

# **Investigation of Agrichemical Contamination in Public Supply Wells, Springfield, CO**

**Colorado Department of Agriculture  
Agricultural Chemicals & Groundwater Protection Program**



**COLORADO**  
**Department of Agriculture**  
Conservation Services Division

## **Executive Summary**

At the request of the City of Springfield, CO, nine public supply wells (PSW) operated by the city were sampled by personnel from the Colorado Department of Agriculture's (CDA) Agricultural Chemicals & Groundwater Protection Program (ACGPP), in May of 2015, to assess agrichemical contamination. Samples were analyzed for select inorganic compounds; nitrogen-15 (<sup>15</sup>N) and oxygen-18 (<sup>18</sup>O) stable isotopes; and a suite of pesticide compounds. Data were evaluated to answer the following questions: Can the nitrate contamination in the city's PSWs be linked to a source and is this source organic or inorganic in composition; and is there evidence to show that the agrichemical contamination impacting PSW #8 could in the future impact other PSWs in the system that are not presently impacted?

Results from the 2015 sampling event were comparable with previous data collected by ACGPP and the City of Springfield. Nitrate was above the drinking water standard in PSW #8 and multiple pesticide active ingredients were also detected in the well. Evidence shows that the negative impacts to water quality in PSW #8 are likely man induced; however, the stable isotope analysis that was used in this evaluation did not provide any insight as to whether the nitrate source was from an inorganic or organic source. What was revealed is that multiple sources are impacting PSW #8 due to the various types of pesticide compounds detected and the elevated nitrate, bromide, chloride, and sulfate discovered.

There appears to be some relationship between PSWs #8, #9, and #10 with regard to the types and concentrations of some constituents, but there is no clear evidence whether PSWs #9 and #10 will be further impacted by the contamination currently impacting PSW #8. There are some hydrogeological characteristics involving Cat Creek, the Dakota Sandstone unit, and storm water runoff which are likely contributing contamination to the Dakota Sandstone aquifer. This discharge, in addition to other possible sources such as fertilizer spills or leaking sewage/septic, could be working in tandem to impact the groundwater quality seen in PSW #8.

The ACGPP, in a collaborative evaluation with the Colorado Department of Public Health and Environment, recommend decommissioning PSW #8 as a drinking water supply, but suggest holding onto it for other uses. Further research efforts could be conducted to attempt to determine more specifically if there is a point source for the nitrate contamination and what are the specific contamination pathways most influential in the local setting; these investigations however, could be costly. These efforts could include storm water runoff sampling, sediment sampling within and outside of the storm water drainage channels emptying into Cat Creek, and monitoring well installation and sampling in strategic locations up- and down-gradient of suspected agrichemical contaminant sources. Ultimately, PSW #8 is being impacted by agrichemicals to a much greater extent than any other well in Springfield's water supply system. A decision on whether additional sampling and evaluation to hone in on where the contamination is originating from will be up to the City of Springfield, though this may not be financially feasible.

A more technically in-depth report follows this Executive Summary.

Karl Mauch, Groundwater Monitoring Specialist

# **FULL REPORT**

## Introduction/Background

The Agricultural Chemicals & Groundwater Protection Program (ACGPP) of the Colorado Department of Agriculture (CDA) was requested to assist the City of Springfield, CO with investigating lingering nitrate contamination concerns within some of the city's public supply wells (PSW). It was decided in conversation with Colleen Williams, a Source Water Specialist with Colorado Rural Water Association whom completed the Source Water Protection Plan for the city, that we would collect samples for the following analyses: anion and pesticide analysis at CDA's biochemistry lab, and analysis of the stable isotopes  $^{15}\text{N}$  and  $^{18}\text{O}$  at the University of California at Davis. The stable isotope analysis was intended to assist in determining if the source of nitrate contamination discovered in wells is of an organic (sewage, manure), an inorganic (fertilizer), or indeterminate/mixed source. Pesticide analysis would be conducted as part of the normal analysis suite that CDA runs on samples collected by the ACGPP

The following brief introduction to stable isotope analysis should serve to familiarize you with the main concepts of it. The elements nitrogen and oxygen have an atomic mass of approximately 14 and 16, respectively. However, all elements have various isotopes, or alternate forms of themselves, due to the process of proton addition or subtraction which changes the atomic mass. These isotopes can be unstable radionuclides (like  $^{14}\text{C}$ ) that can degrade over time, or they can be stable like  $^{18}\text{O}$  and  $^{15}\text{N}$  which withstand degradation. The mass difference between isotopes causes differences in physical, chemical, and biological processes or reactions that these elements may be involved in. Biologically-mediated processes on nitrogen and oxygen like assimilation, nitrification, and denitrification, significantly impact the dynamics of these elements in the soil, and ultimately the groundwater. The lighter isotope of each element is preferentially selected for these processes so there ends up being an enrichment of the heavier isotope of each element in the nitrate or nitrite compounds. An enrichment (or in some cases a depletion) is derived from comparing the measured  $^{15}\text{N}$  or  $^{18}\text{O}$  isotope concentration to a standard of reference. The standard for  $^{15}\text{N}$  is atmospheric  $\text{N}_2$  which has a stable  $^{15}\text{N}$  concentration of 0.3663% (Junk and Svec, 1958) and the standard for  $^{18}\text{O}$  is Standard Mean Ocean Water (Craig, 1961) or the virtually equivalent Vienna-SMOW standard which is 0.002%  $^{18}\text{O}$ . The evaluation of terrestrial material using this methodology has proven to be a useful tool in answering a plethora of questions for researchers over the last 60 years, including the sources of nitrate contamination in water.

From Williams (2003) it was determined that all nine wells (**Figure 1**) to be sampled had a screened interval accessing the Dakota Sandstone unit. Two wells also accessed the Cheyenne Sandstone unit below the Kiowa Shale Aquitard (PSW #10 and PSW #13) and another well accessed those units in addition to the Ogallala Formation which sits above both the Dakota Sandstone and another aquitard of the Colorado Group (when present). Hydrogeologic information for the area suggests that the Colorado Group aquitard is discontinuous and where it is absent there is a hydrologic connection between the Ogallala Formation and Dakota Sandstone units. Furthermore, in places where the Ogallala has been eroded away by fluvial process there is the likelihood that a hydraulic connection exists between the quaternary material of the Cat Creek alluvium and the Dakota Sandstone. While these scenarios are possible, it is not known exactly where they might be occurring. Nonetheless, it is important to keep

these scenarios in mind when deciphering where groundwater contamination could be coming from in the well network.

