | 0.38 | 2.28 |
| Potassium (K) | mg/L | 63 | 0.29 | 1.7 | 2.24 | 13.3 |
| Selenium (Se) | mg/L | 41 | 0.001 | 0.002 | 0.003 | 0.05 |
| Sodium (Na) | mg/L | 63 | 7.54 | 49.4 | 129.09 | 1096 |
| Sulfate ($SO_4$) | mg/L | 63 | 14 | 166 | 336 | 2114 |
| **Other Lab Measurements** | | | | | | |
| Alkalinity (as $CaCO_3$) | mg/L | 63 | 45 | 122 | 187 | 1085 |
| Conductivity | uS/cm | 63 | 0.27 | 1.02 | 1.78 | 11.87 |
| Hardness (as $CaCO_3$) | mg/L | 63 | 3 | 257 | 359 | 931 |
| pH | | 63 | 7.0 | | | 8.1 |
| Sodium Absorption Ratio | | 63 | 0.21 | 1.31 | 3.97 | 75.67 |
| Total Dissolved Solids | mg/L | 63 | 318 | 617 | 915 | 4793 |

**Table 1.** Basic summary information for laboratory analysis of inorganic composition of groundwater sampled in 2009 from domestic wells in the Tri-River Area of Colorado's Western Slope.

| Tri-River Area 2009 Pesticides Detected | | | | | |
|---|---|---|---|---|---|
| **Pesticide** | **# Detects** | **Minimum** | **Median** | **Average** | **Maximum** |
| Acetochlor (ESA) | 1 | 0.0520 | | | 0.0520 |
| Alachlor (ESA) | 9 | 0.0190 | 0.0930 | 0.3193 | 2.0000 |
| Alachlor (OA) | 2 | 0.0110 | 0.0255 | 0.0255 | 0.0400 |
| Chlorsulfuron | 4 | 0.0070 | 0.0115 | 0.0260 | 0.0740 |
| Desethyl atrazine | 2 | 0.0020 | | | 0.0020 |
| Hexazinone | 2 | 0.0080 | | | 0.0080 |
| Imazapyr | 6 | 0.0100 | 0.0160 | 0.0242 | 0.0470 |
| Imazethapyr | 1 | 0.0120 | | | 0.0120 |
| Imidacloprid | 1 | 0.0210 | | | 0.0210 |
| Metolachlor (ESA) | 6 | 0.0048 | 0.0150 | 0.0176 | 0.0460 |
| Prometon | 1 | 0.0150 | | | 0.0150 |

**Table 2.** Summary information for pesticide compounds detected in domestic well groundwater samples collected in the Tri-River Area of Colorado's Western Slope in 2009.

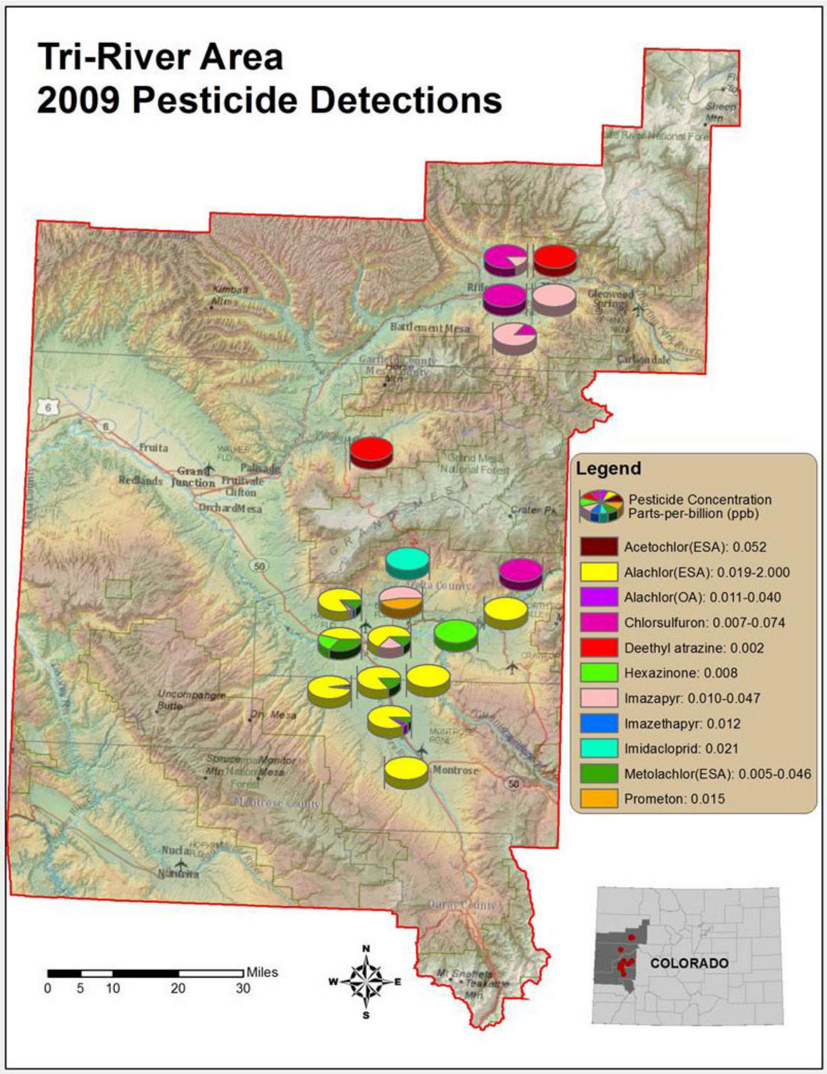


**Figure 3.** Detected pesticide concentrations for domestic well groundwater samples collected in the Tri-River Area of Colorado's Western Slope in 2009. All concentrations are in micrograms per liter (μg/L) or parts-per-billion (ppb).

