

Water Quality Monitoring Survey Results Big Walnut and Alum Creeks Columbus Community Bill of Rights



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Table of Acronyms

ODNR	Ohio Department of Natural Resources
SDWA	(Federal) Safe Drinking Water Act
TMDL	Total Maximum Daily Load
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WQS	Water Quality Standards
WQX	EPA’s National Water Quality Data Exchange

Table of Chemical Abbreviations

Chemical abbreviation	Full name
Li	lithium
Na	sodium
Ca	calcium
Mg	magnesium
Ba	barium
Br	bromine
Cl	chloride
Sr	strontium
SO ₄	sulfate

Motivation

Oil and gas companies have been granted permits to inject toxic, radioactive fracking waste into Class II injection wells within Columbus Metro watersheds, which provide drinking water for more than 1.2 million residents of the greater Columbus area. There are currently 13 injection wells upstream of Columbus metro located in Delaware and Morrow counties which have been injected with millions of gallons of oil and gas waste, euphemistically called “brine”. This waste can contain more than 1,000 different chemicals, of which many are carcinogens, neurotoxins, and endocrine disruptors, and also contains radium 226 and 228, in addition to other radionuclides.

The immediate goal of this water testing initiative is to motivate the need for long-term water quality monitoring of both groundwater and surface water by the City of Columbus near the injection wells.

Columbus Community Bill of Rights (CCBOR) was formed in 2014 by a group of concerned citizens in order to protect their water from oil and gas industrial harms. CCBOR is a grassroots, all-volunteer group that believes all people have inalienable rights to safe water, soil, and air, as well as the right of local self-governance to prohibit substances and activities that would violate those rights. CCBOR also recognizes the rights of ecosystems and natural communities within the city to be free from such harmful activities. CCBOR has led four ballot initiative campaigns to put a Community Bill of Rights on the ballot to ensure that Columbus citizens have these rights. Throughout their initiative campaigns more than 50,000 Columbus residents have signed their petitions.

Project Management & Personnel

Carolyn Harding reached out to Thriving Earth Exchange (TEX), which is a branch of American Geophysical Union (AGU) and obtained a grant with this national non-profit organization that pairs concerned citizen groups with established scientists to initiate citizen science projects. Bill Lyons and Kathy McGlone, along with Carolyn Harding, made

up the citizen science team from CCBOR. TEX connected us with Megan Duffy, a biogeochemist and PhD candidate at the University of Washington School of Oceanography in Seattle as our Project Manager. The citizen science team and Megan Duffy met virtually on a weekly basis. CCBOR reached out to Dr. Chris Spiese, Associate Professor of Chemistry, Ohio Northern University, who designed the site locations for the water monitoring, and to Dr. John Stolz, Director of the Center for Environmental Research and Education and Professor of Environmental Microbiology, Duquesne University, who provided quarterly detailed analysis of water samples. Bi-weekly data collection was performed by various members of CCBOR. Karen L. Knee, associate professor in the Environmental Science department at American University in Washington, DC, advised our team and helped with data analysis and presentation.

Study Area & Methodologies

General Types of Data Collected

General chemical water quality data were collected biweekly between August 2021 and August 2022. These parameters included *in situ* water temperature, salinity, total dissolved solids (TDS) and conductivity by CCBOR. In addition quarterly analyses of 1) major anions (chloride, bromide, sulfate, etc.) and cations (sodium, potassium, magnesium, etc.); 2) dissolved metals (iron, copper, lead, arsenic, etc.) and 3) volatile organic compounds (VOCs, including methane and ethane) were conducted on water samples which were collected and transported by members of Dr. John Stolz's research group.

Sampling Equipment & Methods

CCBOR obtained Extech EC150 water conductivity and total dissolved solids meters for bi-weekly *in situ* water testing. Measurements were recorded on uniform data sheets and then transferred to a spreadsheet managed by Bill Lyons. Also recorded was the previous 48-hour rainfall near each site and water temperature. The bi-weekly data collection took approximately four hours.

