2018 Monitoring Activity
Full Report

Sampling Logistics

The Agricultural Chemicals & Groundwater Protection Program (Program) sampled groundwater of its following monitoring regions in 2018: South Platte, West Slope – Northwest (NW), and North Park (NP). The effort in the South Platte region included monitoring wells (MWs) from the long-term network of Weld County (WLT) and the Lower South Platte (LSP), but also included new wells as part of an initial expansion effort to improve coverage and density across the region. The NW sampling was the first in that part of the state since the Program's initial reconnaissance effort in 1998. Furthermore, this marked the completion of the last of the three West Slope regions created in 2009 (See 2009 Western Slope Tri-Rivers Factsheet and 2017 Monitoring Activity). North Park was last sampled in 2001, so this marked the first sampling in more than a decade for that region.

The effort to conduct multiple sampling events on a subset of WLT monitoring wells, which was initiated in June 2017, continued in 2018 but with some variability – the bi-weekly sampling schedule was completed in January, March, and April, but then changed to monthly for the remainder of 2018 with no samples collected in October or December. Some of the samples collected in the South Platte region are from the Irrigation Innovation Technology Research Consortium (IITRC) project on the eastern edge of Fort Collins, CO and the Subsurface Irrigation Efficiency Project (SIEP) on a portion of the 70 Ranch east of Kersey, CO. The five wells at each of these locations are clustered in areas less than 1/3 of a square mile which results in a higher sample density than is typically used for the Program's monitoring efforts, so it is likely that only some of these wells will be included in the overall expansion in the South Platte region. The last caveat to the 2018 sampling of the South Platte region, is that some of the samples came from locations in Weld County where there are nested wells accessing different depths of the alluvial aquifer.

Other than two irrigation wells sampled at the IITRC, all other samples came from monitoring and piezometer wells. Nearly all of the piezometer wells were constructed with 1-inch PVC risers, and when the static water level was less than 25 ft below the ground surface, Program personnel used a peristaltic pump for purging and sampling. Otherwise, all other samples were collected using 2-inch or 1-inch HydraSleeve™ no-purge sampling devices.

The 233 samples collected in 2018 breakdown as follows: from January to November 107 samples from the WLT subset; in June and July, 67 samples from the South Platte Region in addition to those collected as part of the WLT subset; 33 samples from the NW region mostly in September; 25 from the NP region in October, and one resample of an LSP well in November for confirmation of a pesticide standard exceedance.

Laboratory Logistics

All samples collected in 2018 were analyzed at CDA's Biochemistry Lab for a suite of seven anions and 97 pesticide compounds, except for ten rounds of samples collected from the WLT subset that did not have glyphosate and AMPA analysis conducted. Split samples were collected once per month from the WLT subset for analysis of total soluble phosphorus (TSP) at the Colorado Department of Public Health & Environment (CDPHE) laboratory through the June sampling event. There were also split samples collected from the NW and NP sampling events for analysis of dissolved metals, hardness and alkalinity, and total soluble phosphorus at the ALS Environmental Laboratory in Fort Collins, CO. Due to budget restraints in 2018, the Program was unable to have any samples analyzed for isotopic composition, pharmaceuticals and wastewater indicators, or for a qualitative screening of 600+ pesticide compounds as has been done periodically over the last six years.

Sampling Results

Results from all 2018 sampling events can be easily queried and downloaded from the Program's online database (https://erams.com/co_groundwater). **Table 2**, at the end of this report, shows detection limits for all agrichemical parameters analyzed for in 2018. A discussion of 2018 sampling projects follows.

South Platte Region

In 2018, there were several new monitoring wells sampled in this region **(Figure 1)**. Some were used to begin the process of filling in gaps in the South Platte River alluvial aquifer that haven't been sampled since the early 1990's, and others in Weld County were part of nested well sites or wells within a short distance of regularly sampled wells. Additional sampling was also conducted on a subset of eight Weld County MWs throughout the entire year. Due to this variability in sampling, it will be beneficial to discuss results separately for comparison to historical results seen in the agricultural land use area of this region.

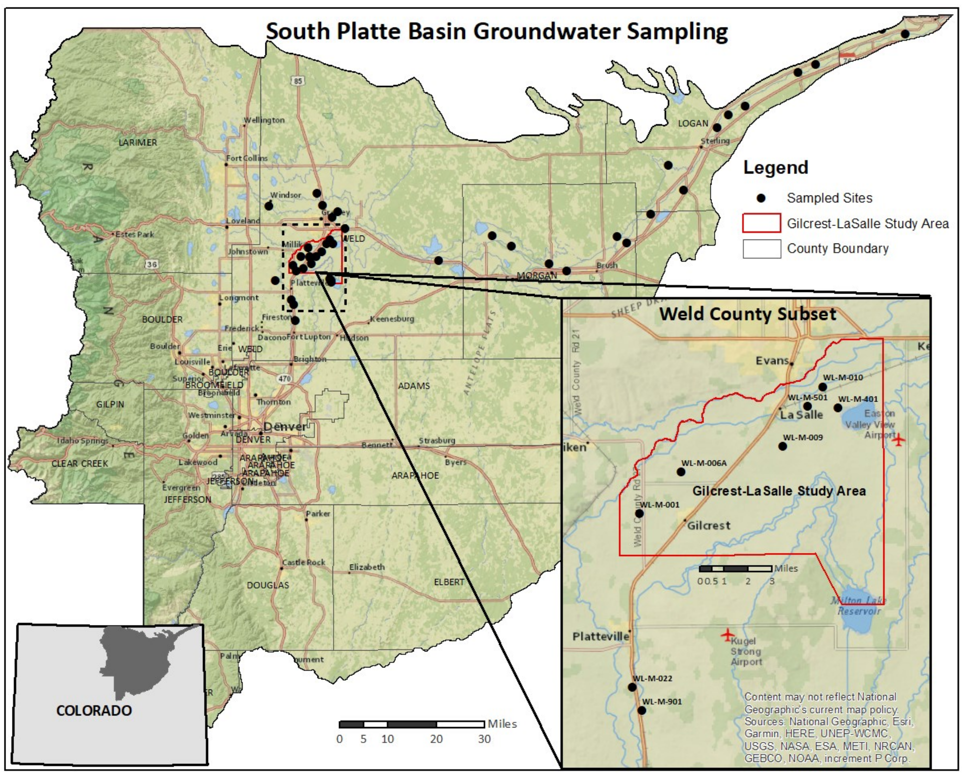

FIGURE 1 MAP OF GROUNDWATER MONITORING WELLS SAMPLED IN THE SOUTH PLATTE BASIN IN JUNE AND JULY OF 2018. MAP INSET SHOWS THE WELLS THAT ARE PART OF THE WELD COUNTY SUBSET SAMPLED MONTHLY FROM JUNE 2017 THROUGH NOVEMBER 2018.

Whole Region: The Program worked with Colorado State University to sample new wells at the IITRC and SIEP properties located in the region. The five wells sampled at each property were within a 0.3 sq mi area, which is a higher sample density than is normally sampled by the Program. It is likely only one well from each property will be included in future sampling events. Therefore, an average of the results for each of these areas was used in comparison to historical results seen in the region. In Weld County, two or three wells at differing depths, but very close areally, were sampled at different locations for the purpose of evaluating stratification of water quality. For each of these nested sites, only results from a single well sampling near the top of the water table (some of the wells at nested sites are drilled all the way to the bottom of the saturated thickness of the alluvial aquifer) are included. Well ID WL-M-501, which is in a part of Weld County where results have tended to show greater impact by agrichemicals, had two additional monitoring wells sampled within 0.10 mi east and 0.20 mi southeast of itself. Due to the variability seen in the concentrations of some analytes between the three wells, the two new locations are both considered. Lastly, WL-M-401 has a set of two nested wells about 0.30 mi east of it, and results from the shallower well at that location are considered.

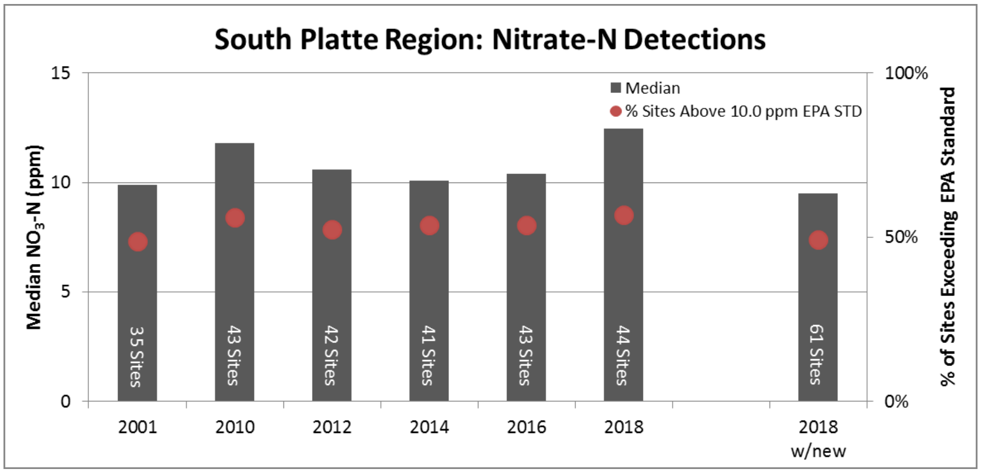

FIGURE 2 NITRATE-N DATA FOR WELLS SAMPLED OVER MULTIPLE YEARS IN THE SOUTH PLATTE REGION.