that there were a higher number of detections in the Uncompahgre Valley and the Parachute to Silt stretch of the Colorado River Valley, suggests that continued, periodic monitoring should occur in these areas. It does not appear to be necessary to increase monitoring intensity in the Plateau Creek Valley given the single pesticide detection.

## Summary

Groundwater sampling by the Program in the Tri-River Area of Colorado's Western Slope in 2009, did not raise overall concern of quality impairment with respect to agrichemicals. Outside of two wells with $NO_3$-N above the EPA standard, most wells contained $NO_3$-N well below five ppm, similar to what was discovered in 1998. This suggests that non-point nitrate contamination is not a major concern in the areas studied. There were 11 different pesticide compounds detected throughout the study area with a majority of those being breakdown products from pesticides commonly used in the area. Fortunately, amidst the variety, no concentrations were above established EPA standards.

The results from the 2009 sampling event were effective in providing a better understanding of where groundwater is more vulnerable to pesticide and nitrate leaching. While sample density could be improved in future sampling events, it was discovered that some areas do not likely need increased sampling. Unfortunately, a representative sampling of the Grand Valley was not obtained in 2009. The results from the agriculturally diverse Uncompahgre Valley points towards the need to more thoroughly involve other areas with similar land use characteristics, such as the Grand Valley. While not conclusive, the six detections of imazapyr in areas of high O&G activity does suggest that increasing monitoring efforts in such areas should be considered, as they may be a source of agrichemical contamination.

## Reference

Bauder, T., R. Waskom, and R. Pearson. 2010. Best Management Practices for Agricultural Pesticide Use to Protect Water Quality. Colorado State University Extension XCM-177.

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.** 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 $L^{-1}$) for fungicide, herbicide, growth-regulator, and insecticide analyte types. Concentrations for inorganic and dissolved metal analyte types are in milligrams per liter (mg $L^{-1}$).

