

# Groundwater Protection Program 2016 Monitoring Activity & Results

### Sampling & Analysis Details

It was a productive monitoring year for The Agricultural Chemicals & Groundwater Protection Program (ACGPP) in 2016. Personnel sampled groundwater in the Front Range Urban Monitoring Network (FRU), Lower South Platte River Basin (LSP), lower Arkansas River Basin (ARB), San Luis Valley Unconfined (SLV), and the normal annual sampling of the irrigation, domestic, and monitoring well networks in Weld County.

However, the sampling year started in May, when the ACGPP assisted the City of Burlington, CO at the encouragement of the Colorado Department of Public Health & Environment (CDPHE) by collecting groundwater samples to be used by the City's hired consultant for assessing the cause of elevated nitrate contamination that is impacting several of the City's public supply wells (PSW). The ACGPP assisted in a similar project in 2015 with the Town of Springfield, CO.

	2016 Sampling Logistics									
Sample Area	Well Types Sampled	# Sample Events	Sample Event Dates	Analysis Completed						
City of Burlington	PSW; DW	17	05/18/16 - 05/20/16	Anions, pesticides, <sup>15</sup> N/ <sup>18</sup> O, <sup>11</sup> B, <sup>257</sup> Sr						
Front Range Urban	MW	64	05/26/16 - 06/30/16	Anions, pesticides						
Weld County	MW	23	07/01/16 - 07/21/16	Anions, pesticides						
Weld County	DW	7	08/30/16 - 08/31/16	Anions, pesticides						
Weld County	IW	3	08/30/16 - 08/31/16	Anions						
Lower South Platte	MW, DW, IW	23	07/19/16 - 08/10/16	Anions, pesticides						
Arkansas River Basin	MW	17	08/15/16 - 08/25/16	Anions, pesticides						
San Luis Valley	MW, DW	39	10/15/2015 - 10/28/2015	Anions, pesticides						

#### TABLE 1 SAMPLING LOGISTICS FOR NETWORKS SAMPLED BY ACGPP IN 2016.

Agrochemical results for the various networks and the ten PSWs and seven domestic wells (DW) sampled in and around the City of Burlington, are uploaded to the online database. However, the results of the City of Burlington study are best summarized in a report by Martin & Wood Water Consultants, Inc., sent in December 2016 to Steven Rabe with the City. The report discusses and provides interpretation of the laboratory results obtained from ACGPP's sampling efforts in May. A copy of the report will not be posted on ACGPP's website but those interested in obtaining a copy can contact Steven Rabe with the City of Burlington, CO. **Table 1** summarizes the sampling logistics with respect to number of sample events, sample dates, and analyses conducted.

As part of a continued investigation into the feasibility of using the HydraSleeve<sup>™</sup> for collecting a groundwater samples from a monitoring well (MW), the ACGPP conducted dual sampling at 36 MW sampling sites in 2016. Included are sites from metropolitan areas in the FRU network, as well as from the



LSP and ARB networks. The in depth study conducted on a selection of MWs in Weld County in 2015, is currently being compiled into a report, and these additional comparisons will be included in ACGPP's evaluation of the effectiveness of the HydraSleeve<sup>™</sup> for sampling in various well networks around Colorado. Therefore, split sample comparisons for these 36 sites will not be elaborated on in this summary, but the results from samples collected at the sites sampled in 2016, using current ACGPP field methodology, will be part of the discussion for each area.

Most MW samples were collected using SOP GPP-1 or SOP GPP-2; however some MWs were sampled only with a HydraSleeve<sup>™</sup>. All but two of 64 FRU sites were sampled using SOP GPP-1 or SOP GPP-2, with the other two sites being sampled with a HydraSleeve<sup>™</sup>. Two MWs installed in September, 2015, in Weld County, were sampled using SOP GPP-1 and the HydraSleeve<sup>™</sup> while the remaining 21 MWs were sampled only with the HydraSleeve<sup>™</sup>. This summary will present the HydraSleeve<sup>™</sup> results for the Weld County MWs compared to historical results to determine if any significant deviation occurred as a result of the methodology change. Only seven Weld County DWs were sampled in 2016. Overall this network is diminishing in size with 6 of 14 wells being dropped from the network over the last five years due to owner request, change of ownership, or well damage. While the ACGPP plans on continuing to sample the remaining wells in the DW network for the purpose of providing well owners with analytical results, there are no plans to expand upon the network. Similarly, ACGPP has significantly cut back on sampling of the Weld County IW network over the last several years, and given that only three samples could be obtained from the network in 2016, it is likely that no further sampling of the IW network will occur, at least in the near-term. MW results along with results from three IWs and seven DWs can be seen in the section *Weld County*.

A total of 23 wells were sampled in the LSP, in 2016, with the majority of those being MWs. One MW could be sampled with only a HydraSleeve due to inaccessibility by personnel. Well LSP-M-009, which sits in the middle of a center-pivot field usually densely planted with corn, was once again not accessible by sampling personnel as has been the case for the last few sample years. As a means of getting groundwater quality data for the area around LSP-M-009, substitution samples were collected from the center-pivot irrigation well itself and a nearby windmill-powered stock watering well. Results from these two substitution wells along with the other wells will be discussed under *Lower South Platte*. Samples from the 17 MWs in the ARB were sampled with nine of those sites being dual sampled with a HydraSleeve™. An additional MW installed near AK-M-019 was sampled using a HydraSleeve™ and those results will be included in the discussion under *Arkansas River Basin*.

The ACGPP sampled 38 DWs and one MW in the SLV, in 2016. This is down from the 40+ wells that were sampled in each of the previous three sampling events since 2009. In 2016, two new DWs were added to improve sample density in part of the network. The MW sample was from a USGS-NAWQA site that has been part of previous collaborative sampling events in 2001 and 2007 with the US Geologic Survey. While it was sampled in 2016 because of the need for getting video footage of water quality sampling for some Regulation 85 video work being done by CSU Extension and CDPHE, the results from the well will be included as part of the discussion of *San Luis Valley*.