The nine wells have a permitted water supply of 3,802 acre-feet, and work to fill the city's four water towers or tanks having a total capacity of 1.28 million gallons. This capacity is capable of serving 1,200 taps, but as of the year 2013 only 890 taps were being served. PSWs #7 and #8 have been shut down since 1993 due to water quality impacts. In the early 1990s, the wells were discovered to have elevated nitrate-nitrogen concentrations above the U.S. EPA Primary Drinking Water Standard of 10.0 mg L<sup>-1</sup>. PSW #8 also had the pesticide active ingredient atrazine above its EPA standard of 3.0 µg L<sup>-1</sup>. According to city monitoring records for PSW #7 (**Figure 2** and **Table 1**) from 1989 to 2014, the average nitrate-nitrogen concentration for the well is just under 12 mg L<sup>-1</sup>; however, concentrations varied from less than 8.0 mg L<sup>-1</sup> before 1999 to more than 14 mg L<sup>-1</sup> since then with only a couple of quarterly sampling events dipping below the U.S. EPA standard. In contrast, PSW #8 has seen an average concentration of 23.4 mg L<sup>-1</sup> since monitoring began in 1994 and shows evidence of an increasing trend from around 20 mg L<sup>-1</sup> to more than 35 mg L<sup>-1</sup> since 2005. PSW #9 has never measured over the EPA standard and averages 5.9 mg L<sup>-1</sup>.

The ACGPP sampled PSW #8 as part of a baseline sampling effort in the High Plains in 1997 and discovered 25 mg L<sup>-1</sup> nitrate-nitrogen (**Table 2**). Additionally, the pesticide active ingredients atrazine, bromacil, and prometon were measured at 3.9, 0.8, and 1.3 µg L<sup>-1</sup>, respectively. The atrazine measurement for this well was over the U.S. EPA Maximum Contaminant Level for drinking water. As can be seen in Table 2 PSWs #12, #9, #7, and #10 also contained measurable atrazine and bromacil was discovered in PSWs #8 and #9. Other notable data from the 1997 sampling event was how elevated other inorganic constituents were in PSW #8 compared to the other wells. Sixty groundwater samples from the late 1940s (McLaughlin, 1954) showed total dissolved solids (TDS) in the Dakota Sandstone ranged from 132 to 5,120 mg L<sup>-1</sup> across Baca County, but approximately 72% of those were less than 500 mg L<sup>-1</sup>. In the same study nitrate-nitrogen was only seen in four of 60 samples to be over the EPA limit of 10 mg L<sup>-1</sup>. The closest groundwater sample collected in 1948 from near Springfield, CO as part of this study was from Well #151 which had a TDS of 478 mg L<sup>-1</sup> and nitrate-nitrogen at 1.15 mg L<sup>-1</sup>. The sulfate ion was measured at 208 mg L<sup>-1</sup> in the well. Given the well's depth of 128 ft and the known geologic stratigraphy of the area, it was likely that Well #151 was accessing groundwater in the Dakota Sandstone unit. Therefore the water chemistry results from this historical study provide a rough idea of what natural background should be for the Dakota Sandstone in the general vicinity of Springfield, CO.

Cat Creek, an intermittent tributary to Bear Creek, runs through the southern part of Springfield and has likely incised through the Ogallala Formation and any existing Colorado Group shale member to provide a direct horizontal recharge pathway into the Dakota Sandstone. Since both PSW #8 and PSW #9 are installed to the same depth and are both screened in the Dakota Sandstone it is plausible that water discharging from Cat Creek would impact both of these wells. McLaughlin (1954) discusses drilling records from a test hole dug for the city of Springfield in the Stewart-Thompson addition at the northern end of Springfield, and shows in succession the Ogallala Formation overlaying varied sandstone stratigraphy common to the Dakota Sandstone unit. Following the Dakota Sandstone was the Kiowa Shale Member and then the Cheyenne Sandstone member which are both part of the Purgatoire

Formation. Additional drilling records for two wells (Driller's Logs #87 and #88 in McLaughlin, 1954) dug for the Atchison, Topeka and Santa Fe Railway Co. in the south-central part of Springfield, showed the Ogallala formation followed by the varied stratigraphy common to the Dakota Sandstone. Not only do these three logs show a rather non-existent Ogallala Formation (maximum of 28ft thickness in northern Springfield record), they also show the lack of a Colorado Group shale member which would serve to impede the hydraulic connection between the Ogallala Formation and the Dakota Sandstone. This provides evidence that Cat Creek very well could be discharging directly to the Dakota Sandstone, both vertically and horizontally, when sufficient flow events occur.

One of the recharge zones most pertinent to this evaluation of water quality impacts, lies west of both PSW #8 and PSW #9, but with the curvature of Cat Creek and the assumed groundwater flow direction of E to ESE, it is possible that groundwater accessed by PSW #8 is influenced more by the recharge events than the groundwater accessed by PSW #9 (see Figure 1). PSW #7, about 800 ft NE of the curve in Cat Creek, has a pumping yield of 50 gallons per minute (gpm) and PSW #8 of 70 gpm. PSW #9 on the other hand has a yield of 167 gpm which is the highest yield for the five PSWs within 1,100 ft of the intersection of Tipton St & W 13<sup>th</sup> Ave (near PSW #7). Not known is if a pumping rate of 167 gpm is sufficient enough to cause increased flow of groundwater in a southerly direction from where it is believed Cat Creek discharges into the Dakota Sandstone. If this was the case then PSW #9 water quality would be more similar to that of PSW #8. Taking this all into consideration, ACGPP was to conduct sampling of the municipal wells and try to determine if the source of nitrate contamination impacting PSW #8 was of organic or inorganic origin. Furthermore, it was to be determined if any evidence exists to suggest that other public supply wells in Springfield's water supply system were likely to be impacted in the future by the same contamination impacting PSW #8.

## **Sampling Methodology**

ACGPP personnel sampled all nine PSWs in Springfield on either May 27 or May 28, 2015 under the supervision of Mike Ingle, Public Works Manager for the Town of Springfield. To assure the wells were adequately purged of any stagnant water existing in the perforated or solid sections of well casing, each well was purged for a time period that allowed for the purging of at least four well volumes. A well volume was defined as the volume of water within a well of a given diameter taking into account the difference in length between the bottom of the well and the static water level. Measured yield estimates for each well were then used to determine how long the well needed to run in order to purge the four well volumes.

A sampling port (usually a spigot) off of the main delivery pipe was configured with Teflon-line LDPE tubing connected to a flow-through cell equipped with a YSI® 556-MPS water quality sonde. Measurements of water temperature, pH, dissolved oxygen, oxidation-reduction potential, and conductivity were measured at three to five minute intervals at some point after the first of four requisite well volumes had been purged. Once three consecutive readings met stabilization criteria the well was declared ready for sampling.

The sample discharge line was connected to a 142-mm stainless steel housing equipped with a 0.45 micron Nylapor® nylon filter disc for collection of the anion and pesticide samples. Then a second stage filtration occurred through a 47-mm stainless steel filter housing equipped with a 0.20 micron Nylapor® nylon filter disc for collection of the stable isotope sample. Samples were then placed in a refrigerator cooler at a temperature between one and four degrees Celsius. Anion and pesticide samples were delivered to the CDA biochemistry lab on May 28, 2015. Analysis of anion was per EPA Method 300.0 methodology and pesticide analysis was completed using the CDA Biochemistry Laboratory SOP PT-METH-027. The stable isotope samples were frozen and shipped overnight to UC Davis Stable Isotope Facility in Davis, CA. Isotope determination for  $^{15}\text{N}$  and  $^{18}\text{O}$  from  $\text{NO}_3^-$  was conducted using a 'denitrifier' method (Sigman et al., 2001; Casciotti et al., 2002; Bohlke et al., 2007).