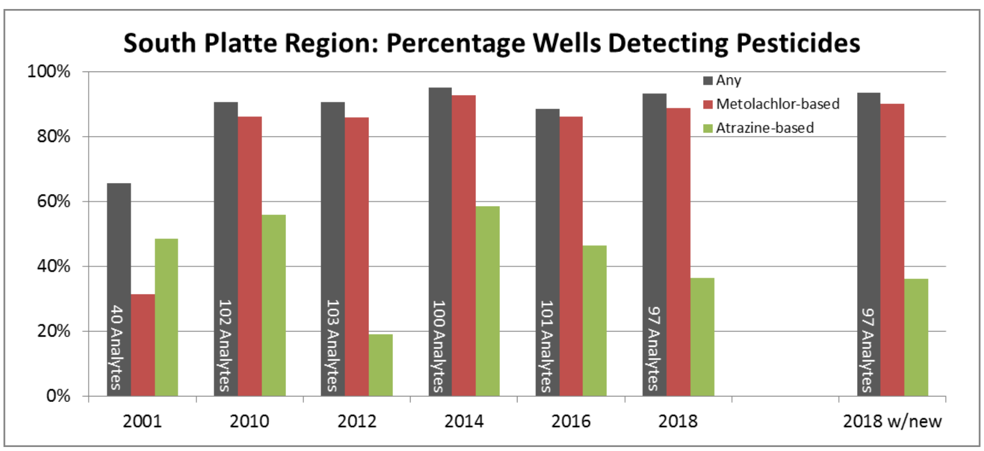

FIGURE 3 PESTICIDE DETECTION FREQUENCY FOR WELLS SAMPLED OVER MULTIPLE YEARS IN THE SOUTH PLATTE REGION.

When only looking at results for sites that have been part of the regular sampling network in 2001, 2010, 2012, 2014, 2016 or 2018; the 2018 results for the South Platte Region, as a whole, are similar to historical results. The median NO_3-N of 12.5 ppm in 2018 and the percentage of sites above the U.S. EPA Drinking Water Standard (EPA STD) of 10.0 ppm (57%) are similar to that seen for other years. When the new sites are considered (**2018 w/new** in **Figure 2**) – taking into account the considerations and restrictions just mentioned - the median NO_3-N sits below the EPA STD with only 49% of sites exceeding it.

The Program plans to increase the number of sites sampled in the region so that upwards of 110 locations are eventually sampled in the agricultural land use area from Ft. Lupton, CO to Julesburg, CO. It is unknown how the median NO_3-N for the region might change due to the addition of new sites; however, by increasing the density and/or coverage within the region, the Program will be able to better understand the extent of agrichemical impacts the South Platte alluvial aquifer is under. This will be an improvement over only commenting on a fairly limited set of about 40 wells.

One or more pesticide compounds have been detected in 88-95% of samples since 2010 **(Figure 3)**. The lower detection frequency seen for 2001 (66%) is mostly due to only 40 pesticide compounds being analyzed for compared to 97 or more in all other years. Metolachlor is an herbicide commonly used in agriculture and has two main breakdown products (metolachlor-Ethane Sulfonic Acid (MESA) and metolachlor Oxanilic Acid) that have been screened for since 2010 when the Program's laboratory expanded its analytical suite of pesticides. This undoubtedly increased the likelihood of a well detecting one or more pesticides and hence the increase in detection frequency from 66% in 2001 to 91% in 2010. Since 2010, metolachlor-based pesticides have seen a detection frequency of 86-93%, the highest frequency by far of all pesticides analyzed for. The median concentration for all detections has ranged from 0.26 to 0.53 ppb since 2010 but the median is greatest for the metolachlor-based compounds (**Figure 4**). While there was no change in the detection frequency of these compounds with the addition of the new sites sampled in 2018, the lower concentrations did prompt a 25% decrease in median from 1.04 to 0.76 ppb. Of the pesticide detections discovered in the alluvial aquifer of the South Platte River, since 2010, approximately 70% of them have been of metolachlor-based and atrazine-based (the herbicide atrazine and its breakdown products desethyl-atrazine, desisopropyl-atrazine, and hydroxy-atrazine) compounds. A single sample collected in July from one of the new sites added to the network, exceeded the U.S. EPA Maximum Contaminant Level of 3.0 ppb for atrazine, but a follow-up sampling in November showed the initial concentration of 4.5 ppb had diminished to below the reporting limit.

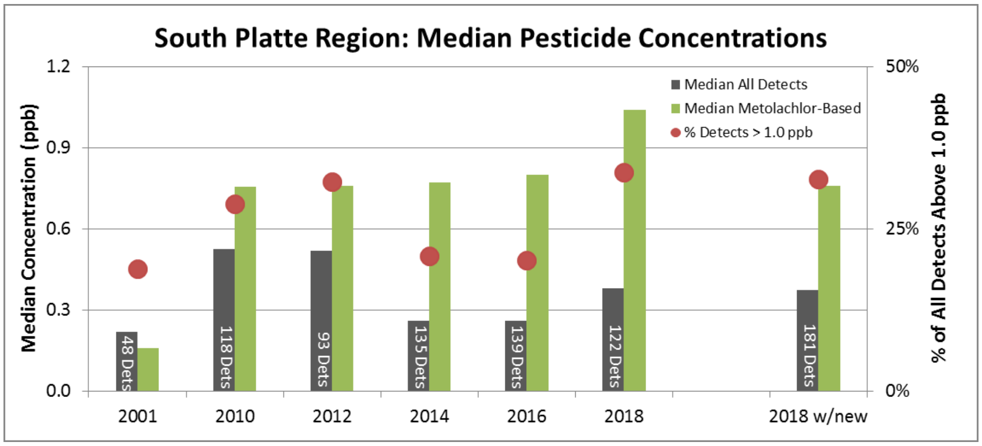

FIGURE 4 PESTICIDE DETECTION DATA FOR WELLS SAMPLED OVER MULTIPLE YEARS IN THE SOUTH PLATTE REGION

***Weld County Subset*: **The Weld County MW Network was established as a long-term monitoring network for evaluating trends in groundwater quality impact nearer the top of the water table due to agrichemicals. When considering the agricultural land-use area within the South Platte River Basin (thereby excluding results from monitoring wells sampled in the Program's Front Range Urban Region), this network study area sits on the upper end of the basin and is in place from Ft. Lupton, CO to just north and east of Greeley, CO (**Figure 1**). The Program has annually sampled the network in June because the likelihood of finding agrichemicals in shallow groundwater is believed to be the greatest at that time due to agricultural management activities occurring in the spring (planting, fertilizing, pre-emergent pesticide application) and the lack of crop root structures allowing for easier movement of some of those compounds through the soil and into the groundwater. The number of wells available for sampling has varied year to year due to accessibility, additions to the network, or re-drilling to fix damaged wells;

however, since 1996 there have been 16 wells that have consistently been sampled. These 16 wells are used to monitor the annual median NO_3-N for the network study area. **Figure 5** shows how the median has varied from 11.1 ppm to 27.7 ppm over the time period. These results show a fairly persistent and consistent impact of nitrate contamination of shallow groundwater in this part of Weld County although there is evidence of a downward trend in concentration.