The CDA **Biochemistry** Lab's 2016 analysis suite for groundwater samples consists of seven anions and 101 pesticide compounds (including separate analysis for glyphosate and its main degradate, AMPA). All

samples collected in 2016 were analyzed for these constituents

except Weld County IWs only being analyzed

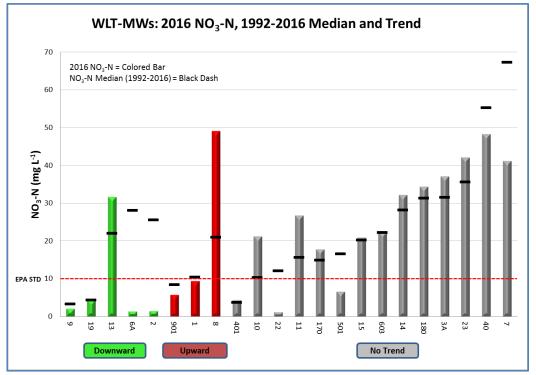
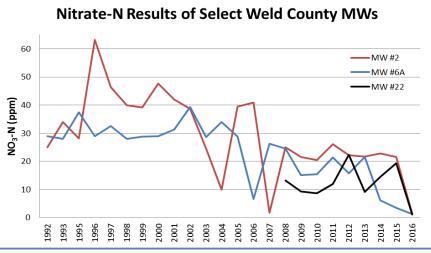


FIGURE 1 NITRATE-N (NO<sub>3</sub>-N) RESULTS IN 2016 COMPARED TO LONG-TERM (1992-2016) MEDIAN CONCENTRATION AND TREND DIRECTION FOR INDIVIDUAL MONITORING WELLS IN WELD COUNTY, COLORADO. FOR EACH WELL, THE TREND IS THE BAR COLOR; THE 2016 CONCENTRATION IS THE MAGNITUDE OF COLORED BAR; AND LONG-TERM MEDIAN IS THE BLACK DASH.

for anions, and Weld County DWs being analyzed for everything other than glyphosate and AMPA. Split samples collected as part of the City of Burlington study were sent to the Stable Isotope Lab at University of California at Davis for <sup>15</sup>N and <sup>18</sup>O determination and to the ICPMS Laboratory at University of Utah for



analysis of the isotopes <sup>11</sup>B and <sup>87</sup>Sr along with 27 other elemental constituents. As a reminder, data from the work in Burlington is not discussed in this summary. The analyte screen at the CDA laboratory and the corresponding reporting limits are presented in **Table 6** at the end of this summary.

#### Weld County

FIGURE 2 NITRATE-N RESULTS FOR WELD COUNTY MWS #2, #6A, AND #22 FROM 1992-2016

Historical

nitrate-nitrogen



(NO<sub>3</sub>-N) values in Weld County MWs from 1992-2015, have seen a median of 19.8 mg L<sup>-1</sup> or parts-permillion (ppm) and a range of 0.6-111.3 ppm. The results for 2016, by way of HydraSleeve sampling, show a median of 21.2 ppm which falls within the historical 95% confidence interval around the median of 19.2-21.5 ppm. Most individual wells did not have any significant deviation from their long-term records for nitrate; however, three wells measured less than 2.0 ppm NO<sub>3</sub>-N – MWs #6A, #2, and #22 - which as seen in Figure 1, is well below each well's long-term median concentration. However, as will be explained below, all three instances are reasonable and not likely due to sampling with the HydraSleeve as is explained for each instance below.

MW #6A measured its all-time lowest NO<sub>3</sub>-N at 1.3 ppm which is far below its long-term median concentration of 28 ppm, but as seen in **Figure 2** the annual June measurements have been decreasing significantly since 2014 whereas the significant concentration drop in 2006 rebounded in 2007. The lack of a rebound since the drop in 2014 is likely due to several augmentation ponds that lay up-gradient of the well. These ponds were initially installed and used in 2012 but additional augmenting capacity has been added since then. It is believed that water collected from this MW in June, when the ponds are being actively used for augmentation, is very young in age and most likely representative of the surface water nitrate concentration instead of regional groundwater concentration. In coming years, ACGPP may collect samples from the augmentation ponds in near timing with collecting MW samples to study this relationship.

Nitrogen & Phosphorus Results for Weld County MWs										
	Nitrate-N (ppm)				diss Orthophosphate (ppm)					
Time Period	% Detect	Min I	Median	Max	% Detect	Min M	Median	Max		
2012-2015	100	0.6	18.4	64.4	55	0.06	1.19	5.05		
2016	100	1.1	21.2	49.1	43	0.10	1.39	3.02		

Another unusual drop in NO<sub>3</sub>-N in 2016 was in MW #22 which measured 1.1 ppm. Similar to MW #6A, this is the all-time lowest concentration seen in this well although it is worth mentioning the shorter historical record of

TABLE 2 NITRATE AND ORTHOPHOSPHATE MEASURED OF ACGPP'SMONITORING WELL NETWORK IN WELD COUNTY, CO SINCE 2012.

monitoring. In the last couple years of monitoring, this well has seen concentration spikes of several pesticide compounds including a detection of atrazine at  $41 \ \mu g \ L^{-1}$  or parts-per-billion (ppb) in June of 2013. One concern with sampling with a no-purge sampling device, such as the HydraSleeve, is that use in wells that may have a tendency to hydraulically disconnect from the saturated geologic formation, unless being actively pumped to encourage flow into and through the well, may result in sampling of stagnant water. If stagnant water with less than 2.0 mg L<sup>-1</sup> of dissolved oxygen (DO) is in the well, then there is a good chance that nitrate concentrations could be diminished relative to saturated formation concentrations due to denitrification. However, this is not believed to be the case for this well nor the reason for the unusually

	Other Anion Inorganic Results for Weld County MWs											
	Fluoride (ppm)			Chloride (ppm)				Sulfate (ppm)				
Time Period	% Detect	Min	Median	Max	% Detect	Min	Median	Max	% Detect	Min	Median	Max
2012-2015	100	0.05	0.94	2.42	100	33	105	307	100	95	274	2820
2016	100	0.29	0.85	1.70	100	49	105	207	100	95	248	1585