## **Results**

Each sampling event's time records and pumping logistics are seen in **Table 3** and **Table 4**. Most wells were turned on at least 18 minutes prior to beginning purging measurements except for the two highest producing wells (PSWs #13 and #10) which only ran for about two minutes prior to beginning purging measurements. Even then, PSWs #13 and #10 had purged one or two casing volumes prior to beginning purging measurements due to their high pumping yield, so the initial stagnant water was likely removed. Although the total time each pump was ran before collecting samples varied, the total number of casing volumes removed before sampling met the requirement of four casing volumes and ranged in number from 8 to 209. **Table 5** shows the final field measured water temperature, pH, conductivity, oxidation-reduction potential, dissolved oxygen, and total dissolved solids collected at Time Stabilized (Table 3). All pH values fell into the normal range for groundwater between 6.0 and 8.5. Dissolved oxygen concentrations were all greater than  $2.0 \text{ mg L}^{-1}$ . This is significant because it indicates that no active denitrification was occurring in close proximity to the wells. Specific conductance measured in each well was higher in some (#1, #3, #12, #13), lower in some (#7, #11) and relatively unchanged in some (#8, #9, #10) when compared to measurements made in 1997 by the ACGPP.

### **Inorganic Ions & Stable Isotopes**

PSW #8 was the only well to contain nitrate-nitrogen above the U.S. EPA standard with  $39.2 \text{ mg L}^{-1}$  (**Table 6**). This result agrees with the increasing concentration trend seen in historical data. Likewise, PSW #9 had  $6.4 \text{ mg L}^{-1}$  nitrate-nitrogen which also agrees with historical findings. The third highest concentration was in PSW #7 at  $5.4 \text{ mg L}^{-1}$  which is one of the lowest concentrations seen in this well since 1994. Other inorganic results, as seen in Table 6, revealed elevated chloride, bromide, and sulfate concentrations in PSW #8 which were all more than two and a half standard deviations above each constituent's mean value for all wells. This exact same response was seen of PSW #8 in 1997 (Table 2). This indicates that results from PSW #8 continue to be an anomaly when compared to statistics for all nine PSWs, and supports a likely conclusion that the elevated ions in PSW #8 are from an anthropogenic source and are not naturally occurring. Furthermore, due to the concurrent presence of these three ions in addition to an elevated nitrate concentration (as well as elevated boron detected in 1997), it would seem the source of contamination is from sewage/septic or manure waste more than any other source

since numerous studies have used these specific ions to determine the influence of septic on water quality (Thurman et al., 1986; Vengosh & Pankratov, 1998; Hudak, 2003; Katz et al., 2011).

Interestingly, the stable isotope results (**Table 7**) which could confirm a septic (organic) signature if present, did not in any of the samples collected. While the average  $\delta^{15}\text{N}$  was just over 8 ‰ which falls into the range of the manure/septic (+4‰ to +25‰), there is not a strong enough signal to identify that as the nitrate source due to overlap with other source classes (**Figure 3**). Additionally, with the exception of three samples, all  $\delta^{18}\text{O}$  values point more toward microbe-produced soil N and a combination of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  results, at best, indicate that the nitrate is coming from a mixed source. It was however interesting that the highest  $\delta^{18}\text{O}$  values were measured in wells that also had the highest  $\text{NO}_3\text{-N}$  concentrations. This might indicate that nitrate from a past fertilizer spill is blending with nitrate from an organic source like leaking sewage lines, and resulting in an indeterminate overall signature.

Another interesting relationship exists when looking at the nitrate concentrations in PSWs #8, #9, and #10. It appears that nitrate concentrations in PSWs #9 and #10 have consistently been about 20% of those measured in PSW #8 over time. This makes sense for the ratio of PSW #10 to PSW #8 because of the fact that PSW #10 is about 0.85 miles down gradient (east) of PSW #8 which would allow for dilution, removal through plant uptake, or denitrification to occur. The relationship between PSW #9 and PSW #8 however does not benefit from the same explanation. Being only about 400 ft SSW of PSW #8, and not directly down gradient of it, it is not clear why PSW #9 nitrate concentrations seem to consistently be about 1/5 of those detected in PSW #8. It is plausible that the higher pumping yield in PSW #9, which is almost 2.5X that of PSW #8, creates a lower pressure which causes groundwater being flowing through PSW #8 to also move towards PSW #9. In this scenario a portion of the water pumped by PSW #9 could be coming from the vicinity of PSW #8 and it would make sense that the measured concentrations in PSW #9 would be a consistent fraction of those measured in PSW #8. However, the rising concentration trend seen in PSW #8 is not clearly reciprocated in PSW #9, so this explanation for the consistency in deviation of concentration between the two wells may not be adequate by itself.

In evaluating for the existence of a spatial relationship of agrichemical contamination to potential sources, the ACGPP looked at the distance and direction of each well from either the area where Cat Creek discharges to the Dakota Sandstone (CCD) and feeds storm water runoff into the aquifer, or from All Seasons Fertilizer Company (ASFC) - a local agrichemical dealer mentioned in the Source Water Protection Plan as a potential agrichemical contaminant source (Williams, 2013). For each location, each well was assigned a rank value, which assuming groundwater flow is easterly, followed the basis that wells closest to and/or aligned in a down-gradient position from the location, would result in the greatest chance of being impacted. Since  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  interpreted independently of one another for determining nitrate source is not reliable, the ratio of  $\delta^{15}\text{N}/\delta^{18}\text{O}$  is used. While not great for either location, the correlation of the ratio CCD is the strongest, especially the top six ranked PSWs which are #8, #9, #10, #7, #3, and #1 respectively (**Figure 4**). While this correlation could be showing the effect of microbial manipulation of the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  over time if these six locations were increasing in distance from but remaining directly down-gradient of CCD, that is not how they are arranged, and the exact reasoning behind why this correlation exists cannot be understood from these data alone. Since the first six points in the CCD correlation are scattered north and south of the CCD location, this likely only



confirms the point made earlier that nitrate discovered in these public supply wells is blending of organic and inorganic isotopic signatures likely coming from multiple sources.

### Pesticides

A total of nine different pesticide compounds were detected at quantifiable concentrations in five of nine wells sampled by the ACGPP in 2015 (**Table 8**). The most commonly detected pesticide compound was desethyl atrazine which is an atrazine degradation product. Atrazine is a non-selective herbicide used mostly on field corn but does have some roadside right-of-way (ROW) use on some product labels. Only Well #12 contained the parent compound atrazine at a quantifiable level of  $0.1 \mu\text{g L}^{-1}$  but five other wells had trace estimates. Deisopropyl atrazine can also be a degradation product of atrazine and was detected in three wells and estimated in another. “Estimated” means that the concentration is above the analytical method detection limit for an analyte but below the reporting limit for that analyte. The reporting limit is usually three to five times greater concentration than the method detection limit. All of these atrazine related compounds being detected or estimated indicate that atrazine at some point has contaminated groundwater resources, but no contaminant source can be determined from these results. Compared to results found by the ACGPP in 1997 where atrazine was detected in five of the nine municipal wells at concentrations ranging from  $0.3$  to  $3.9 \mu\text{g L}^{-1}$ , results from the 2015 indicate significant attenuation of the atrazine contamination has occurred. This decrease in the concentration of atrazine is consistent with ACGPP results from other areas of the state.