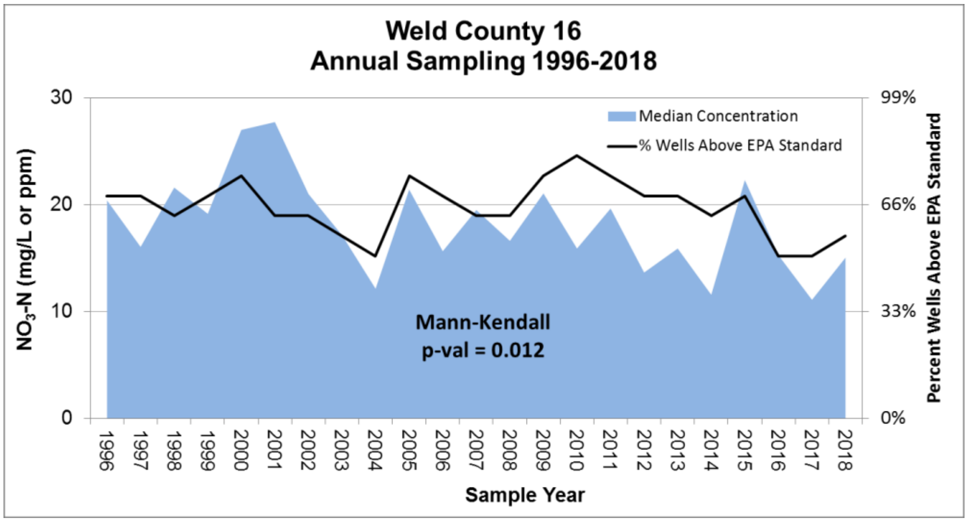

FIGURE 5 ANNUAL MEDIAN NO_3-N AND PERCENTAGE OF WELLS OVER THE U.S. EPA PRIMARY DRINKING WATER STANDARD FOR NO_3-N OF 10.0 PPM, SEEN IN 16 MONITORING WELLS SAMPLED IN WELD COUNTY, CO FROM 1996-2018. MANN-KENDALL P-VALUE INDICATES STATISTICALLY SIGNIFICANT DOWNWARD CONCENTRATION TREND IN NITRATE OVER THE TIME PERIOD.

In the early 2000's, the South Platte Basin was facing a severe to extreme drought and due to issues with less water and unmet water rights, 1000's of irrigation wells were shut down between 2004 and 2006. This curtailment had to occur in order to facilitate restoration of a flow into the South Platte River, which heavily depends on groundwater discharge after spring runoff has mostly subsided by late June to early July. The above normal pumping of the alluvial aquifer during the drought was injuring senior surface water rights downstream. Starting in 2006, the State Engineer's Office allowed for some of the curtailed wells to start pumping again but only after getting an augmentation plan in place for replacement of out-of-priority depletions. While the concept of augmentation wasn't new to Colorado or the South Platte Basin, the density of augmentation ponds increased dramatically in the basin at this time. The increase of augmentation structures in the upper part of the aquifer sampled by the Program's Weld County well network was not as great as that seen further downstream (due to the limited availability of replacement sources in the upper part of the basin which are required for securing an augmentation plan), but nonetheless, the increase was still significant for the area.

1992-2018	NO_3 as N (since 1992)				ort-PO_4 as PO_4 (since 2012)			
Well ID	AVG	MED	Conc Range	Conc Trend	AVG	MED	Conc Range	Conc Trend
WL-M-001	9.9	10.3	4.3 - 16.7	Upward	1.3	1.2	0.6 - 2.0	Downward
WL-M-006A	22.2	27.1	1.3 - 39.2	Downward	0.3	0.3	BDL - 0.6	None
WL-M-009	3.4	3.1	0.6 - 9.4	Downward	1.3	1.4	0.6 - 1.8	Downward
WL-M-010	12.1	9.9	3.0 - 31.3	None	2.9	2.9	2.6 - 3.3	None
WL-M-022*	14.3	13.2	1.1 - 25.4	None	1.2	1.5	0.4 - 1.7	None
WL-M-401	3.6	3.2	1.9 - 6.7	None	1.2	1.3	0.4 - 1.9	None
WL-M-501	24.8	16.5	6.5 - 80.8	None	3.4	2.9	2.5 - 5.1	None
WL-M-901	10.8	9.4	3.8 - 23.0	Upward	1.5	1.5	1.0 - 2.2	None

TABLE 1 CONCENTRATIONS MEASURED IN WELD COUNTY MONITORING WELLS FOR NITRATE-N (NO_3-N) SINCE 1992 AND FOR ORTHOPHOSPHATE AS PO_4 (ORT-PO_4) SINCE 2012. 'MED' IS MEDIAN. 'CONC RANGE' IS CONCENTRATION RANGE. 'CONC TREND' IS THE RESULT OF A MANN-KENDALL TREND TEST.

Normally, the Program might not pay attention to augmentation projects that deal primarily with issues surrounding delivery and security of water rights. However, in 2014 when the network median NO_3-N dipped to its all-time lowest of 13.9 ppm, and one specific well (WL-M-006A) near a new augmentation pond facility dipped from its normal double digit NO_3-N concentrations down to 6.1 ppm, it caused the Program to consider how the increase in groundwater recharge projects might be impacting its water quality monitoring.

Starting in June 2017, eight MWs were selected for the purpose of evaluating two key items: 1) to determine if the variability seen throughout the year was remarkably different than the long-term median NO_3-N or pesticide detections seen for each well; and 2) to obtain a higher frequency of sampling results for comparison to water level elevations in order to determine the degree of correlation between the variability in groundwater elevation and concentration of nitrate and other detected agrichemicals. The eight wells were selected primarily due to one or more of the following factors:

- Presence of a statistically significant upward or downward trend in NO_3-N
- Yearly NO_3-N concentrations consistently below the U.S. EPA Primary Drinking Water Standard of 10.0 ppm since 1992
- Location next to significant groundwater recharge structures like augmentation ponds or seeping irrigation canals/ditches
- Persistent detection of orthophosphate (ort-PO_4), since lab reporting of this parameter began in 2012, with concentrations upwards of 1.7 ppm as phosphorus.

A total of 28 sampling events were conducted on the subset from June 2017 through November 2018 with the one exception being the event on 10/2/2017 was skipped for well WL-M-901 due to inaccessibility. Initially, the wells were sampled approximately every two weeks, but the frequency was tapered back to once per month starting in May 2018. As was discussed earlier, the long-term nitrate data for wells in this Weld County network has been analyzed extensively and **Table 1** shows some simple statistics for the long-term nitrate and orthophosphate seen in the subset wells along with whether a statistically significant trend is present for either compound. A 95% confidence interval around the median concentration provides a gauge of the typical concentrations seen when the Program normally samples in June/July. This interval is represented in the nitrate graphs in **Figure 7** with red horizontal lines, while the all-time maximum and minimum concentrations, as measured in June/July, are represented with black horizontal lines. Each site's groundwater elevation over the same 28 events is also shown.

Nitrate concentrations showed significant variability over the last year and a half in most wells with concentrations dipping above and below the median confidence interval and even reaching outside the all-time minimum and maximum values. This higher frequency of data shows that there is seasonality in nitrate concentrations of the shallow groundwater in this area. While there was no doubt that such phenomena exists in an area under seasonally active agriculture, what is made a bit clearer is the fact that reporting on agrichemical concentrations seen in only June and July, may not always be representative of the greatest impacts the South Platte alluvial aquifer could be under. However, it is important to remember that one of the reasons these particular wells were selected was because of their location in areas that can be under significant influence of groundwater recharge through augmentation ponds or canal seepage. While it is likely that the seasonality of water conveyance within the study area contributes to the variability in NO_3-N concentrations seen throughout the year, it is not clear on how much of that variability is due just to water conveyance or is a result of transport lag time through the