On site measurements by John Stolz's group for temperature, dissolved oxygen, pH, and specific conductivity ($\mu\text{S}/\text{cm}$) were made using a YSI Professional Plus handheld multimeter with Quatro cable (Fondriest Environmental Products, Fairborn OH). Total dissolved solids were calculated from the specific conductivity (factor of 0.65). The YSI multimeter was calibrated prior to the field work.

Samples for anion analysis were collected in a sterile 1 L French square bottle (VWR International, Bridgeport, NJ). Samples for cation analysis were collected in a 60 mL glass bottle (VWR International, Bridgeport, NJ) with 8-10 drops of nitric acid (10 M HNO_3). Samples for light hydrocarbon analyses were taken in 40 ml amber butyl septum bottles, making sure no air bubbles were trapped. Samples were stored in coolers with ice packs while in the field, then kept at 4 °C in the Duquesne University lab until analysis was completed.

Analysis for the light hydrocarbons, methane, ethane, ethene, and propane, was done by Gas Chromatography and Flame Ionization Detection using the Shimadzu Nexis GC-2030 AF with LabSolutions software (Columbia, MD, USA) following a modified version of PA DEP procedure 9243.

Anions (Cl^- , Br^- , NO_3^- , NO_2^- , PO_3^- , SO_4^-) were determined by EPA method 300.1, using a Dionex ICS-1100 equipped with DS6 heated conductivity cell and DAD-3000 UltiMate 3000 Diode Array programmable UV/VIS detector (Thermo Scientific, Sunnyvale CA). Anions were separated using the Dionex IonPac AS22A Carbonate Eluent Anion-Exchange Column, 2x250 mm, 6.5- μm particle diameter, with a Dionex IonPac AG22 Guard Column (2x50 mm) coupled to an anion self-regenerating Dionex ASRS 300 suppressor (Thermo Scientific, Sunnyvale CA). The limit of detection for bromide with the UV detector is 0.035 mg/L.

Cations were determined by EPA method 200.7, performed on a Perkin Elmer NexION 300x ICP-MS with Perkin Elmer S10 Autosampler and the NexION 300x ICP-MS software.

Quality Control/Quality Assurance

All CCBOR meters were calibrated on the day of use and were rinsed with distilled water before each testing. Regular blanks were analyzed to eliminate carryover. Non-detected data were recorded as “below detection limits” or “not determined”. Field blanks and field duplicates were collected and analyzed.