TABLE 3 INORGANICS NUTRIENTS MEASURED OF ACGPP'S MONITORING WELL NETWORK IN WELD COUNTY, CO SINCE 2012.





low nitrate concentration measured in 2016. *In situ* measurement of DO prior to retrieval of the HydraSleeve showed 3.02 mg/L which would prevent anaerobic bacteria from facilitating denitrification. Other evidence of this well not suffering from poor hydraulic connectivity with the saturated formation is that a confirmation sampling in July of 2013, to follow up on the atrazine exceedance seen 30 days earlier, revealed that the atrazine concentration had diminished from 41 ppb to less than two ppb. This is indicative of significant local groundwater flow velocity both around and through the well. Therefore, it is believed this low nitrate measurement is accurate.

The last instance of nitrate measured below two ppm in a Weld County MW in 2016, was in well MW #2 at 1.4 ppm. As can be seen in **Figure 2**, this MW also saw a similarly low concentration of 1.7 ppm in 2007, and a 2004 result of 9.9 ppm which was very low at the time given that all prior annual measurements ranged 25-63 ppm. Due to this history which reflects instances of nitrate concentrations dropping significantly in

MW #2, it is reasonable to assume the 2016 concentration was not due to the use of the HydraSleeve.

Since 2012, in addition to nitrate, the ACGPP has been analyzing groundwater samples for five other anionic inorganic nutrients - fluoride, chloride, bromide, dissolved orthophosphate  $(dOrt-PO_4),$ and sulfate. Tables 2 & 3, show a few statistics for some of these nutrients measured in primary sampling events from 2012-2016. Of these five anionic nutrients,  $dOrt-PO_4$  is the only one not detected in all Weld County MWs. More specifically, the majority of nine MWs that have regularly detected dOrt-PO<sub>4</sub> are all located very near canals or ditches conveying South Platte River water through irrigated row crops in Weld County as can be seen in the map in Figure 3. The ACGPP is beginning to look closer into why there are elevated concentrations of dOrt-PO₄ consistently showing up in some areas of Weld County since the characteristics of phosphate usually inhibit leaching. MW #10 has seen the

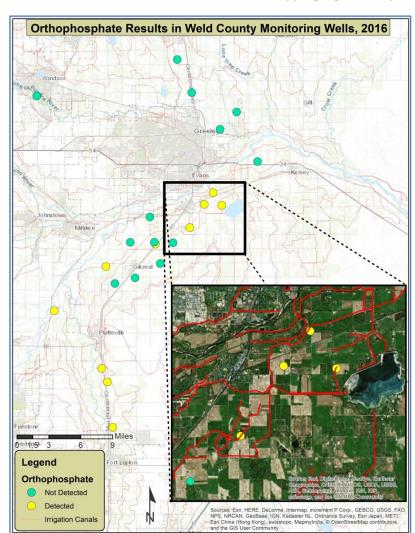


FIGURE 3 DISSOLVED ORTHOPHOSPHATE DETECTION RESULTS FOR MONITORING WELLS SAMPLED IN WELD COUNTY, CO IN 2016. MOST WELLS WITH DETECTION ARE INSTALLED NEAR SEEPING IRRIGATION CANALS AND DITCHES.



highest median concentration (0.95 ppm dOrt-PO<sub>4</sub> as P) and the lowest standard deviation (0.03), resulting in nearly 1 ppm of dissolved P being consistently detected since 2012. Interestingly, if surface water recharge of groundwater by means of canal seepage is a potential source for these concentrations, it would not make sense for this particular location since the canal that MW #10 is near, is actually believed to be hydraulically down-gradient of the well. This would stand to reason that the high concentrations being detected in this well are entering groundwater from locations south of the well. ACGPP will be taking a closer look into the fate and transport of this ion in shallow groundwater systems which may include adjustment of the analysis suite to incorporate other constituents related to phosphorus behavior, such as calcium and iron. For now, it is obvious that the factors influencing nitrate movement within this part of the South Platte alluvial aguifer are not the same as those influencing the movement of dOrt-PO<sub>4</sub>.

The seven DWs sampled in Weld County in 2016 saw nitrate levels very similar to each well's historical results. Three DWs were over the U.S. EPA Standard of 10.0 ppm, and the maximum concentration of 12.9 ppm remains well below the NO<sub>3</sub>-N median seen in the MW network. The three IWs also saw concentrations that were typical of their individual historical results.

A total of 95 detections of 17 different pesticide active ingredients were discovered in 2016. This is a comparable number of detections and types seen in primary annual sampling periods of Weld County MWs (mid-June to early July) since the pesticide screening list was expanded to around 100 compounds in 2009. It has been discussed before in ACGPP's recent monitoring activity summaries that the non-selective herbicide metolachlor's breakdown products of ethane sulfonic acid (MESA) and oxanilic acid (MOA) typically account for about one-quarter of the total pesticide detections seen in Weld County MWs between June and mid-July. In similar fashion, these pesticides accounted for about 41% of all detections seen in 2016. MESA had a detection frequency of 96% which has been the norm for Weld County MWs since analysis for the compound began in 2009. All of the pesticide active ingredients detected in 2016 have

been seen in Weld County MWs one or more times since 2012. so it is believed that data resulting from the use of the HydraSleeve in 2016 is comparable to prior data. Pesticide concentrations discovered in 2016 are

unremarkable

Nitrogen & Phosphorus Results for Networks Sampled in 2016 Nitrate-N diss Orthophosphate Area **#Samples** % Detect Min Median Max % Detect Min Median Max Front Range Urban 64 97% 0.12 6.32 36.58 16% 0.06 0.23 0.78 3 100% 0.39 5.42 8.84 0% Greeley 100% 0.12 2.58 36.58 Fort Collins 14 7% 0.11 0.11 0.11 10 80% 3.12 11.84 32.05 10% 0.51 0.51 0.51 **Colorado Springs** 35 Denver-Metro 100% 0.27 4.56 25.63 23% 0.06 0.15 0.78

TABLE 4 ANALYSIS RESULTS FOR NITRATE AND DISSOLVED ORTHOPHOSPHATE ANALYZED IN SAMPLES COLLECTED FROM MONITORING WELLS IN THE FRONT RANGE URBAN NETWORK IN 2016.

compared to historical results and no established U.S. EPA maximum contaminant level (MCL) was exceeded. A full listing of which pesticide were detected in this network can be found in Table 5 at the end of this summary.