Bromacil and prometon are non-selective herbicides commonly used in roadway and railroad ROW vegetation control or beneath new concrete/asphalt installations. In 1997, one or both of these compounds were discovered in PSWs #8, #9, and #10 at concentrations ranging from  $0.1$  to  $1.3 \mu\text{g L}^{-1}$ . In 2015, four wells had estimated concentration evidence of prometon being present (but no quantifiable concentration) while bromacil was detected in PSW #8 and PSW #9 at  $3.94$  and  $0.98 \mu\text{g L}^{-1}$  respectively. Additional pesticide compounds detected in PSW #8 were diuron, imazapyr, norflurazon, picloram and tebuthiuron (all herbicide active ingredients commonly used in industrial areas where bare ground is desired). Of all the pesticides detected or estimated in PSW #8 in 2015, five are Restricted Use Pesticides (atrazine, bromacil, diuron, picloram, and prometon) that are very unlikely to be applied by residential consumers due to purchasing restrictions placed on products containing these active ingredients. Concentrations of these compounds were all less than  $0.4 \mu\text{g L}^{-1}$  except for a  $0.97 \mu\text{g L}^{-1}$  for imazapyr and  $2.6 \mu\text{g L}^{-1}$  for picloram. All told, PSW #8 accounted for nearly half of the 17 total pesticide detections discovered in five of the nine sampled wells.

Atrazine and picloram were the only compounds detected in 2015 that have an established U.S. EPA Maximum Contaminant Level (MCL) for drinking water of  $3.0$  and  $500 \mu\text{g L}^{-1}$ , respectively, but the detected concentrations for these two compounds were well below these levels. Concentrations of the other two detected compounds that have a U.S. EPA lifetime health advisory level (HALT), were also well below those levels. A detection of bromacil in PSW #8 at  $3.94 \mu\text{g L}^{-1}$  was the closest to its HALT, but even so was only a fraction of the  $70 \mu\text{g L}^{-1}$  level (**Table 8**).

## **Conclusions/Recommendations**

With PSW #8 being the only well with nitrate well above the U.S. EPA standard, having detections of eight pesticide compounds and estimates of three others, it is obvious that it should be, as is the case, the primary water quality concern for the City of Springfield. The presence of a multitude of agrichemical compounds and the presence of an indeterminate isotopic signature for the nitrate ion, suggests that agrichemical contamination is coming from multiple sources. With most of the detected pesticide compounds being pesticides that are commonly used for railroad or roadside ROW applications, it is likely those application areas are a source, but to what extent is not known. What is known is that wherever pesticides are applied to kill all vegetation there is not concurrent use of a fertilizer intended to promote vegetative growth, so the nitrate contamination is likely coming from a separate source(s). While possible that resident properties with septic systems, or even the city's sewage infrastructure, could contribute some of the detected pesticide compounds along with nitrate due to filling or cleaning out of application equipment, or because of spills near septic leach beds, this is not likely since the vast majority of the pesticides detected are unlikely to be used by residential consumers.

Given that Springfield currently is only providing water for about 75% of its 1,200 tap capacity and given that PSW #8 accounts for about 7% of the city's total adjudicated water right of approximately 3,800 ac-ft per year, and <4% of the potential pumping yield (as measured by Mike Ingle in May, 2015), it is the recommendation of the ACGPP that PSW #8 be decommissioned as a drinking water supply. The well could still be utilized for other purposes so it doesn't need to be abandoned. While there appears to be a consistent relationship of the nitrate concentration in PSWs #9 and #10 when compared to PSW #8, the ACGPP's sampling efforts did not provide any evidence that suggests either of those two wells could be significantly impacted in the future; however, the full extent of the nitrate source impacting PSW #8 is unknown. Therefore, the ACGPP also recommends that further testing of sediment, storm water runoff, and groundwater will be necessary if the City of Springfield desires to hone in on the nitrate contamination source(s).

To evaluate the scenario of Cat Creek discharging water and consequently any dissolved contaminants into the Dakota Sandstone during storm events, multiple sampling approaches could take place. Groundwater samples could be collected from any existing domestic, stock, or irrigation wells that are completed in roughly the same portion of the Dakota Sandstone as is PSW #8, but to the west of where storm water runoff enters Cat Creek. If similar contaminants and/or concentrations are measured west of Cat Creek as those in PSW #8, then the hydraulic connection may not be a primary contributor to contamination. A second approach is to collect surface water samples of runoff during or shortly after adequate precipitation events at multiple points along the drainage channel, which according to imagery in Google Earth™ looks to originate up-gradient of both suspected contaminant sources and flows through or near those sources before discharging into Cat Creek (see Figure 1). These samples should be analyzed and evaluated for similarity to contamination found in PSW #8. Due to results discovered by the ACGPP in 2015, it is plausible that runoff is a key source of pesticide contamination to the Dakota Sandstone, but not likely for nitrate.

Evaluation of the groundwater age might also provide evidence as to the existence of this hydraulic connection since groundwater that deep percolates over time into the Dakota Sandstone, which is actually a stratigraphy of sandstone with multiple shale lenses, should easily be hundreds of years old while water recharging horizontally into the Dakota Sandstone from Cat Creek would be much younger.

Collection of soil/sediment samples may provide more evidence of where contamination is coming from. Sediment samples collected from various locations within the drainage channel that empties into Cat Creek, if determined to have the same contaminants found in the Dakota Sandstone accessed by PSWs #7, #8, and #9, could confirm a storm water influence. However, additional soil core samples should be collected from outside the drainage channel and in strategically placed locations up- and down-gradient of suspected contaminant sources to determine if a spill may be to blame for contaminating groundwater. Soil cores drilled ten or more feet (below the root-zone of any local vegetation) and analyzed for residual nitrate concentrations as well as  $^{15}\text{N}$  &  $^{18}\text{O}$  analysis could assist in determining the existence of a nitrate contamination plume. Remembering that the stable isotope signature found by the ACGPP in 2015 was indeterminate in all nine PSWs, likely because of blending of organic and inorganic sources, it may be useful to try and acquire groundwater samples in strategic locations that might help split out each suspected nitrate source. This would likely require the installation of several monitoring wells into the Dakota Sandstone at an average depth of 140ft, which would undoubtedly be the most costly next step that could be taken by the City of Springfield.