Permit Requirements

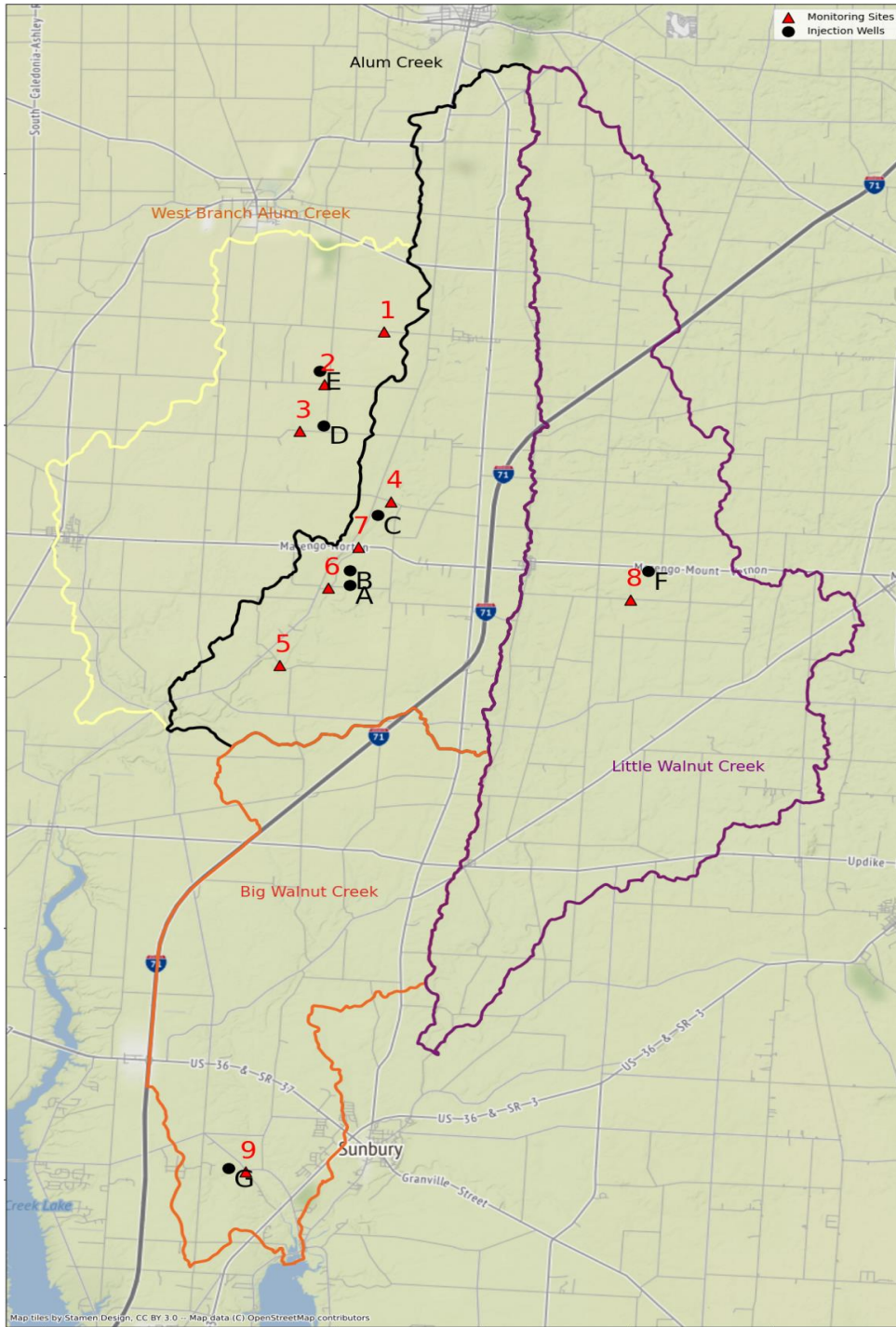


Figure 1 CCBOR study sites and injection wells

No collection permits were required for this study plan as no invertebrate or vertebrate samples were collected. All monitoring sites were accessed at road crossings. The Morrow

County engineer was contacted by phone and email about the project but CCBOR received no response.

Results and Analysis

Nine monitoring sites were selected by Dr. Christopher Spiese at Ohio Northern University. Injection well location and injection data were obtained from the ODNR Well Database for the most recent injection volumes available (Quarter 4, 2019). Well depths were not recorded in the database but should be considered in the evaluation of potential groundwater contamination.

Table 1 Class II injection wells within study area.

Well Lable (A-G)	Well ID # API10	Owner company name	Latitude (N)	Longitude (W)	County	Depth (ft)	Total injected volume through 2022 (gal)
A	3411721444	Maram Energy Inc.	40.39585606	-82.8653692	Morrow	3195	29,347,878
B	3411723020	Maram Energy Co.	40.39984365	-82.86548962	Morrow	3200	14,050,218
C	3411721901	Woodcock III George W DBA West Drilling Co	40.41496033	-82.85685507	Morrow	3304	92,352,960
D	3411722109	Fishburn Producing, Inc.	40.43933696	-82.87351156	Morrow	3150	29,569,428
E	3411722829	Fishburn Producing, Inc.	40.45415583	-82.87467276	Morrow	3050	46,010,622
F	3411723388	Fishburn Producing, Inc.	40.39961353	-82.77338553	Morrow	3986	224,381,766
G	3404120160	Patricia Harman	40.2370729	-82.90278834	Delaware	3010	0

Table 2 CCBOR water monitoring site coordinates.