#### Front Range Urban



ervation Services Division

The 2016 effort is the fourth sampling of the FRU monitoring network since it was expanded in 2008 and the seventh overall sampling effort by ACGPP concentrated in urban areas. While the majority of anion results for sampled wells are comparable to historical results, there are a few observations worth discussing. As can be seen in **Table 3**, the median NO<sub>3</sub>-N for all wells sampled in FRU is 5.2 ppm which is comparable past results seen of this network. The distribution of nitrate results can be seen in the map in **Figure 4**. The maximum concentration came from a MW installed near the Nix Farm Natural Area Facility in east-central Fort Collins which has seen NO<sub>3</sub>-N above 10 ppm in prior sampling events, but not to the extent of the nearly 37 ppm seen in 2016. There are a multitude of potential sources for this increased nitrate, but discussions in 2010 with Natural Area personnel led to the discovery that cleaning of pesticide application equipment up-gradient of the monitoring well was likely a source of several detected pesticide active

ingredients in May of that year. And while the discussion didn't include nitrate since the concentrations were not too alarming in 2010, now that the concentration has ballooned nearly three times higher since 2013, the ACGPP may work with Natural Area personnel to determine if any fertilizer application equipment is cleaned out near the well in order to rectify any source impacts to the shallow aquifer. The median NO<sub>3</sub>-N of 11.8 ppm from the ten wells sampled in Colorado Springs, while not unusual for it to be the highest median amongst the various metropolitan areas in the FRU, is the highest median seen for that portion of the network since sampling began back in 2008.

Most of the other inorganic results for 2016 are unremarkable aside from ten MWs that detected dOrt-PO<sub>4</sub> at a median concentration of

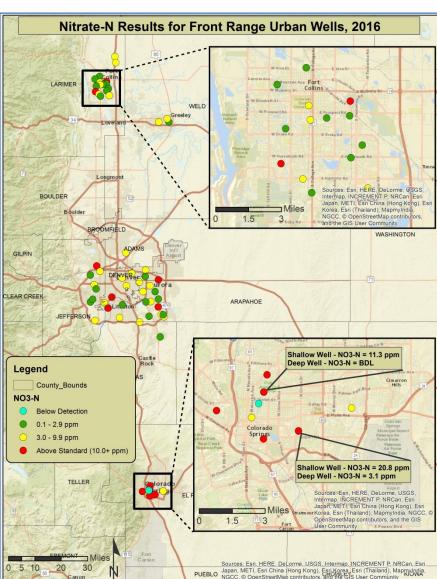


FIGURE 4 NITRATE-N RESULTS FOR URBAN AREAS IN COLORADO SAMPLED AS PART OF THE FRONT RANGE URBAN MONITORING NETWORK IN 2016.



0.07 ppm as P, and a range of 0.02-0.25 ppm as P. Eight of those wells were in the Denver-Metro area, and the maximum concentration was found in a well installed alongside the South Platte River, downstream of the Metro Waste Water Reclamation Plant. This max concentration is roughly only one-half of the 0.45 ppm median dOrt-PO<sub>4</sub> as P seen of the Weld County MWs. The only well to detect dOrt-PO<sub>4</sub> in Colorado Springs has also been one of the wells in that portion of the FRU with some of the highest NO<sub>3</sub>-N concentrations since 2008.

There were 42 detections of 12 different pesticide active ingredients in 2016 as can be seen in Table 5 near the end of this summary. The most frequently detected active ingredient was imazapyr, a non-selective herbicide with usage that includes some aquatic sites, maintenance of wildlife corridors, bare-ground weed control, and weed control beneath some paved surfaces. The maximum concentration of 0.57 ppb, was discovered in the well installed at Nix Farm Natural Area Facility, and was associated with the maximum concentration of this compound in 2010 and 2013 as well. While it is believed that practices have changed, the area this well is located near has been used by city personnel for cleaning out pesticide application equipment in the past. Similar to previous years, this well had the greatest number of different pesticide active ingredients detected in 2016 which includes the only detection of chlorsulfuron, one of only two detections of picloram, and one of only a few detections of imazapic. All three of these herbicide active ingredients can be used in right-of-way areas, wildlife corridors, and other non-crop areas. Chlorsulfuron was the only one not detected in previous sampling events. With characteristics like a typical half-life of 160 d, a very high solubility, and no observed degradation by means of hydrolysis, it is unclear whether detection of this pesticide is indicative of current cleaning operations continuing to impact shallow groundwater, or if this pesticide entered the groundwater at some point hydraulically up-gradient of the area used for cleaning application equipment. Regardless, the concentrations of these various pesticides, and all others detected in the FRU in 2016, are well below any established U.S. EPA drinking water standards or human health benchmarks for pesticides.

#### Lower South Platte

Most of the wells sampled in the LSP network have been sampled historically by ACGPP since 2001, but as described in Sampling and Analysis Details, an irrigation well and a stock well were sampled in 2016 in order to obtain a measure of water quality in the area around LSP-M-009 which has often been inaccessible due to its location in the center of a center-pivot irrigated field. The median NO<sub>3</sub>-N in 2016 is 8.8 ppm which is comparable to the long-term median of 8.3 ppm, even with the addition of these two wells.