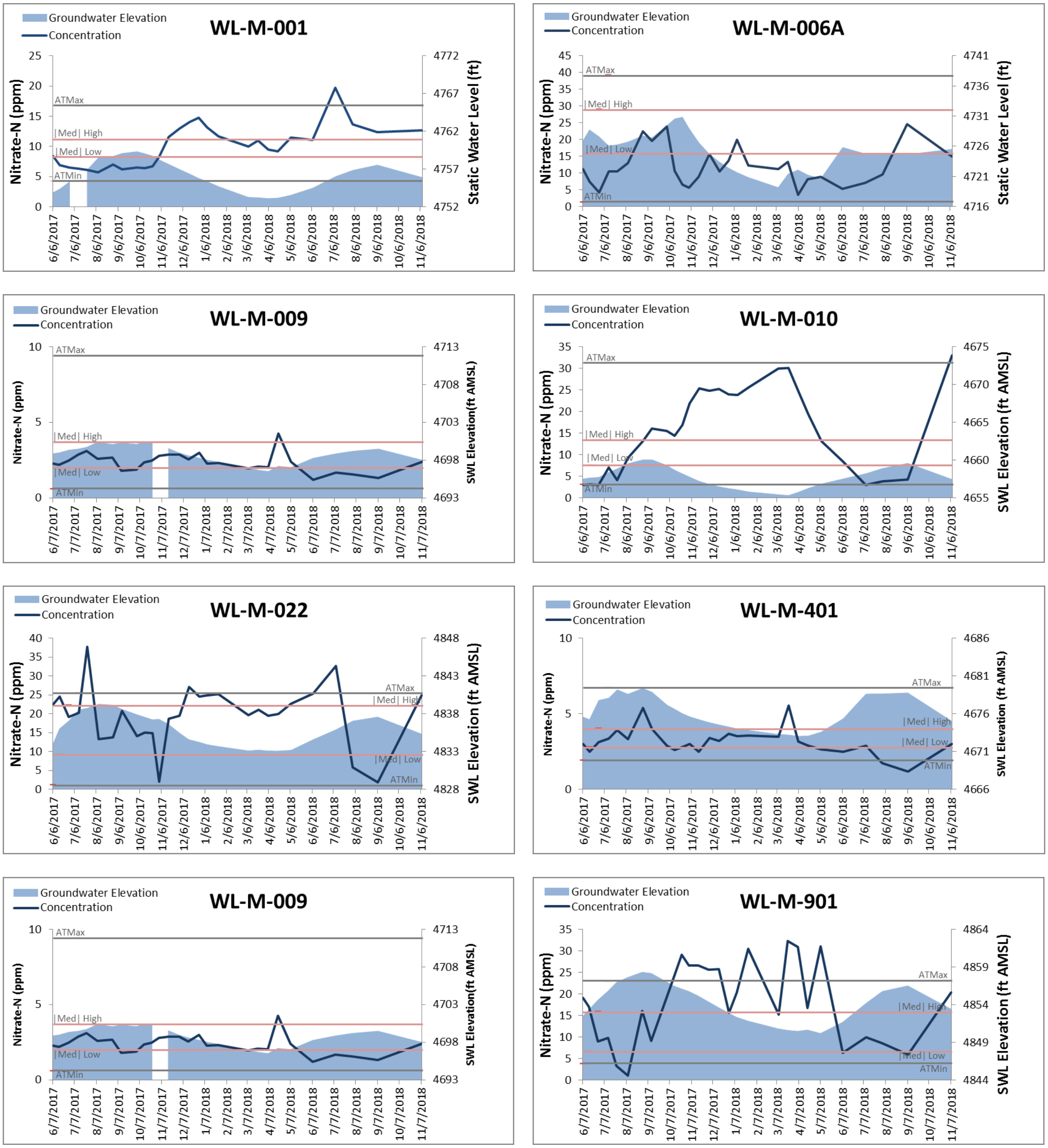

Figure 7 Nitrate concentration and groundwater elevation measured across 28 sampling events from June 2017 through November 2018 on eight monitoring wells in the South Platte alluvial aquifer within Weld County, Colorado. |Med|High and |Med|Low, are the upper and lower bounds of a 95% confidence interval around the long-term median nitrate concentration for each well, and ATMax and ATMin, are the minimum and maximum nitrate concentrations for each well as measured annually in June or early July from 1992 to 2018. Top value on SWL Elevation axis is the land elevation.

unsaturated zone, variability in agricultural management practices, and even spatial and temporal variability in precipitation. If other monitoring wells from Weld County, not believed to be as heavily influenced by groundwater recharge, would have been selected, it is possible the nitrate variability may not have breached outside of the median confidence intervals or range thresholds for those wells. These are questions that will require additional work to answer, but for the purpose of this summary, some additional observations are worth discussing as point of proof for the need to further study these questions.

While there is not a consistent response between water level elevation change and nitrate concentrations between wells, some wells show good response with respect to the theory that lower water levels in the aquifer minimizes the dilution of contaminant concentrations, specifically wells WL-M-010, WL-M-022, WL-M-501, and WL-M-901. These results allow for a better understanding of what baseline nitrate concentrations for these wells may be. Interestingly, the baseline concentrations in these wells seem to behave more like what is typically seen in a surface water time series – higher concentrations coinciding at times of lower flows. What is made somewhat clearer for these sites is that it is not likely that nitrate concentrations in the augmentation ponds or irrigation canals are a major contributor to nitrate in groundwater, but rather only serve to dilute the concentrations of agrichemicals flowing towards the well from the various non-point sources. This realization does create a conundrum with regard to how baseline groundwater quality results for this area should be studied and discussed, as the highest concentrations tend to be found outside of the growing season instead of at the front end of it.

While only two wells showed significant trends for ort-PO_4 **(Table 1)**, it is noteworthy that prior to the June 2018 measurement, WL-M-010 was also trending upward but then had a decrease for the June 2018 value that resulted in a non-significant trend **(Figure 8)**. Keep in mind that trend monitoring for the wells in the Weld County MW Network considers single measurements, typically in June. All seven wells regularly detecting ort-PO_4 (WL-M-006A has infrequent, low-concentration detections) saw a decrease from May 2018 to June 2018, but the decrease of 1.4 ppm seen in WL-M-010 was second largest only to the 2.2 ppm decrease seen in WL-M-501. This is just one indication of a unique relationship between these two wells which will be discussed in further detail later.

The responses seen in WL-M-901 and WL-M-001 further add to the complexity. While the nitrate concentrations in WL-M-901 were highest, on average, when the water level elevation was lowest, the nearly 15 ppm undulation that occurred multiple times, from January to May in 2018, is not mimicked by changing water table elevation. This monitoring well is located next to an irrigation well which when running could likely induce a sudden change in water quality measured in the monitoring well; however, it is unlikely this irrigation well is operated during the winter months and it was never running during a sampling event. Dissolved oxygen concentrations over this time frame were well above the 2.0 mg/L upper threshold that inhibits denitrifying bacteria from actively breaking down nitrate, so it is difficult to know what might have caused this pattern. And while there was an increase in nitrate for WL-M-001, between October and December in 2017, which coincides with the increase seen in several other wells when the water table elevation was beginning to fall, the statistically significant upward trend observed for that well seemed to disregard the recovery of water table elevation.