Site	Latitude	Longitude	Watershed	Location to well
1	40.464786	-82.854767	West Branch Alum Creek	Upstream of Wells
2	40.45042	-82.87316	West Branch Alum Creek	Downstream 1 of Well E
3	40.43778	-82.88076	West Branch Alum Creek	Downstream 2 of Wells E,D
4	40.418595	-82.852719	Headwaters Alum Creek	Upstream
5	40.374121	-82.887075	Headwaters Alum Creek	Downstream 3 of Wells C,B,A
6	40.3952	-82.87199	Headwaters Alum Creek	Downstream 2 of Wells C,B
7	40.40617	-82.86286	Headwaters Alum Creek	Downstream 1 of Well C
8	40.39195	-82.778737	Headwaters Big Walnut Creek	Downstream of Well F
9	40.23605	-82.89748	Little Walnut Creek	Downstream of Well G

Table 3 Conductivity analysis at CCBOR sites.

Location	Mean (uS/cm)	Minimum (uS/cm)	Maximum (uS/cm)	Standard deviation (uS/cm)
Site 1: Upstream West Branch Alum Creek	637	217	1365	291
Site 2: Downstream 1 West Branch Alum Creek	668	272	969	216
Site 3: Downstream 2 West Branch Alum Creek	337	76	481	118
Site 4: Upstream Alum Creek	317	94	432	83
Site 5: Downstream Alum Creek 3	320	148	465	75
Site 6: Downstream Alum Creek 2	308	107	455	83
Site 7: Downstream Alum Creek 1	323	94	593	101
Site 8: Downstream Big Walnut Creek	374	182	653	113
Site 9: Downstream Little Walnut Creek	1107	275	1696	445

Drainage 1: West Branch Alum Creek

Three sites were monitored in the West Branch of Alum Creek, also called 'Turkey Run'. Site 1 is upstream of two Class II injection wells. Sites 2 and 3 were each immediately downstream of one of the injection wells.