The depth of LSP-M-009 is 37.6 ft below ground surface which is about 30 ft shallower than the irrigation and stock wells. The irrigation well saw NO<sub>3</sub>-N at 13.5 ppm which is a little higher than the 8.6 ppm seen back in 2010 in LSP-M-009, but is a reasonable increase that is likely representative of the area. Definitely more so than the stock well that only saw 0.8 ppm NO<sub>3</sub>-N. With natural groundwater flow likely to the north-northwest and no agriculture south-southeast of the stock well as can be seen in inset 1B of **Figure 5**, it would be reasonable to assume this amount of nitrate is naturally occurring. However, the stock well also detected two pesticide compounds that were seen in the irrigation well, and measurable  $dOrt-PO_4$ , so it could be that the stock well is indeed providing representative measurement of local irrigated agriculture



impacts on shallow groundwater. There were nine MWs with measurable *d*Ort-PO<sub>4</sub>, which is a similar detection frequency seen of Weld County MWs.

Another result of interest for the LSP network is from a collection of wells installed down-gradient from a rural home community with individual septic systems (inset 1A of **Figure 5**). When these wells were first sampled in 2008 the median concentration was 9.0 ppm. Results from 2016, show a median of 11.3 ppm

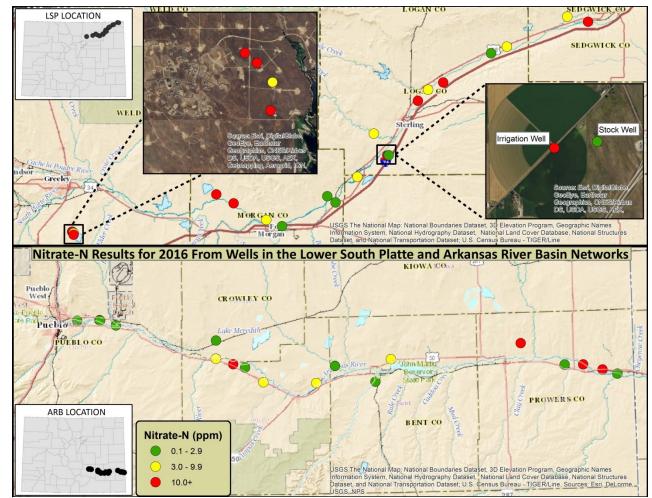


FIGURE 5 MAP SHOWING DISTRIBUTION OF NITRATE IN THE LOWER SOUTH PLATTE (#1) AND ARKANSAS RIVER BASIN (#2) NETWORKS SAMPLED IN 2016.

for these same wells. While there is some center-pivot irrigated agriculture about one and half miles northwest of these wells that could be contributing nitrate, it is more likely that the increasing nitrate being discovered is linked to the increase in the number of homes being built up-gradient of the wells.

All together there were 58 detections of 14 different pesticide active ingredients in the LSP network. The most frequently detected was MESA with an 83% detection frequency. This is similar to results seen of South Platte Basin alluvial groundwater in Weld County. Alachlor ESA was another commonly detected pesticide at a 48% detection frequency. While most of the wells average two to three pesticide detections, well LSP-M-016 near Ovid, CO, detected ten of the fourteen different pesticide compounds seen in the LSP network in 2016. Six of the ten compounds were also seen in 2014 and at very similar concentrations. The



other compounds seen in 2016 have been seen at some point historically in this well except for imidacloprid, a systemic neonicotinoid insecticide used as a pre-applied seed treatment in corn and soybean. No pesticide concentrations were above established US EPA drinking water standards.

#### <u>Arkansas River Basin</u>

The ARB monitoring network, while being distributed throughout irrigated agriculture, has consistently seen low nitrate concentrations and few pesticide detections. The most notable observation for NO<sub>3</sub>-N concentrations in 2016 was that three wells previously never seeing the compound over 8 ppm, saw concentrations ranging 11.2-18.2 ppm. The two eastern red circles seen in the bottom map of **Figure 5**, each contained more than 15 ppm which is nearly two times greater than any previously measured concentrations. All told there were 28% of ARB wells over the US EPA standard of 10.0 ppm, but the median NO<sub>3</sub>-N hardly changed from 2.5 ppm in 2012 to 2.7 ppm in 2016. Even the average NO<sub>3</sub>-N of 5.7 ppm in 2016 was not as high as the 6.3 ppm average seen in 2008. So for the most part, the 2016 results add to the consistent record of low nitrate impacts in the ARB network.

There was a larger number of detections seen in 2016 (25) and more variety (11 compounds) than has ever been seen previously. A matter of fact, since the ARB monitoring well network was installed in 2004, only 29 total pesticide detections have been seen in five sampling events, with 12 of those being seen in 2010. Most of the different compounds detected in 2016, have been detected previously in the ARB. The four new compounds seen of the network in 2016 (each with only a single detection), have been seen consistently in other irrigated agriculture land use areas that ACGPP monitors, so while the sudden variety is interesting, it is not unreasonable. The most frequently detected compound was imazapyr with a 44% detection rate. Imazapyr was also the most frequently detected pesticide in the FRU network in 2016; however, it is worth noting that it had only been previously detected one time in the ARB whereas the FRU has seen it more consistently. Pesticide concentrations were all below established US EPA drinking water standards.

#### San Luis Valley

The median NO<sub>3</sub>-N of 2.4 ppm for 2016 is higher than the all-time median (1.5 ppm) for this network of domestic wells that was first established and sampled in 2009. The map in **Figure 6** shows the distribution of nitrate results seen in 2016 from the DW network compared to those seen in 2007 from the US Geologic Survey's NAWQA MW network. Historically, the area of greatest nitrate concentration has tended to be east of the town of Center, CO, but as can be seen in the map, the max concentration of 33 ppm in 2007 and 41 ppm in 2016 have both been located more southeast of Center, CO. It is reasonable to assume that the DW called out on the map even though there is a 30 ft difference in where the screened intervals are for each of the wells.