## **References**

- Bohlke J., R. Smith and J. Hannon. 2007. ***Isotopic analysis of N and O in nitrite and nitrate by sequential selective bacterial reduction to N<sub>2</sub>O***. Anal. Chem. 79(15): 5888-95.
- Casciotti K., D. Sigman, M. Hastings, J. Bohlke and A. Hilkert. 2002. ***Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method***. Anal. Chem. 74(19): 4905-12.
- Craig, H. 1961. ***Isotopic variations in meteoric waters***. Science, 133: 1702-1703
- Hudak, P. 2003. ***Chloride/bromide ratios in leachate derived from farm-animal waste***. Env. Poll. 121: 23-25.
- Junk, G. and H. Svec. 1958. ***The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources***. Geochim. Cosmochim. Acta, 14, 234-243.
- Katz, B., S. Eberts, L. Kauffman. 2011. ***Using Cl/Br ratios and other indicators to assess potential impacts on groundwater quality from septic systems: A review and examples from principal aquifers in the United States***. J. Hyd. 397: 151-166.

McLaughlin, T. 1954. ***Ground-Water Resources of Baca County, Colorado***. Geological Survey Water-Supply Paper 1256.

Sigman D, K. Casciotti, M. Andreani, C. Barford, M. Galanter and J. Bohlke. 2001. ***A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater***. Anal. Chem. 73(17): 4145-53.

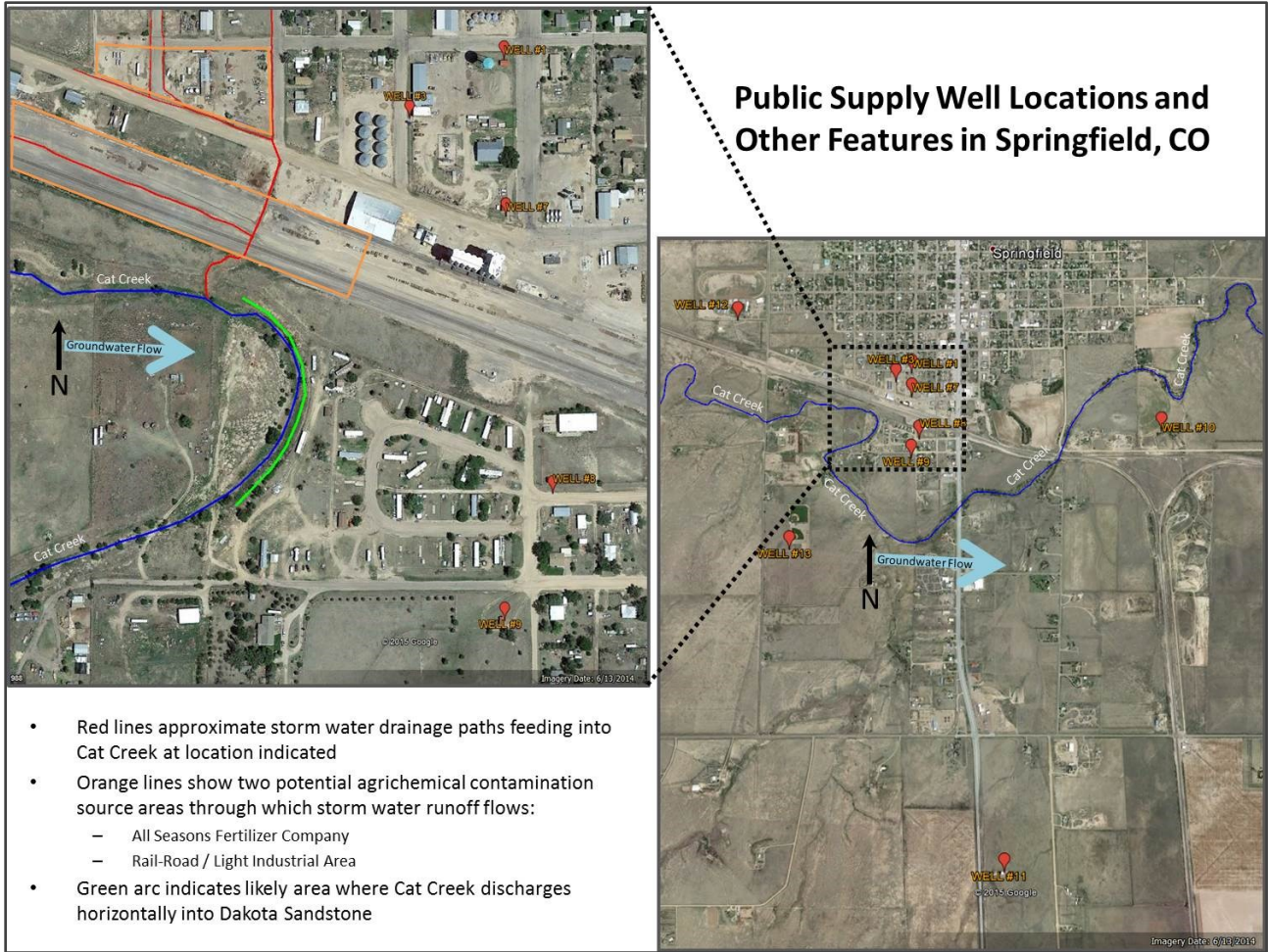
Thurman, E.M., L. Barber Jr and D. LeBlanc. 1986. ***Movement and fate of detergents in groundwater: a field study***. J. Contam. Hyd. 1: 143-161.

Vengosh, A. and I. Pankratov. 1998. ***Chloride/Bromide and Chloride/Fluoride ratios of domestic sewage effluents and associated contaminated ground water***. Groundwater 36(5): 815-824