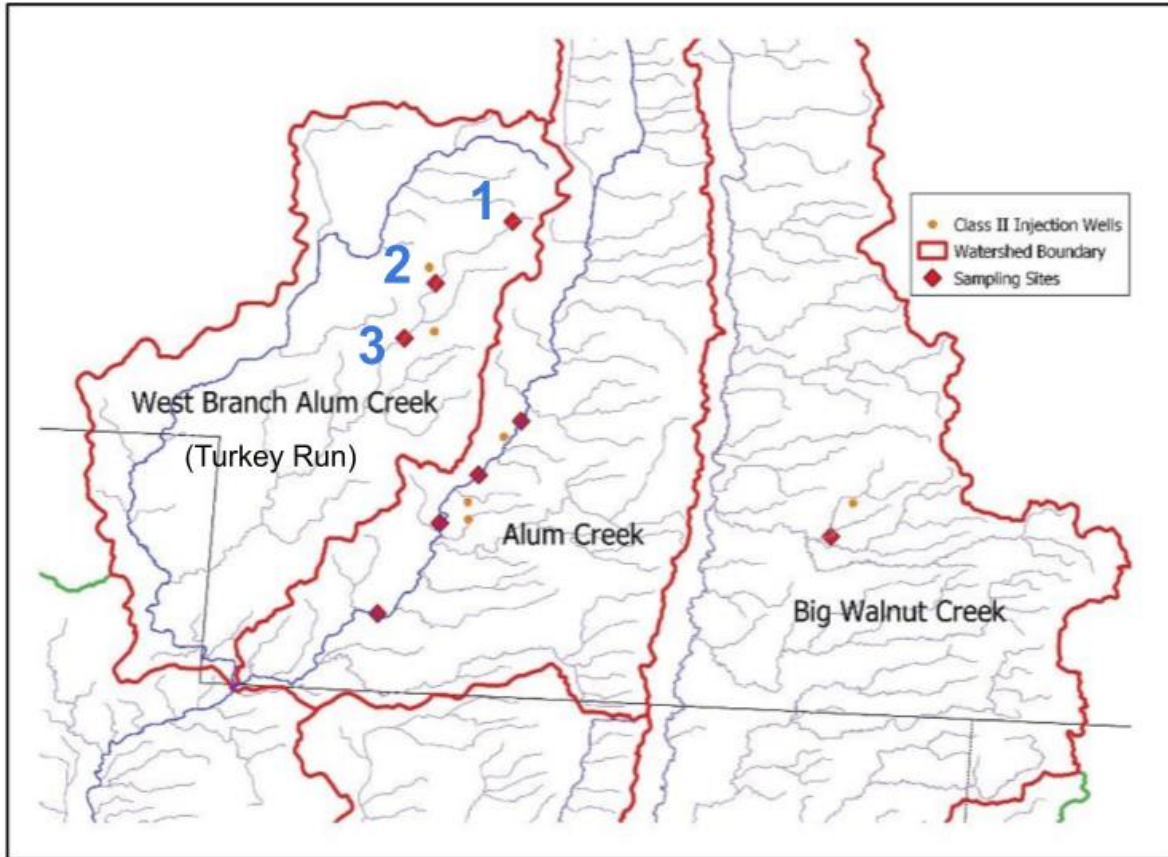


Figure 2 Site map of West Branch Alum Creek.