There was a detection rate of 74% for *d*Ort-PO4 in 2016 with concentrations ranging 0.02-0.32 ppm as P and a median of 0.04 ppm as P. One of the new wells added to the sampling network in 2016, contained the maximum dOrt-PO<sub>4</sub> measurement, but interestingly nitrate and sulfate were both below the detection



limit in the well. While sulfate is usually always detected in wells sampled by ACGPP, this result is not unreasonable given that several other wells had concentrations < 3.0 ppm. The well with the maximum  $NO_3$ -N of 40.9 ppm also had high chloride (102 ppm) and high sulfate (603 ppm); however, another well with chloride of 271 ppm and sulfate of 1489 ppm, only saw  $NO_3$ -N at 2.8 ppm. These results show the overall complexity and variety that can be seen in water quality of the SLV.

Only 15 detections of three different pesticide compounds were seen in 2016 with the vast majority (93%) of those being the metolachlor degradation products MESA and MOA. Since 2011, these two compounds have essentially been the only two pesticide compounds discovered in the SLV. Single detections of MCPP in 2013 and 2,4-D in 2016 are the only other pesticides discovered over the last three sampling events.

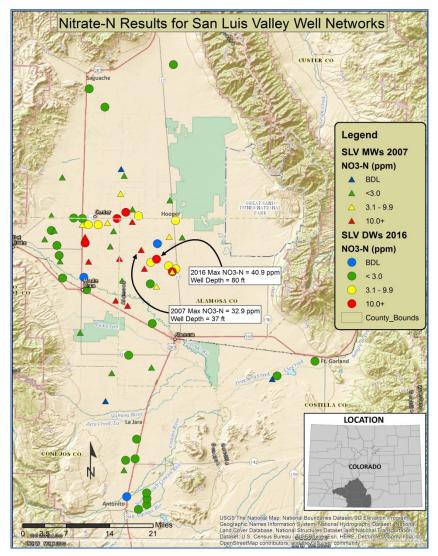


FIGURE 6 NITRATE-N RESULTS FOR MONITORING WELLS AND DOMESTIC WELLS SAMPLED IN 2007 AND 2016, RESPECTIVELY, IN THE SAN LUIS VALLEY WHICH LIES IN THE RIO GRANDE RIVER BASIN OF SOUTH-CENTRAL COLORADO.

#### **Conclusion**

The ACGPP sampled five monitoring networks and assisted the City of Burlington, CO as part of its work in 2016 to monitor Colorado's groundwater for the presence of agricultural chemicals. The results of the work with City of Burlington can be requested from Steve Rabe, Public Relations Office with the City of Burlington. The use of the HydraSleeve sampling device for sampling the Weld County MWs was found to provide results comparable to previous years as was expected after a 2015 study of the device proved it to have that capability. There was an increase in the number of wells detecting nitrate over the US EPA standard in the ARB network compared to earlier monitoring efforts with some of the increases being fairly substantial, but for the most part, anion results for the networks sampled were not remarkably different from results seen of sampling efforts in prior years.

Pesticide results did not reveal



detection of any compounds that had not been previously detected by the ACGPP. While there was an increase in the number of detections and types of compounds seen in the ARB network, no pesticide concentrations in any of the networks sampled were above established US EPA standards. As has been the case since 2009 for most sampling of areas within irrigated agriculture, the ESA and OA breakdown products of the herbicide metolachlor, were the most frequently detected. The most frequently detected pesticide in the urban environment for 2016 was the herbicide imazapyr which has similar usage potential as prometon which was the most frequently detected pesticide in 2013.

All of the data seen and/or discussed in this monitoring summary can be queried and downloaded from the Program's online water quality database and map viewer which can be accessed at: <u>http://www.erams.com/co\_groundwater</u>. Program personnel contact information and other information can be found on the Program's main website <u>http://www.co.gov/ag/gw</u>.



TABLE 5 CONC RANGE (MEDIAN), CONCENTRATION RANGE FOR DETECTED PESTICIDES, AND MEDIAN IN PARENTHESES FOR 3+ DETECTIONS; HAL, HEALTH ADVISORY LEVEL; MCL, MAXIMUM CONTAMINANT LEVEL; HHBP, HUMAN HEALTH BENCHMARK FOR PESTICIDES (NON-ENFORCEABLE); CONCENTRATIONS ARE IN  $\mu$ G L<sup>-1</sup>.