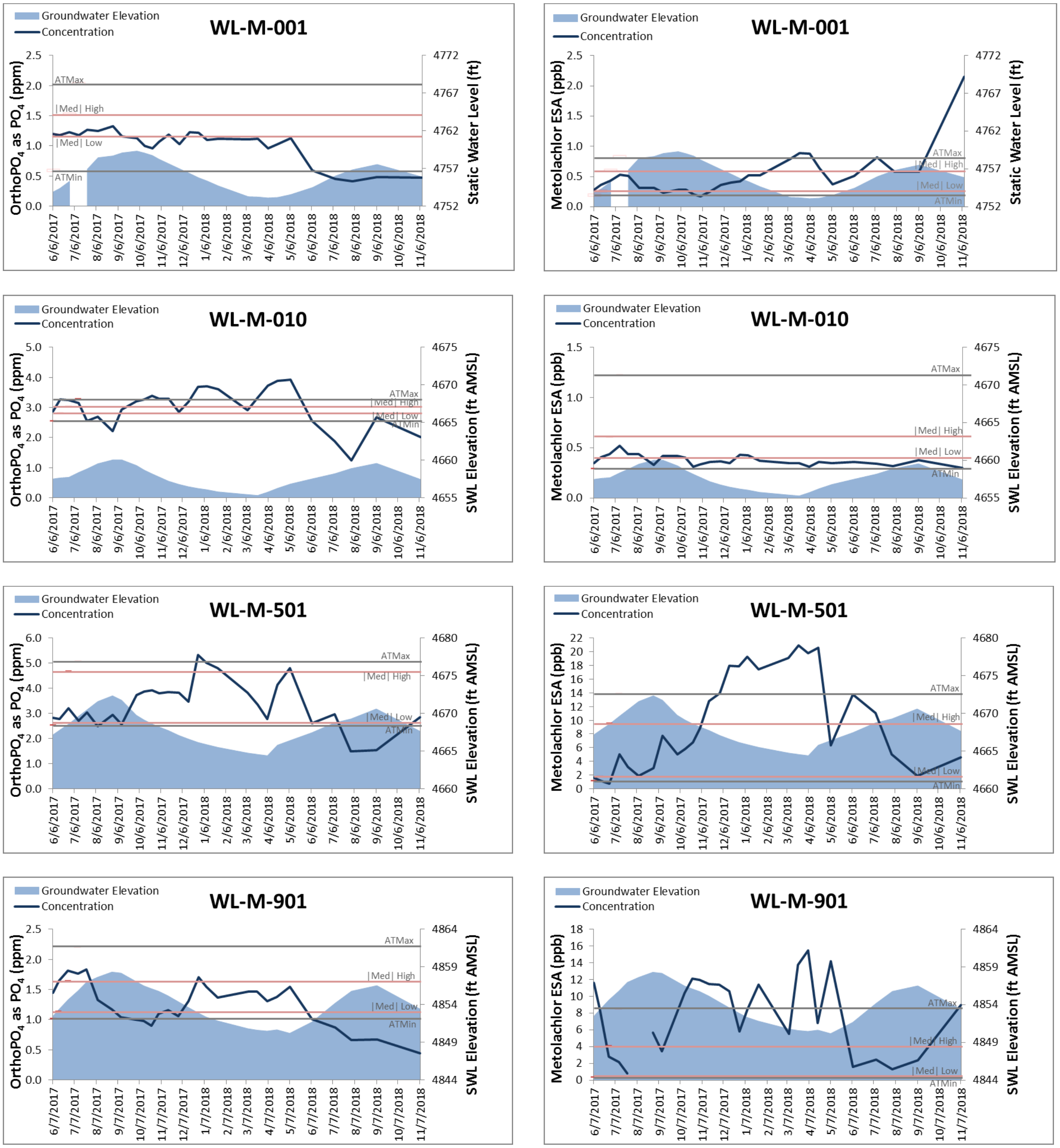

Figure 8 Concentration of orthophosphate as PO_4 (left graph) and the pesticide active ingredient metolachlor-ESA (right graph) compared to groundwater elevation measured across 28 sampling events from June 2017 through November 2018 on four monitoring wells in the South Platte alluvial aquifer within Weld County, Colorado. |Med|High and |Med|Low, are the upper and lower bounds of a 95% confidence interval around the long-term median concentration of parameter on left x-axis, and ATMax and ATMin, are the long-term minimum and maximum concentration of parameter on left x-axis. Long-term orthophosphate measured since 2012 and metolachlor-ESA since 2009. Top value on SWL Elevation axis is the land elevation.

It is understood that the chemical and physical properties of different compounds determine their fate and transport through the rhizosphere, vadose zone, and even once a compound is in groundwater. And while the Program has not yet dug deeper into the details of fate and transport, it is obvious by what is seen in the subset sampling over the last year and half, that the relationships between different compounds, or physical measurements taken in the field (pH, electrical conductivity (EC), water temperature, dissolved oxygen, etc.) are not consistent across all wells in the subset. For example, NO_3-N and ort-PO_4 in WL-M-001 are inversely correlated, but for several other wells they are positively correlated. Ultimately, ort-PO_4 should not be showing up in shallow groundwater on a consistent basis since it has an affinity for adhering to soil particles and is therefore more of a surface water contamination concern due to sediment transport. However, soils due have a limited capacity to store phosphorus, and once that capacity is exceeded, dissolved forms of phosphorus , like ort-PO4, can move more freely in water like nitrate tends to do. But even when ort-PO_4 becomes mobilized, the subset data don't seem to suggest that its mobility mimics that of nitrate. With concentrations of ort-PO_4 in alluvial groundwater reaching upwards of 1.7 ppm as P, and with the South Platte River relying on groundwater discharge to sustain flow, it will be important to continue evaluating why ort-PO_4 is showing up at several locations in Weld County, but the reasons may be tied more to site-specific conditions than to overall regional influences.

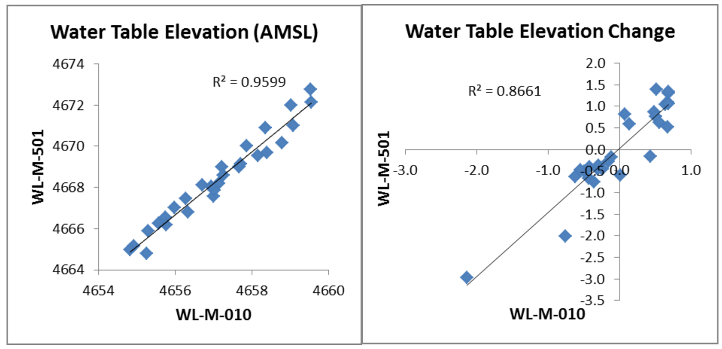

FIGURE 9 SCATTERPLOTS OF GROUNDWATER ELEVATION AND CHANGE IN ELEVATION OVER TIME BETWEEN WELL WL-M-501 AND WELL WL-M-010 IN THE WELD COUNTY SUBSET SAMPLED FROM JUNE 2017 THROUGH NOVEMBER 2018.

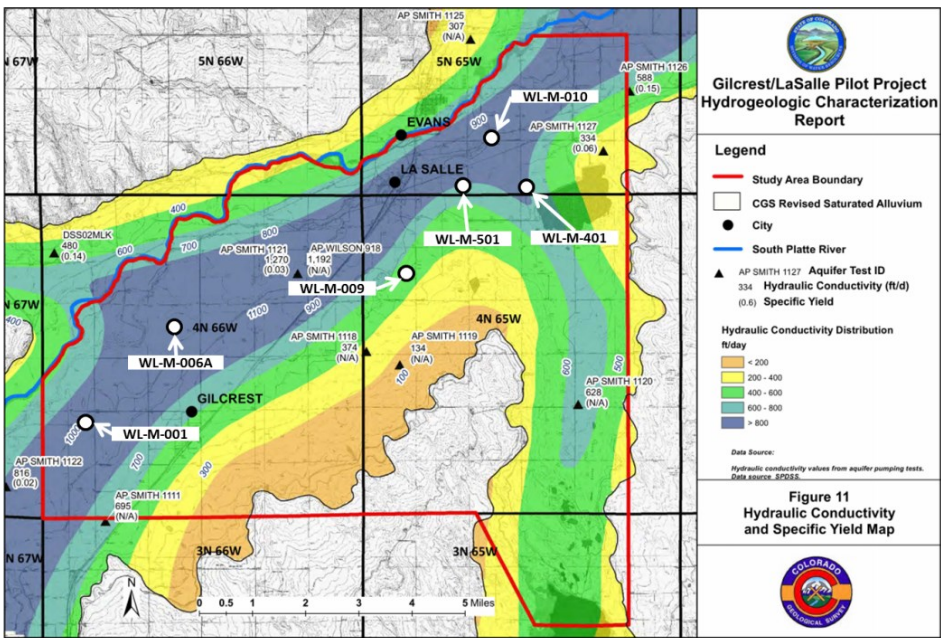

FIGURE 10 EXCERPT FROM BARKMANN ET AL. (2014) OVERLAID WITH WELD COUNTY SUBSET MONITORING WELLS WITHIN THE GILCREST-LASALLE STUDY AREA.

Another example of the inconsistency in responses between compounds, are several of those seen for WL-M-010 and WL-M-501. As mentioned earlier, these two wells have a unique relationship with one another in that WL-M-501 is one mile, seemingly directly up-gradient of WL-M-010 and along the same groundwater flow path. This is believed to be the case primarily because of the similar water table elevations over time and even the same rate of change in elevation seen in both wells (**Figure 9**). The transit time between these two wells is not specifically known; however, hydrogeologic characterization data from the Gilcrest-LaSalle study area (a study area created in 2012 as a result of Colorado House Bill 12-1278 aimed at evaluating concerns with high groundwater levels impacting residential dwellings and inundating crops) as seen in the map in **Figure 10**, from Barkmann et al. (2014), shows that these two wells are in an area with hydraulic conductivity likely exceeding 800 ft/day, or ½ a foot per minute. The transmissivity in the area is projected to be 300,000 gpd/ft or greater. With this volume of water moving through the area so quickly, it may be a bit more surprising when concentrations of compounds between the two wells are similar than when they are dissimilar since there could be a compounding effect of dilution and/or rapid plume migration impacting the results.

However, some similar responses do exist between these two wells with one being a positive correlation in NO_3-N concentration between the two wells (R^2 = 0.72). Aside from an unexpected spike in WL-M-010, from September to November, which is not evident in WL-M-501, the concentrations are similar; although, the rate of change at each site is not. The spike in concentration in WL-M-010 could reasonably be due to the farmland lying between it and WL-M-501, contributing a load of nitrate. For the most part there does appear to be decrease in concentration of various agrichemicals as groundwater moves north-northeast from WL-M-501 to WL-M-010. This is profoundly evident in the difference in concentration of MESA between the two sites, although the response is also somewhat perplexing. The MESA concentrations in WL-M-501 are strongly correlated to the NO_3-N results (R^2 = 0.89), and as was mentioned above, the NO_3-N concentrations between WL-M-010 and WL-M-501 are and have temporal concentration trends that mimic each other fairly well given that these two sites are mile apart. So it would stand to reason that a similar temporal pattern would be seen for MESA as well; however, through the 28 sampling events, the MESA concentrations for WL-M-010 never exceeded 0.5 ppb while WL-M-501 ranged from 0.7 to 20.9 and followed a similar temporal pattern to that of NO_3-N. This response is peculiar and shows that fate and transport of agrichemicals in high energy alluvial systems, such as that of the South Platte River Basin, is very complex.