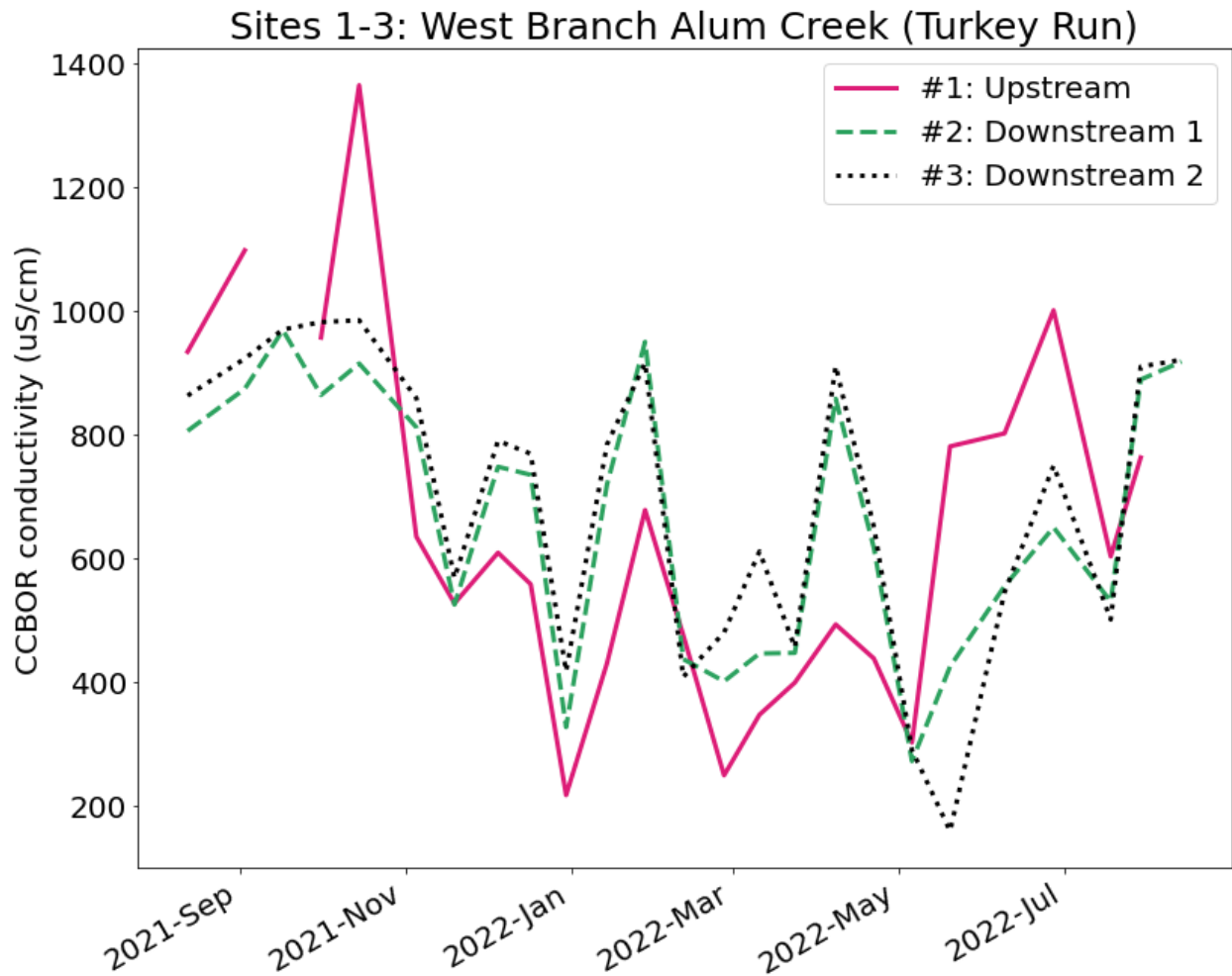


Figure 3 Conductivity at West Branch Alum Creek (Turkey Run).

From August 2021 to August 2022. The upstream, site 1 line is broken near the beginning and at the end of its plot because there was no water at this site for the corresponding data collection dates.