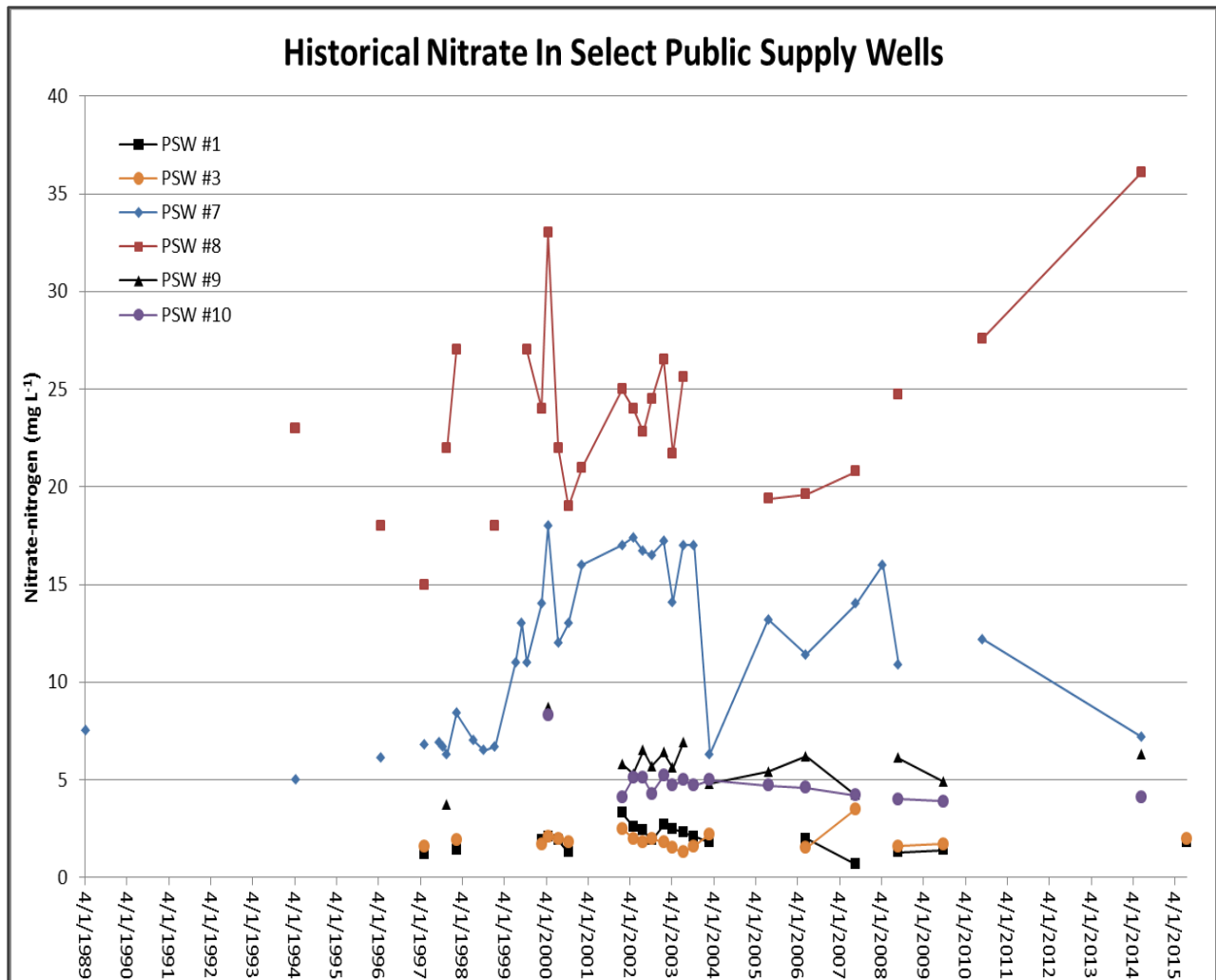
Xue, D., J. Botte, B. De Baets, F. Accoe, A. Nestler, P. Taylor, O. Van Cleemput, M. Berglund, P. Boeckx. 2009. ***Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater***. Water Res. 43: 1159-1170.

Williams, C. 2013. ***Town of Springfield Source Water Protection Plan***.

## **FIGURES & TABLES**

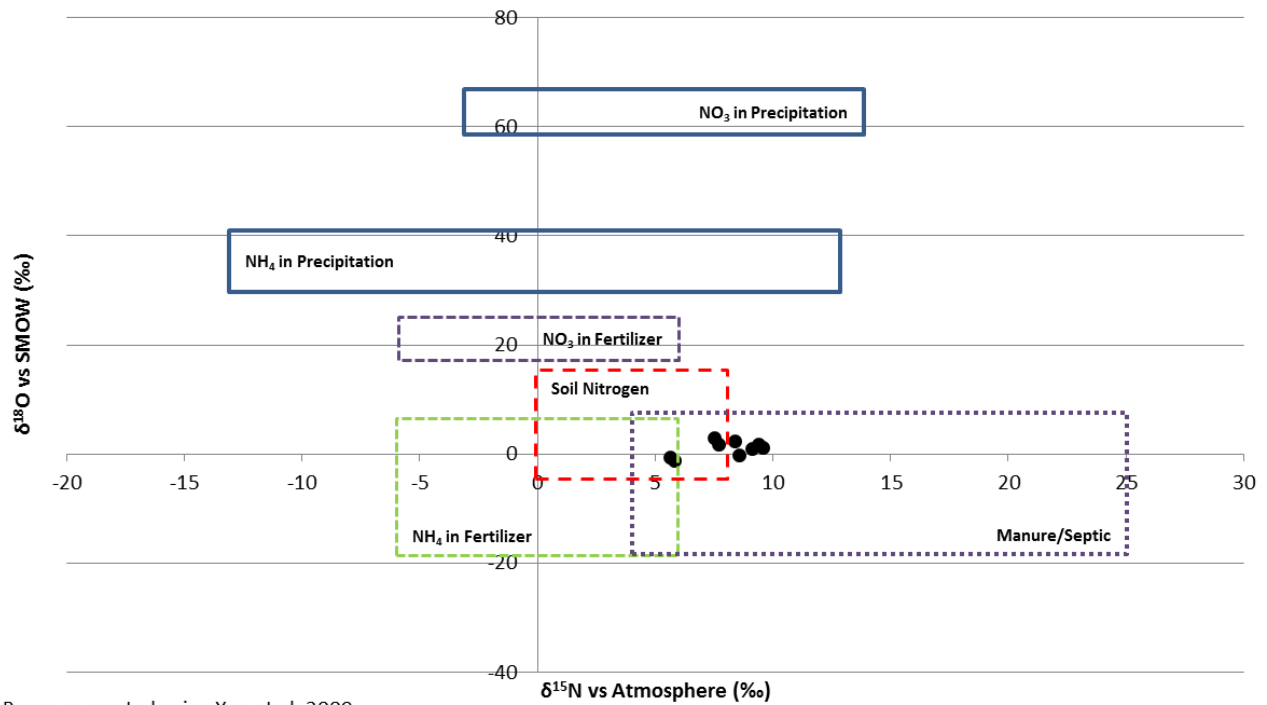


**Figure 1** Map on right shows locations of public supply wells in Springfield, CO sampled in May, 2015. Inset, on left, shows approximate storm water drainage paths, potential agricultural contamination source areas through which storm water likely flows before emptying into Cat Creek, and likely area where Cat Creek discharges horizontally into Dakota Sandstone aquifer up-gradient of Wells #8 and #9.