Pesticide Compounds Detected in Various Networks Sampled in 2016 Pesticide Active Ingredient Network % Detection Conc. Range (Median) Note								
Pesticide Active Ingredient			• • •					
2,4-D	San Luis Valley	2.6%	0.22	U.S. EPA Drinking Water MCL 70 $\mu$ g L <sup>-1</sup>				
Acetochlor ESA	Lower South Platte	17.4%	0.15 - 0.69 (0.34)	No Drinking Water Standard				
Acetochlor OA	Lower South Platte	4.3%	0.12	No Drinking Water Standard				
Alachlor ESA	Weld County MW	13.0%	0.16 - 0.65 (0.22)	No Drinking Water Standard				
	Lower South Platte	47.8%	0.11 - 1.51 (0.29)					
Aminopyralid	Front Range Urban	3.1%	0.14 - 0.53 (0.34)	U.S. EPA HHBP Chronic 3,500 $\mu$ g L <sup>-1</sup>				
Atrazine	Weld County MW	4.3%	0.34	U.S. EPA Drinking Water MCL 3.0 µg L <sup>-1</sup>				
	Lower South Platte	4.3%	0.91					
	Arkansas River Basin	5.9%	0.71					
Chlorantraniliprole	Weld County MW	8.7%	0.18 - 0.31 (0.25)	U.S. EPA HHBP Chronic 11,060 µg L <sup>-1</sup>				
Chlorsulfuron	Front Range Urban	1.6%	0.15	U.S. EPA HHBP Chronic 140 $\mu$ g L <sup>-1</sup>				
	Weld County MW	4.3%	0.10					
Desethyl Atrazine	Front Range Urban	17.2%	0.10 - 0.36 (0.10)	No Drinking Water Standard				
	Weld County MW	26.1%	0.10 - 0.17 (0.13)					
	Lower South Platte	17.4%	0.11 - 1.04 (0.27)					
	Arkansas River Basin	17.6%	0.10 - 0.32 (0.25)					
Deisopropyl Atrazine	Weld County MW	13.0%	0.11 - 0.24 (0.18)	No Drinking Water Standard				
	Lower South Platte	4.3%	0.35					
	Arkansas River Basin	5.9%	0.18					
Dicamba	Weld County MW	4.3%	0.21	U.S. EPA Drinking Water HAL 4000 µg I				
Dimethenamid ESA	Weld County MW	8.7%	0.13 - 0.17	No Drinking Water Standard				
	Lower South Platte	4.3%	0.36					
	Arkansas River Basin	5.9%	0.20					
Dinotefuran	Front Range Urban	1.6%	0.12	U.S. EPA HHBP Chronic 140 $\mu$ g L <sup>-1</sup>				
Diuron	Arkansas River Basin	5.9%	0.11	No Drinking Water Standard				
Hexazinone	Arkansas River Basin	5.9%	0.12	U.S. EPA Drinking Water HAL 400 μg L				
Hydroxy Atrazine	Front Range Urban	4.7%	0.04 - 0.06 (0.06)	U.S. EPA HHBP Chronic 70 µg L <sup>-1</sup>				
	Weld County MW	52.2%	0.04 - 0.18 (0.06)					
	Lower South Platte	21.7%	0.06 - 0.11 (0.08)					
	Arkansas River Basin	17.6%	0.04 - 0.06 (0.05)					
Imazamox	Front Range Urban	1.6%	0.11	No Drinking Water Standard				
	Arkansas River Basin	11.8%	0.10 - 0.10	6				
Imazapic	Front Range Urban	6.3%	0.10 - 0.29 (0.14)	U.S. EPA HHBP Chronic 3,500 µg L <sup>-1</sup>				
	Weld County MW	8.7%	0.10 - 0.10					
Imazapyr	Front Range Urban	29.7%	0.10 - 0.57 (0.17)	U.S. EPA HHBP Chronic 17,500 $\mu$ g L <sup>-1</sup>				
	Weld County MW	47.8%	0.10 - 0.19 (0.14)					
	Lower South Platte	4.3%	0.13					
	Arkansas River Basin	47.1%	0.10 - 0.22 (0.11)					
Imazathapyr	Arkansas River Basin	5.9%	0.21	U.S. EPA HHBP Chronic 17,500 $\mu$ g L <sup>-1</sup>				
Imidocloprid	Front Range Urban	1.6%	0.31	U.S. EPA HHBP Chronic 339 µg L <sup>-1</sup>				
	Weld County MW	8.7%	0.13-0.37					
	Lower South Platte	8.7%	0.16 - 0.24					
Metolachlor	Weld County MW	26.1%	0.14 - 3.43 (0.59)	U.S. EPA Drinking Water HAL 700 µg L				
	Lower South Platte	4.3%	0.72	5				
Metolachlor ESA	Front Range Urban	3.1%	0.14 - 0.27	No Drinking Water Standard				
	Weld County MW	95.7%	0.15 - 7.65 (2.64)	0				
	Lower South Platte	82.6%	0.18 - 9.69 (0.36)					
	Arkansas River Basin	17.6%	0.10 - 0.82 (0.13)					
	San Luis Valley	23.1%	0.10 - 2.63 (0.28)					
Metolachlor OA	Weld County MW	73.9%	0.14 - 3.95 (1.13)	No Drinking Water Standard				
	Lower South Platte	26.1%	0.12 - 4.06 (0.37)	0				
	San Luis Valley	12.8%	0.11 - 2.05 (0.13)					
Nicosulfuron	Weld County MW	4.3%	0.14	U.S. EPA HHBP Chronic 8,750 $\mu$ g L <sup>-1</sup>				
Picloram	•	3.1%		U.S. EPA Drinking Water MCL 500 µg L				
Tebuthiuron	Front Range Urban		0.16 - 0.23 0.10 - 0.11					
	Front Range Urban	3.1%		No Drinking Water Standard				
Thiamethoxam	Weld County MW	13.0%	0.19 - 0.36 (0.19)	U.S. EPA HHBP Chronic 84 µg L <sup>-1</sup>				
	Lower South Platte	4.3%	0.28					



## TABLE 6 PESTICIDE AND ANION REPORTING LIMITS FOR ANALYSIS CONDUCTED IN 2016 AT THE BIOCHEMISTRY LABORATORY IN THE ICS DIVISION OF THE COLORADO DEPARTMENT OF AGRICULTURE