It could be argued that the differences in correlation between NO_3-N and electrical conductivity (EC) at each of these sites (WL-M-010 R^2 = 0.65; WL-M-501 R^2 = 0.86) is indicative of land-use practices between the wells influencing the differences. It is known that EC has the tendency to be positively correlated with nitrate, but the subset data suggests that the degree of correlation is site-dependent. For example, wells WL-M-001, WL-M-501, and WL-M-901 all have R^2 values greater than 0.8 for these two variables, but wells WL-M-009 and WL-M-401 show zero evidence of correlation. While it would be great if the Program could save laboratory costs by just estimating nitrate from a simple EC measurement that is impractical in an environment where anthropogenic influence trumps natural occurrence. However, the strong correlations seen at several sites in the subset over the last year and a half, does present the feasibility of using EC as a way of knowing when an ion-specific electrode installed in a well is in need of recalibration. And while this leans heavily on the assumption that the relationship between variables will not degrade, it could be beneficial to take advantage while they are present. Well WL-M-901 presents the best opportunity with not only strong correlation between EC and NO_3-N (R^2 = 0.90) but also a nearly perfect linear relationship between the rate of change in nitrate being equal to that of the pesticide MESA (R^2 = 0.97), even amidst the unexplained undulation seen from January through May in 2018. This seems to indicate that similar processes are affecting the change in concentration of both nitrate and MESA at this location which as has been discussed, is not a pattern that holds true for all wells.

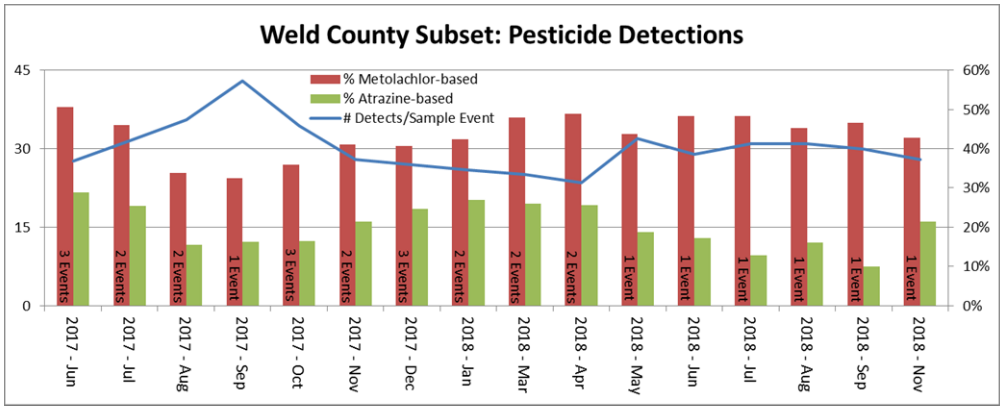

Figure 11 Detection frequency of pesticide active ingredients and the number of types, found in a set of eight Weld County monitoring wells sampled monthly from June 2017 through November 2018. Metolachlor-Based compounds include the parent compound and major breakdown products metolachlor–ESA and –OA. Atrazine-based compounds include the parent compound and major breakdown products desethyl– , desisopropyl–, and hydroxy–atrazine. Numbers in red columns indicate the number of sampling events conducted in each month.

While looking at the results for the individual wells reveals a good level of inconsistency in response between variables and shows that variability of some agrichemicals can indeed breach outside the typical concentrations seen long-term in June, when the subset is looked at collectively as a group, the results tend to agree with historical results seen in the Basin, depending on which spatial scale is evaluated. The median NO_3-N for all 223 samples collected from June 2017 through November 2018, is 10.7 ppm which is in good agreement with the median seen for the South Platte Basin in 2018 and even the all-time median for the eight wells in the subset since 1992 (9.1 ppm). However, this accounts for only half of the 20 ppm median typically seen of the Weld County MW network as a whole since 1992.

Only one of the 223 samples resulted in no pesticide detection. Twenty-two percent of samples contained a single detection of the MESA but no other pesticides. And for the remaining samples detecting two or more pesticides, MESA was detected in every sample. At least for these eight wells, this finds MESA having nearly 100% detection frequency throughout the year, with concentrations ranging from 0.1 to 20.9 ppb and an average of 3.0 ppb. Through 28 sampling events, metolachlor-based pesticides accounted for, on average, 43% of all detections although that percentage did dip down into the thirties in August through October of 2017. And while there was a range from 49 to 80%, the percentage of detections accounted for by metolachlor-based and atrazine-based compounds together, averaged 64% of all detections which is similar to the 70%

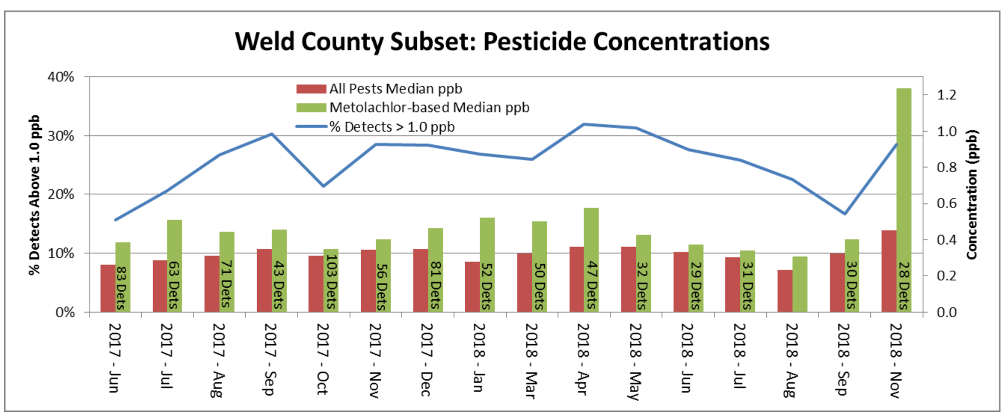

Figure 12 Concentrations of detected pesticides in a set of eight Weld County monitoring wells sampled monthly from June 2017 through November 2018. Metolachlor-based compounds include the parent compound and major breakdown products metolachlor–ESA and –OA. Number in green column is the total number of detections found in the well subset in the given month. In months where multiple sampling events were conducted, the number represents the average number of detections per sampling event.

seen in the South Platte Region since 2010.

Well Clusters: The final point of discussion for the South Platte Region is a brief summary of results seen from a couple clustered well sites in Weld County. Site WL-M-006, which is near a large augmentation pond facility, was visited multiple times as part of the Weld County Subset sampling. The initial reasoning behind sampling the additional wells at the site was to try and see how water quality was being impacted by the groundwater recharge occurring directly up-gradient from the well cluster. Three sampling events were conducted on all three wells at the site from late-March to early-April. However, due to the need to limit sample numbers and the fact that the deepest well had an obstruction preventing successful deployment of the YSI ProDSS for *in situ* measurements, only the shallow and middle depth wells were sampled from May through November.

For the three wells sampled March 22nd, April 5th, and April 19th, the concentration gradients seen for all analytical parameters mostly followed a common trend – concentrations decreasing with depth. The most

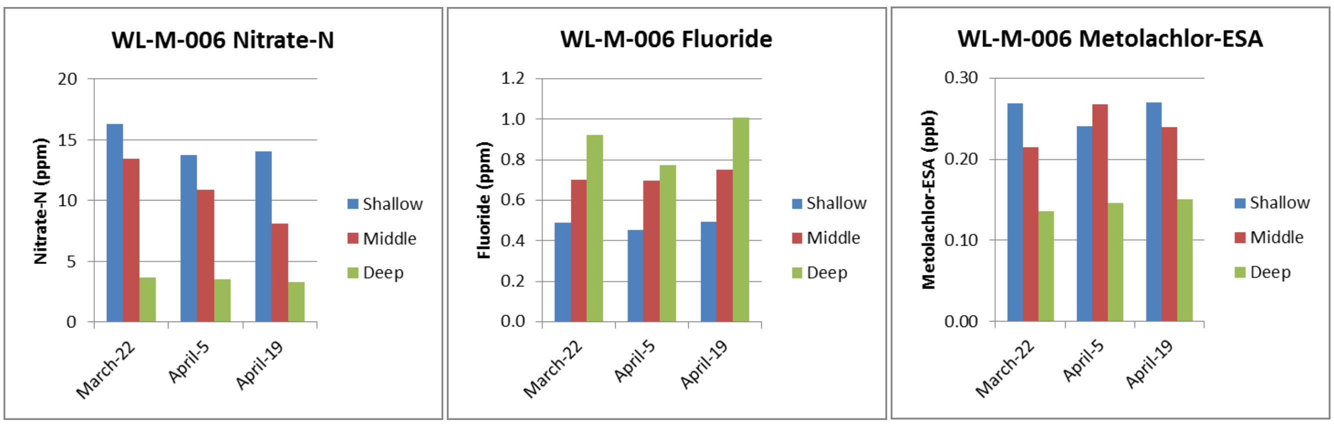

FIGURE 13 BAR GRAPHS SHOWING CONCENTRATIONS OF NITRATE-N, FLUORIDE, AND METOLACHLOR-ESA SEEN IN A CLUSTER OF MONITORING WELLS INSTALLED AT DIFFERENT DEPTHS AT A SITE IN WELD COUNTY, CO. SHALLOW WELL DEPTH IS 31.2 FT, MIDDLE WELL DEPTH IS 41.8 FT, AND DEEP WELL DEPTH IS 59.8 FT. ALL WELLS HAVE 10-FT SCREENED INTERVALS. RESULTS SEEN OVER THREE SAMPLING EVENTS FROM MARCH 22ND THROUGH APRIL 19TH, 2018.