**Reporting Limits for Analytes Tested in Tri-River Area - Sampling Year 2009**

| Analyte | Tradename[1] | Analyte Type | Reporting Limit | Analyte | Tradename | Analyte Type | Reporting Limit |
|---|---|---|---|---|---|---|---|
| Acetochlor | Harness | Herbicide | 0.14 | Imazamethabenz acid | Assert | Herbicide | 0.005 |
| Acetochlor (ESA) | Metabolite | Herbicide | 0.01 | Imazamethabenz ester | Assert | Herbicide | 0.001 |
| Alachlor | Lasso | Herbicide | 0.11 | Imazamox | Raptor | Herbicide | 0.012 |
| Alachlor (ESA) | Metabolite | Herbicide | 0.011 | Imazapic | Plateau | Herbicide | 0.011 |
| Alachlor(OA) | Metabolite | Herbicide | 0.004 | Imazapyr | Arsenal | Herbicide | 0.011 |
| Aldicarb | Temik | Insecticide | 0.003 | Imazethapyr | Pursuit | Herbicide | 0.010 |
| Aldicarb sulfone | Metabolite | Insecticide | 0.001 | Imidacloprid | Admire | Insecticide | 0.002 |
| Aldicarb sulfoxide | Metabolite | Insecticide | 0.056 | Isoxaflutole | Balance | Herbicide | 0.130 |
| Aluminum | | Inorganic | 0.010 | Lead | | Dissolved Metal | 0.005 |
| Aminopyralid | Milestone | Herbicide | 0.053 | Linuron | Afalon | Herbicide | 0.011 |
| Atrazine | Aatrex | Herbicide | 0.002 | Malathion | Malathion | Insecticide | 0.028 |
| Azinphos methyl | Guthion | Insecticide | 0.037 | Magnesium | | Inorganic | 0.010 |
| Azinphos methyl (OA) | Metabolite | Insecticide | 0.031 | Manganese | | Dissolved Metal | 0.010 |
| Azoxystrobin | Amistar | Fungicide | 0.001 | MCPA | MCPA | Herbicide | 0.002 |
| Barium | | Dissolved Metal | 0.010 | MCPP | Kilprop | Herbicide | 0.002 |
| Bentazon | Basagran | Herbicide | 0.001 | Metalaxyl | Allegiance | Fungicide | 0.012 |
| Bicarbonate ($HCO3^-$) | | Inorganic | 0.100 | Methomyl | Lannate | Insecticide | 0.002 |
| Boron | | Inorganic | 0.010 | Metolachlor | Bicep | Herbicide | 0.012 |
| Bromacil | Hyvar X | Herbicide | 0.007 | Metolachlor (ESA) | Metabolite | Herbicide | 0.003 |
| Cadmium | | Dissolved Metal | 0.005 | Metolachlor (OA) | Metabolite | Herbicide | 0.021 |
| Calcium | | Inorganic | 0.010 | Metsulfuron methyl | Ally | Herbicide | 0.026 |
| Carbonate | | Inorganic | 0.100 | Molybdenum (Mo) | | Dissolved Metal | 0.010 |
| Carbaryl | Sevin | Insecticide | 0.040 | Nickel (Ni) | | Dissolved Metal | 0.010 |
| Carbofuran | Furadan | Insecticide | 0.005 | Nicosulfuron | Accent | Herbicide | 0.011 |
| Chlorpyrifos | Lorsban | Insecticide | 0.031 | Nitrate as nitrogen ($NO_3$-N) | | Inorganic | 0.05 |
| Chloride | | Inorganic | 0.010 | Nitrite as nitrogen ($NO_2$-N) | | Inorganic | 0.05 |
| Chlorsulfuron | Glean | Herbicide | 0.006 | NOA 407854 | Metabolite | Herbicide | 0.005 |
| Chromium | | Dissolved Metal | 0.010 | NOA 447204 | Metabolite | Herbicide | 0.010 |
| Clodinafop acid | Topik | Herbicide | 0.013 | Picloram | Tordon K | Herbicide | 0.140 |
| Clopyralid | Lontrel | Herbicide | 0.022 | Potassium (K) | | Inorganic | 0.010 |
| Copper | | Dissolved Metal | 0.010 | Prometon | Pramitol | Herbicide | 0.005 |
| Cyproconazole | Alto | Fungicide | 0.005 | Propachlor | Ramrod | Herbicide | 0.003 |
| 2,4-D | Weed B Gone | Herbicide | 0.005 | Propachlor (OA) | Metabolite | Herbicide | 0.009 |
| 2,4-DB | Butyrac | Herbicide | 0.091 | Propiconazole | Banner | Fungicide | 0.010 |
| Deethyl atrazine | Metabolite | Herbicide | 0.002 | Prosulfuron | Peak | Herbicide | 0.005 |
| Deisopropyl atrazine | Metabolite | Herbicide | 0.010 | Pyrasulfatole | Pyrasulfatole | Herbicide | 0.023 |
| Dicamba | Banvel D | Herbicide | 0.051 | Pyroxsulam | XDE-742 | Herbicide | 0.027 |
| Difenoconazole | Dividend | Fungicide | 0.020 | Selenium (Se) | | Dissolved Metal | 0.001 |
| Dimethenamid | Frontier | Herbicide | 0.010 | Simazine | Primatol S | Herbicide | 0.003 |
| Dimethenamid (OA) | Metabolite | Herbicide | 0.004 | Sodium (Na) | | Inorganic | 0.010 |
| Dimethoate | Cygon | Insecticide | 0.001 | Sulfate ($SO_4$) | | Inorganic | 0.010 |
| Diuron | Karmex | Herbicide | 0.010 | Sulfometuron methyl | Oust | Herbicide | 0.010 |
| Epoxyconazole | Epic | Fungicide | 0.028 | Sulfosulfuron | Certainty | Herbicide | 0.005 |
| Ethion | Nialate | Insecticide | 0.390 | Tebuconazole | Elite | Fungicide | 0.010 |
| Ethofumesate | Solera | Herbicide | 0.025 | Tebuthiuron | Graslan | Herbicide | 0.001 |
| Ethoprop | Mocap | Insecticide | 0.012 | Tembotrione | Tembotrione | Herbicide | 0.220 |
| Fenbuconazole | Enable | Fungicide | 0.005 | Tetraconazole | Eminent | Fungicide | 0.006 |
| Flucarbazone | Everest | Herbicide | 0.001 | Thifensulfuron | Harmony | Herbicide | 0.026 |
| Flucarbazone sulfonamide | Metabolite | Herbicide | 0.001 | Tralkoxydim | Achieve | Herbicide | 0.005 |
| Flufenacet (OA) | Metabolite | Herbicide | 0.005 | Tralkoxydim acid | Achieve | Herbicide | 0.005 |
| Flumetsulam | Broadstrike | Herbicide | 0.063 | Triadimefon | Amiral | Fungicide | 0.006 |
| Glutamic acid | L-Glutamic acid | Growth Reg | 0.007 | Triadimenol | Baytan | Fungicide | 0.026 |
| Hydroxy Atrazine | Metabolite | Herbicide | 0.006 | Triallate | Avadex BW | Herbicide | 0.300 |
| Halosulfuron methyl | Permit | Herbicide | 0.010 | Triasulfuron | Amber | Herbicide | 0.026 |
| Hexazinone | Velpar | Herbicide | 0.006 | Triclopyr | Garlon | Herbicide | 0.011 |
| Iron | | Dissolved Metal | 0.010 | Triticonazole | Charter | Fungicide | 0.032 |
| Imazalil | Deccozil | Fungicide | 0.010 | | | | |

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