Analytes Measured of Groundwater Samples at Colorado Department of Agriculture's Biochemistry Lab in 2016								
Analyte Name	Reporting Limit	Units	Laboratory	Analyte Name	Reporting Limit	Units	Laboratory	
2,4-D	0.1	0.	CDA Groundwater Lab	Imazamox	0.1	ug/L	CDA Groundwater Lab	
2,4-DB	0.1	<u>.</u>	CDA Groundwater Lab	Imazapic	0.1	ug/L		
2,4-DP	0.1	ug/L	CDA Groundwater Lab	Imazapyr	0.1	ug/L		
3-Hydroxycarbofuran	0.1	ug/L		Imazethapyr	0.1	ug/L	CDA Groundwater Lab	
Acetochlor	0.1	ug/L	CDA Groundwater Lab	Imidacloprid	0.1	ug/L	CDA Groundwater Lab	
Acetochlor ESA	0.1	0.	CDA Groundwater Lab	Isoxaflutole	0.1	ug/L		
Acetochlor OA	0.1	ug/L	CDA Groundwater Lab	Kresoxim methyl	0.1	ug/L	CDA Groundwater Lab	
Acifluorfen	0.1	ug/L	CDA Groundwater Lab	Linuron	0.5	ug/L	CDA Groundwater Lab	
Alachlor	0.1	ug/L	CDA Groundwater Lab	Malathion	0.1	ug/L	CDA Groundwater Lab	
Alachlor ESA	0.1	ug/L	CDA Groundwater Lab	МСРА	0.1	ug/L	CDA Groundwater Lab	
Alachlor OA	0.1	ug/L	CDA Groundwater Lab	МСРР	0.1	ug/L	CDA Groundwater Lab	
Aldicarb	0.1	ug/L	CDA Groundwater Lab	Metalaxyl	0.1	ug/L	CDA Groundwater Lab	
Aldicarb sulfone	0.2	ug/L	CDA Groundwater Lab	Metconazole	0.1	ug/L	CDA Groundwater Lab	
Aldicarb sulfoxide	0.1	ug/L	CDA Groundwater Lab	Methomyl	0.1	ug/L	CDA Groundwater Lab	
Aminopyralid	0.2	ug/L	CDA Groundwater Lab	Metolachlor	0.1	ug/L	CDA Groundwater Lab	
AMPA	2.0	ug/L	CDA Groundwater Lab	Metolachlor ESA	0.1	ug/L	CDA Groundwater Lab	
Atrazine	0.1	ug/L	CDA Groundwater Lab	Metolachlor OA	0.1	ug/L	CDA Groundwater Lab	
Azoxystrobin	0.1	ug/L	CDA Groundwater Lab	Metribuzin	0.1	ug/L	CDA Groundwater Lab	
Bentazon	0.25	ug/L	CDA Groundwater Lab	Metsulfuron methyl	0.1	ug/L	CDA Groundwater Lab	
Bromacil	0.2	ug/L	CDA Groundwater Lab	Nicosulfuron	0.1	ug/L	CDA Groundwater Lab	
Carbaryl	0.2		CDA Groundwater Lab	Norflurazon	0.2	ug/L	CDA Groundwater Lab	
Carbofuran	0.1	ug/L	CDA Groundwater Lab	Norflurazon desmethyl	0.5	ug/L	CDA Groundwater Lab	
Chlorantraniliprole	0.1		CDA Groundwater Lab	Oxamyl	0.2	ug/L	CDA Groundwater Lab	
Chlorimuron ethyl	0.1	ug/L	CDA Groundwater Lab	Oxydemeton methyl	0.1	ug/L	CDA Groundwater Lab	
Chlorsulfuron	0.1	ug/L	CDA Groundwater Lab	Picloram	0.1	ug/L	CDA Groundwater Lab	
Clopyralid	0.1		CDA Groundwater Lab	Prometon	0.1	ug/L	CDA Groundwater Lab	
Cyanazine	0.1	ug/L	CDA Groundwater Lab	Propazine	0.1	ug/L	CDA Groundwater Lab	
Cyproconazole	0.1	ug/L		Propoxur	0.1	ug/L	CDA Groundwater Lab	
Cyromazine	0.1	ug/L	CDA Groundwater Lab	Prosulfuron	0.1	ug/L	CDA Groundwater Lab	
Desethyl Atrazine	0.1	ug/L	CDA Groundwater Lab	Pyrimethanil	0.1	ug/L	CDA Groundwater Lab	
Desisopropyl Atrazine	0.1		CDA Groundwater Lab	Quinclorac	0.1	ug/L		
Dicamba	0.1	ug/L	CDA Groundwater Lab	Simazine	0.1	ug/L	CDA Groundwater Lab	
Diflufenzopyr	0.25	ug/L		Sulfentrazone	0.2	ug/L		
Dimethenamid	0.1	ug/L	CDA Groundwater Lab	Sulfometuron methyl	0.1	ug/L	CDA Groundwater Lab	
Dimethenamid ESA	0.1	ug/L	CDA Groundwater Lab	Sulfosulfuron	0.1	ug/L	CDA Groundwater Lab	
Dimethenamid OA	0.1		CDA Groundwater Lab	Tebuconazole	0.1		CDA Groundwater Lab	
Dimethoate	0.1	ug/L	CDA Groundwater Lab	Tebufenozide	0.1	ug/L	CDA Groundwater Lab	
Dinotefuran	0.1		CDA Groundwater Lab	Tebuthiuron	0.1	<b>U</b> .	CDA Groundwater Lab	
Disulfoton sulfone	0.1	ug/L	CDA Groundwater Lab	Terbacil	0.1		CDA Groundwater Lab	
Disulfoton sulfoxide	0.1		CDA Groundwater Lab	Thiamethoxam	0.1	0.	CDA Groundwater Lab	
Diuron	0.1	0,	CDA Groundwater Lab	Triadimefon		0.	CDA Groundwater Lab	
Ethofumesate	0.1	<u> </u>		Triallate	0.1	<b>U</b> .	CDA Groundwater Lab	
		-	CDA Groundwater Lab		0.1			
Ethoprop	0.1	<u> </u>	CDA Groundwater Lab	Triasulfuron	0.1	-	CDA Groundwater Lab	
Fenamiphos	0.1	ug/L		Trichlorfon	0.2	0.	CDA Groundwater Lab	
Fenamiphos sulfone	0.1	ug/L	CDA Groundwater Lab	Triclopyr	0.2	0.	CDA Groundwater Lab	
Florasulam	0.1	<u> </u>	CDA Groundwater Lab	Triticonazole	0.1	0.	CDA Groundwater Lab	
Flufenacet	0.1	ug/L		Bromide	0.05	-	CDA Groundwater Lab	
Flumetsulam	0.1	<u> </u>	CDA Groundwater Lab	Chloride	0.05		CDA Groundwater Lab	
Glyphosate	1.0	ug/L		Fluoride	0.05		CDA Groundwater Lab	
Halofenozide	0.1	ug/L	CDA Groundwater Lab	Nitrate as N	0.011		CDA Groundwater Lab	
Halosulfuron methyl	0.1	<u> </u>	CDA Groundwater Lab	Nitrite as N	0.015	0.	CDA Groundwater Lab	
Hydroxy Atrazine	0.04	ug/L	CDA Groundwater Lab	Ortho-phosphate (Dissolved)	0.05		CDA Groundwater Lab	
Imazamethabenz ester	0.1	ug/L	CDA Groundwater Lab	Sulfate	0.05	mg/L	CDA Groundwater Lab	