notable exception was for fluoride which saw the opposite trend and likely suggests a natural source of fluoride coming from the Pierre Shale formation which is the bottom limit of this alluvial aquifer and where the deepest well at each of the clustered sites is typically drilled down to **(Figure 13)**. Metolachlor-

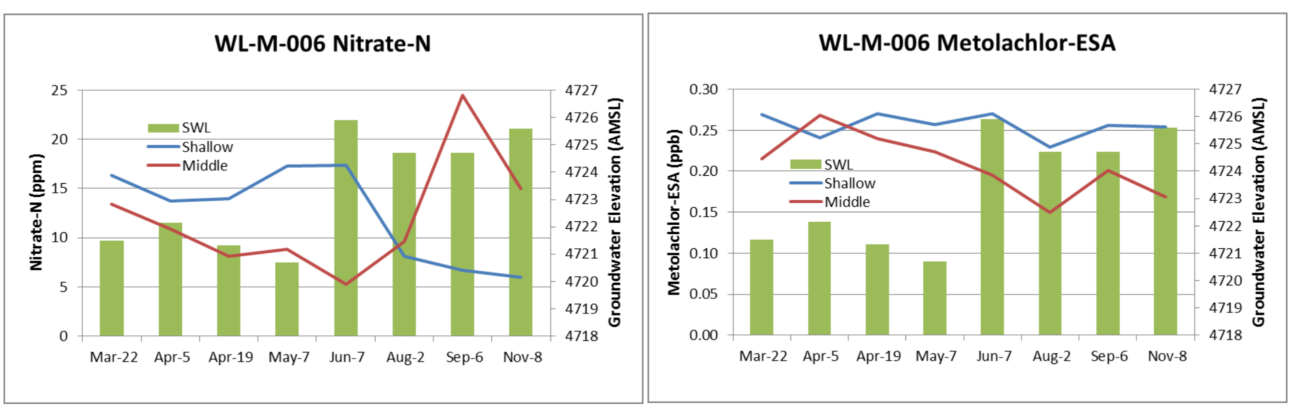

FIGURE 14 GRAPHS SHOWING VARIABILITY OF NITRATE-N AND THE PESTICIDE ACTIVE INCREDIENT METOLACHLOR-ESA AT A SITE WHERE WELLS AT TWO DIFFERENT DEPTHS WERE SAMPLED FROM MARCH 22ND THROUGH NOVEMBER 8, 2018. CONCENTRATIONS ARE COMPARED TO GROUNDWATER ELEVATION. THE TOP VALUE ON THE RIGHT Y-AXIS IS THE APPROXIMATE LAND ELEVATION AT THIS SITE IN WELD COUNTY, CO.

ESA saw the concentration in the middle well on April 5th exceed that of the shallowest well.

This seems to be a response to a change in groundwater elevation; however, it is not clear why the concentration was higher in the middle well than the shallow well but the near overlap of the screened interval for these two wells could be partially explanative. Fluctuation in groundwater elevation as a result of augmentation had a noticeable impact on nitrate concentrations over the course of eight sampling events from March 22nd through November 8th as seen in **Figure 14**; however, for MESA, the concentration continued to trend downward even when the groundwater elevation increased more than five feet.

Another cluster site, WL-M-603, showed similar decrease in concentration from the shallow to the middle depth wells, but the deeper well had slightly higher concentrations of nitrate, MESA, and MOA concentrations. That is not too remarkable; however, the Program's first ever detection of glyphosate's main degradate, AMPA, was found only in the deep well at this site. An initial detection of 18.2 ppb of AMPA was confirmed by another sample collected 47 days later that measured even higher at 32.3 ppb. The top of the screened interval for the deep well is 20 ft deeper than the bottom of the screen in the middle well, and the fact that the dissolved oxygen is only 0.1 ppm in the deep well compared to 6.5 in the middle well, makes it plausible that groundwater from the deep well is either separated from the groundwater being measured by the shallower wells by a aquitard or is much older. It will be of interest to the Program to see if AMPA is still present in this well during the 2019 monitoring season.

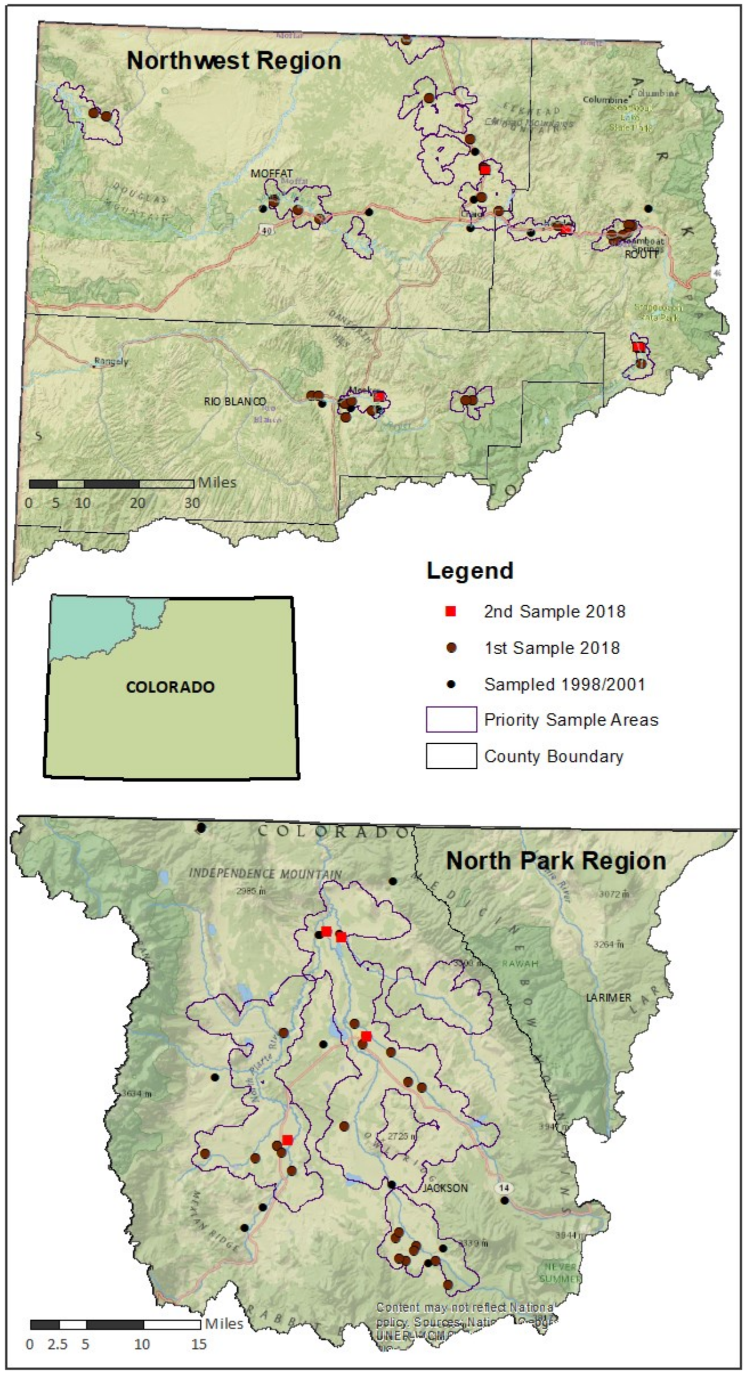

FIGURE 15 MAP SHOWING LOCATIONS SAMPLED IN THE PROGRAM'S NORTHWEST REGION AND NORTH PARK REGION IN SEPTEMBER AND OCTOBER, 2018. PRIORITY SAMPLING AREAS WERE USED TO FOCUS THE SAMPLING EFFORTS INTO THE MOST VULNERABLE AREAS WITHIN EACH REGION. SITES WITH A RED SYMBOL WERE SAMPLED FOR THE 2ND TIME BY THE PROGRAM IN 2018.