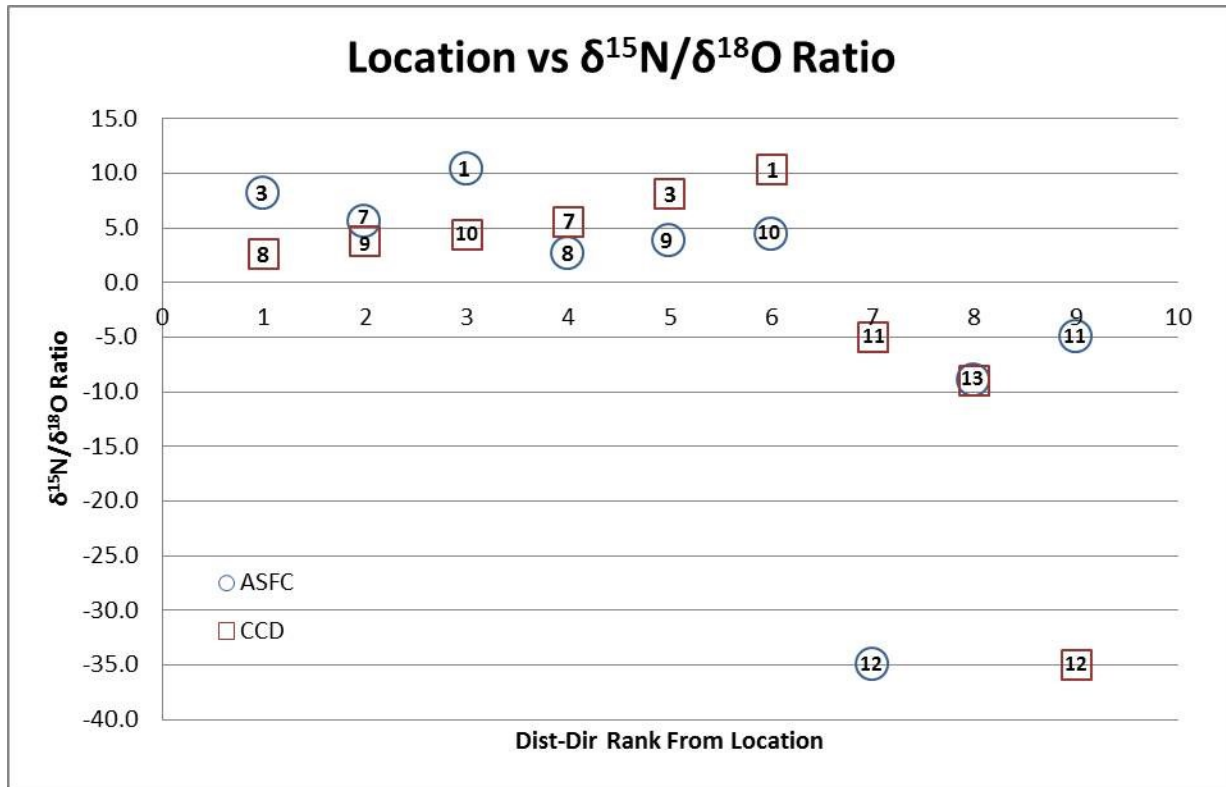
**Figure 2** Line graph showing nitrate-nitrogen concentration measured over time by City of Springfield in select public supply wells (PSW) sampled over the period 1989-2014

### $\delta^{15}\text{N}$ vs $\delta^{18}\text{O}$ Springfield PSWs in May 2015



**Figure 3** Stable isotope scatter plot showing nine groundwater samples collected from public supply wells (PSW) in Springfield, CO in May, 2015. This graph shows where the data points fall amongst various isotopic signature source classes. The boxes and their extents are according to the cited reference.





**Figure 4** Comparison of ranked location to the stable isotope ratio of  $\delta^{15}\text{N}/\delta^{18}\text{O}$  to evaluate spatial relationship between two potential nitrate contamination pathways: **ASFC** is All-Seasons Fertilizer Company and **CCD** Cat Creek Discharge into the Dakota Sandstone aquifer. For each location's dataset, the symbols are aligned with the rank on the X-axis (#1-#9) and the number inside the symbol indicates the public supply well identification number used by City of Springfield, CO.

Historical Nitrate-nitrogen Concentrations						
Statistic	PSW #1	PSW #3	PSW #7	PSW #8	PSW #9	PSW #10
Average	1.9	1.9	11.6	23.4	5.9	4.7
STD	0.6	0.5	4.3	4.7	1.2	1.0
Median	1.9	1.8	12.1	23.0	5.8	4.7
Minimum	0.7	1.3	5.0	12.0	3.7	3.5
Maximum	3.3	3.5	18.0	36.1	8.7	8.3
N	33	33	35	33	25	21

**Table 1.** Nitrate-nitrogen statistics for select public supply wells (PSW) in Springfield, CO as measured by city personnel from 1989-2014. **STD** is standard deviation; **N** is the number of results reported over the time period. All values are in  $\text{mg L}^{-1}$ .

Groundwater Chemistry of Springfield Public Supply Wells Sampled in November 1997																
Wellcode	PSW #	Water T °C	ECS Hardness $\mu\text{S cm}^{-1}$	TDS	HCO <sub>3</sub>	Ca	Cl	B	K	Mg	Na NO <sub>3</sub> -N	SO <sub>4</sub>	Atrazine	Bromacil	Prometon	
HP-117	1	15.3	957	451	893	160.4	115.0	23.8	0.27	4.8	40.0	81.7	1.4	465.4	BDL	BDL
HP-116	3	12.3	983	526	881	164.3	145.0	21.1	0.22	4.4	40.0	68.2	1.8	435.6	BDL	BDL
HP-118	7	14.8	1263	590	1130	161.2	170.6	66.1	0.31	4.5	40.0	93.7	6.9	586.9	2.8	BDL
HP-115	8	15.0	3000	1360	2860	260.1	329.0	207.7	1.33	5.5	131.0	360.1	25.0	1540.2	3.9	0.8
HP-114	9	15.2	838	397	725	147.2	118.6	23.3	0.21	3.8	24.5	49.8	4.0	354.0	2.4	0.5
HP-119	10	13.4	1214	652	1173	203.5	187.0	2.4	0.38	4.0	45.1	82.9	5.5	641.8	1.3	BDL
HP-113	11	14.4	700	411	605	112.1	129.2	31.8	0.07	4.0	21.5	15.5	4.2	286.5	BDL	BDL
HP-111	12	15.3	1120	560	991	171.3	146.8	19.7	0.25	4.3	47.1	77.6	1.4	522.5	0.3	BDL
HP-112	13	12.1	364	208	352	129.0	69.4	4.2	0.06	3.1	8.4	9.7	2.8	125.1	BDL	BDL

**Table 2.** Groundwater chemistry results for samples collected by Colorado Department of Agriculture (CDA) in November 1997 from nine public supply wells in Springfield, CO. **Wellcode** corresponds to CDA's identification of each public supply well (**PSW**). **Water T** is water temperature. **ECS** is specific conductance. **Hardness** is measured as CaCO<sub>3</sub>. **TDS** is total dissolved solids. **BDL** is below detection limit.

Sampling Event Timing					
PSW #	Date Sampled	Time Pump Start	Time Purge Start	Time Stabilized	Time Sampled
1	5/27/2015	7:00:00	11:40:00	11:54:00	11:57:00
3	5/27/2015	11:15:00	12:29:00	12:44:00	12:47:00
7	5/27/2015	11:10:00	13:17:00	13:29:00	13:45:00
8	5/27/2015	14:00:00	15:05:00	15:14:00	15:17:00
9	5/28/2015	7:46:00	8:09:00	8:33:00	8:34:00
10	5/28/2015	10:09:00	10:11:00	10:44:00	10:45:00
11	5/27/2015	14:10:00	15:59:00	16:11:00	16:14:00
12	5/27/2015	13:48:00	14:06:00	14:27:00	14:30:00
13	5/28/2015	9:06:15	9:08:00	9:29:00	9:45:00

**Table 3.** Recorded sample event timing for the nine public supply wells sampled in the city of Springfield, CO in May, 2015. **Time Pump Start** represents the time when city personnel turned on the pump; **Time Purge Start** represents the time when CDA personnel began measuring purging criteria in the discharge; **Time Stabilized** represents the time when produced groundwater had met stabilization requirements and was ready for sampling.