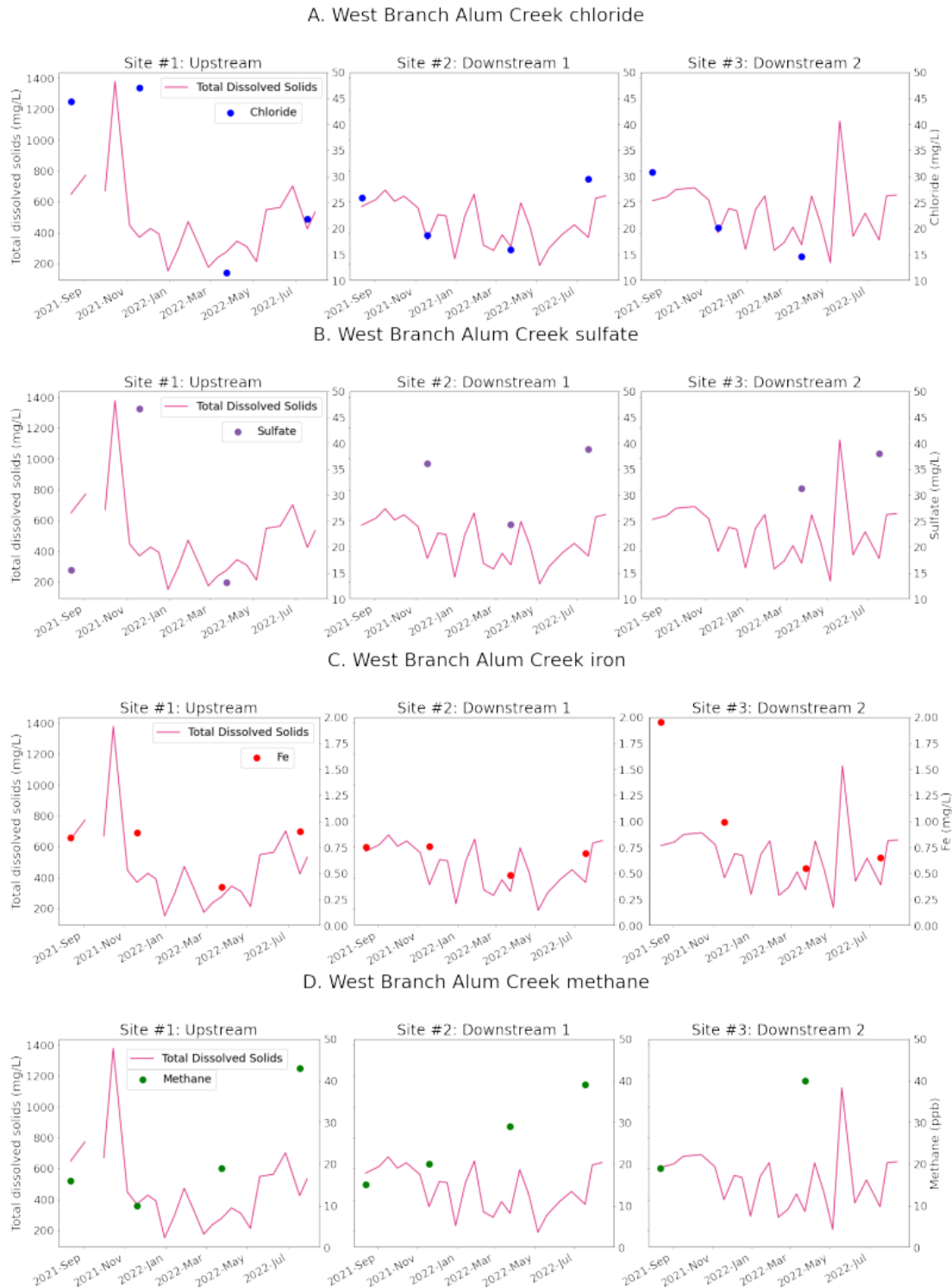


Figure 4 West Branch Alum Creek water quality.

Plots show chloride (A), sulfate (B), iron (C), and methane (D) plotted with biweekly total dissolved solids at West Branch Alum Creek (Turkey Run) for sites 1-3 from August 2021 to

August 2022. If four measurements don't appear on a graph, that parameter was under the detection limit. At the West Branch Alum Creek sites, no measurements were above EPA Secondary Maximum Contaminant Levels (SMCL) in drinking water.

Drainage 2: Alum Creek

Four sites were monitored in the main branch of Alum Creek. Site 4 is upstream of three Class II injection wells. Sites 7 is immediately downstream of one well and site 6 is further downstream additionally to two additional wells. Site 5 is the furthest downstream in the watershed.

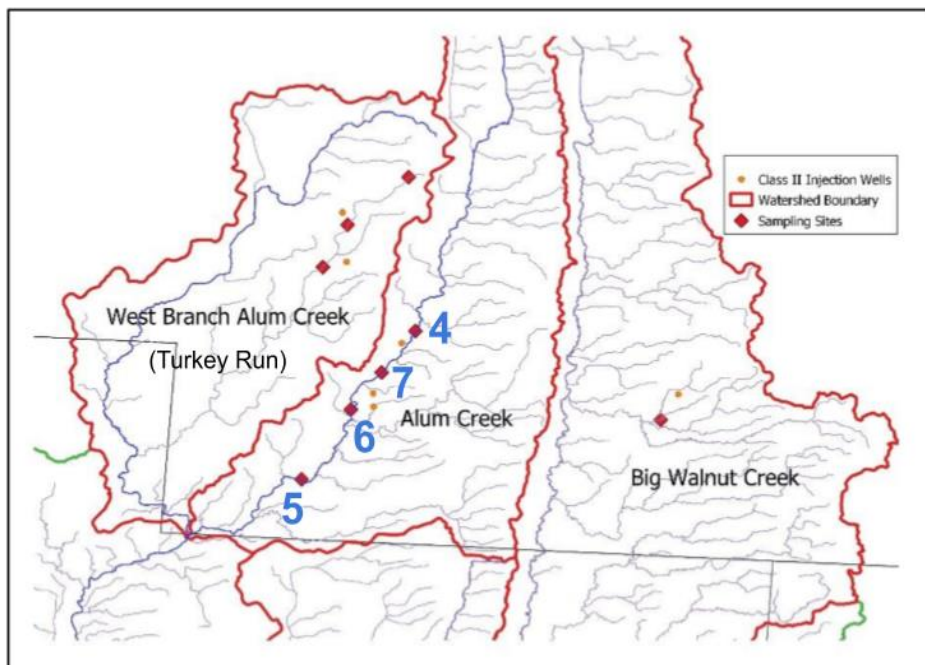


Figure 5 Site map of Alum Creek.