Northwest & North Park Regions

The Program does not visit the lower vulnerability areas of the state very frequently, and when it does, sample counts are fairly limited, which forces the Program to focus on obtaining samples from the most vulnerable areas. Both the Northwest (NW) and North Park (NP) Regions have very low overall vulnerability to agrichemical contamination compared to other parts of the state. This is due primarily because of the discontinuous pockets of vulnerability that are intermittently dispersed amongst the more pristine landscapes of the national forests, open sagebrush-rich rangelands, and mountainous terrain. And even in the more vulnerable alluvial systems along rivers in the regions, since only grass/alfalfa hay production and cattle grazing are the predominant activities, there is lower concern for contamination compared to other alluvial aquifers of the state growing a greater variety of row crops that are more intensely fertilized and managed for pests.

The map seen in **Figure 15,** shows the priority sample areas that were derived from the inclusion of various geospatial data like alluvial aquifers, irrigated acres, oil & gas (O&G) activity, and groundwater vulnerability. Unlike what was seen in the Tri-Rivers and Southwest Regions of Colorado's western slope - O&G activity occurring within or topographically up-gradient of agricultural areas – the largest densities of O&G activity in NW and NP were situated in areas where groundwater was typically deeper than 100 ft. Therefore, no areas with high density O&G activity were sampled in 2018. The final distribution of sample sites in both regions was a result of willing participants and lack of suitable wells, which unfortunately, didn't allow for sampling of all priority areas. Compared to the last sampling effort in 1998 for the NW and 2001 for NP, coverage and density did improve and sample locations were better targeted to the more vulnerable areas in these regions. Due to these improvements, ownership changes or well abandonment, only a handful of wells sampled in 1998 or 2001 were able to be sampled for a second time in 2018.

The average well depth in the NW was 54 ft with four of 33 wells installed deeper than 100 ft. For the NP Region the average well depth was about 100 ft with nearly half of 25 wells installed deeper than 100 ft. For wells in the NW with adequate well permit information, the average screened interval is about 25 ft while the average length for wells sampled in NP is about 50 ft. The deeper wells and long screened intervals sampled in NP indicate that more samples were coming from the quaternary aquifer than from the shallower alluvial aquifers. Given how much more contiguous alluvial systems are in NP compared to the NW region, this is somewhat surprising but likely doesn't impact the water quality results for these areas.

Both regions saw a median NO_3-N of 0.8 ppm and no pesticide detections. There were 12% of wells in NW and 32% of the wells in NP that did no detection of nitrate. When compared to 95-99% detection frequencies seen for the South Platte Basin, this confirms that lower vulnerability to nitrate contamination in this part of the state. Two wells in NP and one in NW had NO_3-N greater than 5 ppm but no wells exceeded the EPA Standard. The only remarkable discoveries from an overall water quality standpoint were a few minor detections of lead, selenium, and a couple other dissolved metals, but no drinking water standards were exceeded. Hardness (as $CaCO_3$) measured in NW averaged 350 ppm and ranged from 3 to 1600 ppm while NP averaged 228 ppm and ranged from 58 to 1800 ppm. One well in NW contained 14 ppm of iron and more than 1,500 ppm of sulfate, but a NP well saw more than 2,100 ppm sulfate and also measured the greatest concentrations of magnesium (200 ppm), calcium (450 ppm), sodium (430 ppm), and chloride (234 ppm) seen in NP, along with the only detection of nickel and cobalt seen in either region. Overall water quality discovered in these regions of Colorado demonstrate that while naturally occurring impacts due to variations in hydrogeology are obvious for some wells, impacts from agrichemicals are fairly unmeasurable which validates the use of an infrequent sampling interval.

All results discussed in this summary can be queried and downloaded from the Program's online water quality database which can be found at: http://www.erams.com/co_groundwater. Program personnel contact information and other program information can be found at http://www.co.gov/ag/gw.

2018 Analyte Reporting Limits					
Analyte Name	**Reporting Limit**	**Units**	**Analyte Name**	**Reporting Limit**	**Units**
2,4-D	0.1	ug/L	Imazamox	0.1	ug/L
2,4-DB	0.1	ug/L	Imazapic	0.1	ug/L
2,4-DP	0.1	ug/L	Imazapyr	0.1	ug/L
3-Hydroxycarbofuran	0.1	ug/L	Imazethapyr	0.1	ug/L
Acetochlor	0.1	ug/L	Imidacloprid	0.1	ug/L
Acetochlor ESA	0.1	ug/L	Isoxaflutole	0.1	ug/L
Acetochlor OA	0.1	ug/L	Kresoxim methyl	0.1	ug/L
Acifluorfen	0.1	ug/L	Linuron	0.5	ug/L
Alachlor	0.1	ug/L	Malathion	0.1	ug/L
Alachlor ESA	0.1	ug/L	MCPA	0.1	ug/L
Alachlor OA	0.1	ug/L	MCPP	0.1	ug/L
Aldicarb	0.1	ug/L	Metalaxyl	0.1	ug/L
Aldicarb sulfone	0.2	ug/L	Metconazole	0.1	ug/L
Aldicarb sulfoxide	0.1	ug/L	Methomyl	0.1	ug/L
Aminopyralid	0.2	ug/L	Metolachlor	0.1	ug/L
AMPA	2.0	ug/L	Metolachlor ESA	0.1	ug/L
Atrazine	0.1	ug/L	Metolachlor OA	0.1	ug/L
Azoxystrobin	0.1	ug/L	Metribuzin	0.1	ug/L
Bentazon	0.25	ug/L	Metsulfuron methyl	0.1	ug/L
Bromacil	0.2	ug/L	Nicosulfuron	0.1	ug/L
Carbaryl	0.2	ug/L	Norflurazon	0.2	ug/L
Carbofuran	0.1	ug/L	Norflurazon desmethyl	0.5	ug/L
Chlorantraniliprole	0.1	ug/L	Oxamyl	0.2	ug/L
Chlorimuron ethyl	0.1	ug/L	Oxydemeton methyl	0.1	ug/L
Chlorsulfuron	0.1	ug/L	Picloram	0.1	ug/L
Clopyralid	0.1	ug/L	Prometon	0.1	ug/L
Cyanazine	0.1	ug/L	Propazine	0.1	ug/L
Cyproconazole	0.1	ug/L	Propoxur	0.1	ug/L
Cyromazine	0.1	ug/L	Prosulfuron	0.1	ug/L
Desethyl Atrazine	0.1	ug/L	Pyrimethanil	0.1	ug/L
Desisopropyl Atrazine	0.1	ug/L	Quinclorac	0.1	ug/L
Dicamba	0.1	ug/L	Simazine	0.1	ug/L
Diflufenzopyr	0.25	ug/L	Sulfentrazone	0.2	ug/L
Dimethenamid	0.1	ug/L	Sulfometuron methyl	0.1	ug/L
Dimethenamid ESA	0.1	ug/L	Sulfosulfuron	0.1	ug/L
Dimethenamid OA	0.1	ug/L	Tebuconazole	0.1	ug/L
Dimethoate	0.1	ug/L	Tebufenozide	0.1	ug/L
Dinotefuran	0.1	ug/L	Tebuthiuron	0.1	ug/L
Disulfoton sulfone	0.1	ug/L	Terbacil	0.1	ug/L
Disulfoton sulfoxide	0.1	ug/L	Thiamethoxam	0.1	ug/L
Diuron	0.1	ug/L	Triadimefon	0.1	ug/L
Ethofumesate	0.2	ug/L	Triallate	0.1	ug/L
Ethoprop	0.1	ug/L	Triasulfuron	0.1	ug/L
Fenamiphos	0.1	ug/L	Trichlorfon	0.2	ug/L
Fenamiphos sulfone	0.1	ug/L	Triclopyr	0.2	ug/L
Florasulam	0.1	ug/L	Triticonazole	0.1	ug/L
Flufenacet	0.1	ug/L	Bromide	0.05	mg/L
Flumetsulam	0.1	ug/L	Chloride	0.05	mg/L
Glyphosate	1.0	ug/L	Fluoride	0.05	mg/L
Halofenozide	0.1	ug/L	Nitrate as N	0.011	mg/L
Halosulfuron methyl	0.1	ug/L	Nitrite as N	0.015	mg/L
Hydroxy Atrazine	0.04	ug/L	Ortho-phosphate (Dissolved)	0.05	mg/L
Imazamethabenz ester	0.1	ug/L	Sulfate	0.05	mg/L

Table 2 Reporting limits for agrichemicals analyzed by the Biochemistry Lab of the Colorado Department of Agriculture in 2018.