Sampling Event Pumping Logistics							
PSW #	Recent SWL (ft TOC)	Well Depth (ft)	Case Dia (in)	Case Vol (gal)	Well Yield (gpm)	Total Purge Time (min)	Case Vol Purged (#)
1	74	108	10	138	97	297	209
3	75	128	10	214	81	92	35
7	72	138	16	693	50	155	11
8	67	129	16	643	70	77	8
9	66	127	16	632	167	48	13
10	40	122	16	848	1,000	36	42
11	210	360	16	1,570	106	124	8
12	81	115	7	58	40	42	29
13	104	210	16	1,112	585	39	20

**Table 4.** Purging logistics for sampling of nine public supply wells in the city of Springfield, CO in May, 2015. **Recent SWL** represents the static water level measured in May, 2015 by city personnel; **Case Dia** is the well casing diameter; **Case Vol** is the volume of water in the casing between the bottom of the well and the static water level; **Well Yield** is the pumping yield measured in May, 2015 by city personnel; **Total Purge Time** is the total elapsed time between when the pump was initiated and the purging criteria had stabilized; **Case Vol Purged** is the total number of casing volumes purged from the well over the total purge time period.

Sampling Event Stabilized Purging Parameters						
PSW #	Water T (°C)	pH	ECs ( $\mu\text{S cm}^{-1}$ )	ORP (mV)	DO ( $\text{mg L}^{-1}$ )	TDS ( $\text{g L}^{-1}$ )
1	15.8	6.84	1,334	6.8	3.5	0.89
3	15.4	6.95	1,131	19.7	2.3	0.76
7	15.4	7.08	1,067	6.1	4.3	0.72
8	15.4	7.28	3,221	3.7	5.8	2.16
9	15.1	7.08	881	(1.2)	5.6	0.59
10	14.9	7.20	1,196	2.4	5.8	0.80
11	15.7	7.78	361	(3.4)	6.4	0.24
12	15.8	6.91	1,493	51.4	3.2	1.00
13	15.0	7.47	437	15.8	7.6	0.29

**Table 5.** Final stabilized measurements for purging parameters utilized to indicate adequate purging of nine public supply wells in Springfield, CO in May, 2015. **Water T** is water temperature; **ECs** is specific conductance; **ORP** is oxidation-reduction potential; **DO** is dissolved oxygen; **TDS** is total dissolved solids

Measured Anion Concentrations in Springfield Public Supply Wells					
PSW #	F	Cl	Br	NO <sub>3</sub> -N	SO <sub>4</sub>
1	1.4	38	0.46	1.9	536
3	1.4	23	0.30	2.2	427
7	0.7	32	0.36	5.4	367
8	0.7	122	1.11	39.2	1486
9	0.6	23	0.24	6.4	271
10	0.9	31	0.29	4.4	421
11	0.5	7	0.07	2.5	44
12	1.4	28	0.35	3.1	652
13	0.4	10	0.11	3.2	74

**Table 6.** Concentrations of inorganic nutrient anions measured in groundwater samples collected from nine public supply wells in Springfield, CO and analyzed at CO Dept. of Agriculture's Biochemistry Lab in May, 2015. All concentrations are in units of  $\text{mg L}^{-1}$ . Dissolved orthophosphate and nitrite-nitrogen were also measured but all results were below the detection limit of  $0.05 \text{ mg L}^{-1}$ .

Stable Isotope Results		
PSW #	$\delta^{15}\text{N}$ vs. Air	$\delta^{18}\text{O}$ vs. V-SMOW
1	9.15	0.88
3	9.57	1.18
7	9.38	1.68
8	7.51	2.89
9	8.41	2.23
10	7.72	1.77
11	5.86	-1.16
12	8.59	-0.25
13	5.66	-0.63

**Table 7.**  $^{15}\text{N}$  and  $^{18}\text{O}$  isotope results measured in nine public supply well (PSW) samples collected in Springfield, CO in May, 2015. **Air** indicates the standard for comparing the  $^{15}\text{N}$  results to is the concentration of  $^{15}\text{N}$  in atmospheric air. **V-SMOW** is the Vienna Standard Mean Ocean Water standard used to compare  $^{18}\text{O}$  results to. Values are in units of ‰ which represents the difference ( $\delta$ ) between the sample concentration and the concentration of the recognized standard for each isotope.

Pesticide Results for Springfield Public Supply Wells												
Pesticide	Standard	PSW #1	PSW #3	PSW #7	PSW #8	PSW #9	PSW #10	PSW #11	PSW #12	PSW #13		
Atrazine (0.10)	EPA MCL 3.0	BDL-E	BDL	BDL-E	BDL-E	BDL-E	BDL-E	BDL	BDL	BDL	BDL	0.10 BDL
Bromacil (0.20)	EPA HALT 70	BDL	BDL	BDL	3.94	0.98	BDL	BDL	BDL	BDL	BDL	BDL
Desethyl atrazine (0.10)	None	BDL-E	BDL-E	0.21	0.19	0.19	0.14	BDL	BDL-E	BDL-E	BDL-E	BDL-E
Desisopropyl atrazine (0.10)	None	BDL	BDL	0.10	0.16	BDL-E	0.11	BDL	BDL	BDL	BDL	BDL
Diuron (0.10)	None	BDL	BDL	BDL	0.16	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Hexazinone (0.10)	None	BDL	BDL	BDL	BDL	BDL	BDL-E	BDL	BDL	BDL	BDL	BDL
Imazapyr (0.10)	None	BDL	BDL	BDL	0.97	BDL-E	BDL-E	BDL	BDL	BDL	BDL	BDL
Metsulfuron-methyl (0.10)	None	BDL	BDL	BDL	BDL-E	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Norflurazon (0.20)	None	BDL	BDL	BDL	0.38	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Picloram (0.10)	EPA MCL 500	BDL	BDL	BDL	2.60	0.19	BDL	BDL	BDL	BDL	0.15	BDL
Prometon (0.10)	None	BDL	BDL	BDL	BDL-E	BDL-E	BDL-E	BDL	BDL-E	BDL	BDL-E	BDL
Tebuthiuron (0.10)	EPA HALT 500	BDL	BDL	BDL	0.27	BDL-E	BDL-E	BDL	BDL	BDL	BDL	BDL

**Table 8.** Pesticide analysis results for nine public supply wells (PSW) sampled in Springfield, CO in May, 2015 and analyzed at CO Dept. of Agriculture's Biochemistry Laboratory in Denver, CO. **Standard** indicates if the U.S. Environmental Protection Agency (EPA) has established a maximum contaminant level (MCL) or life-time health advisory level (HALT) in drinking water for a pesticide; **BDL** is below detection limit; **BDL-E** represents that the pesticide had some estimate concentration evidence of presence in the sample. Detection limit for each pesticide compound is in parentheses next to pesticide name. All values are in concentration units of  $\mu\text{g L}^{-1}$ .