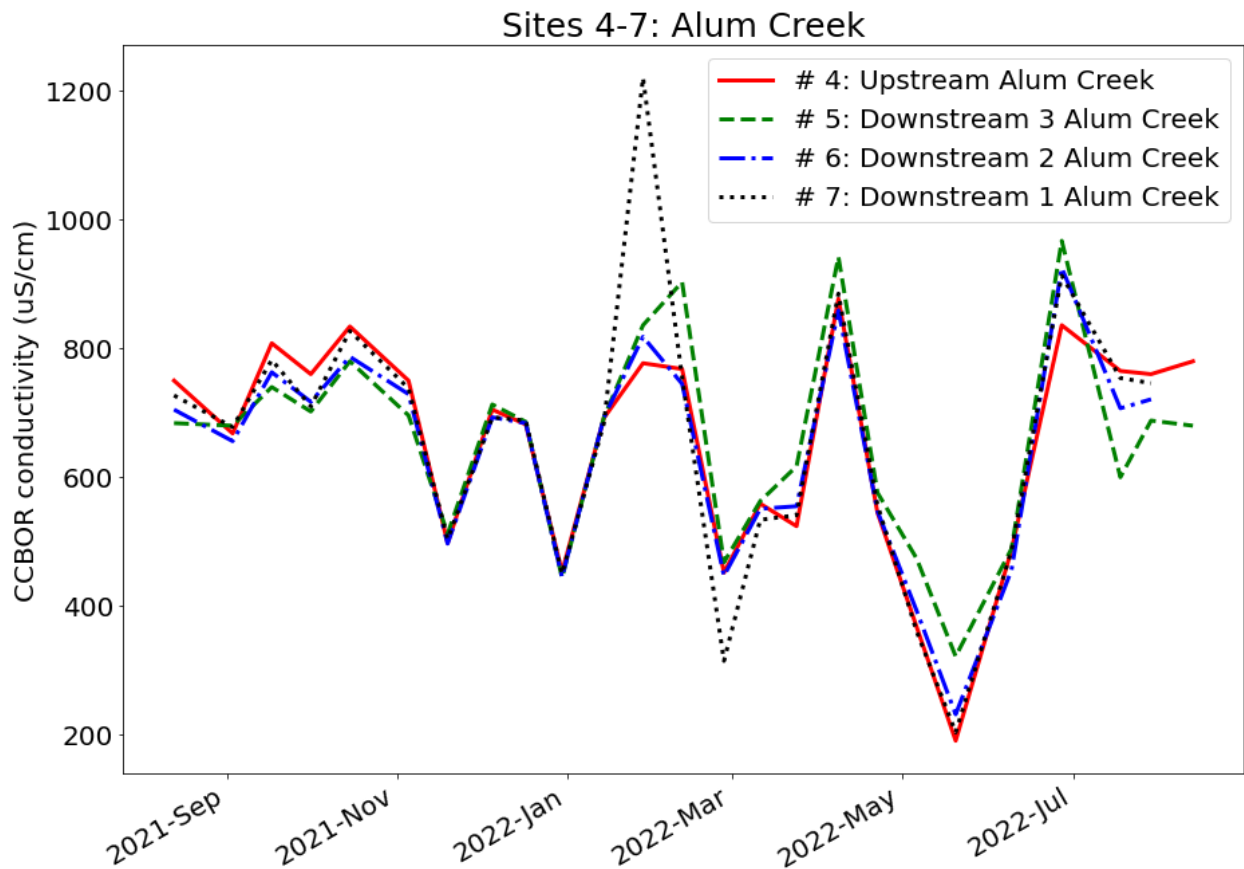


Figure 6 Conductivity at Alum Creek.

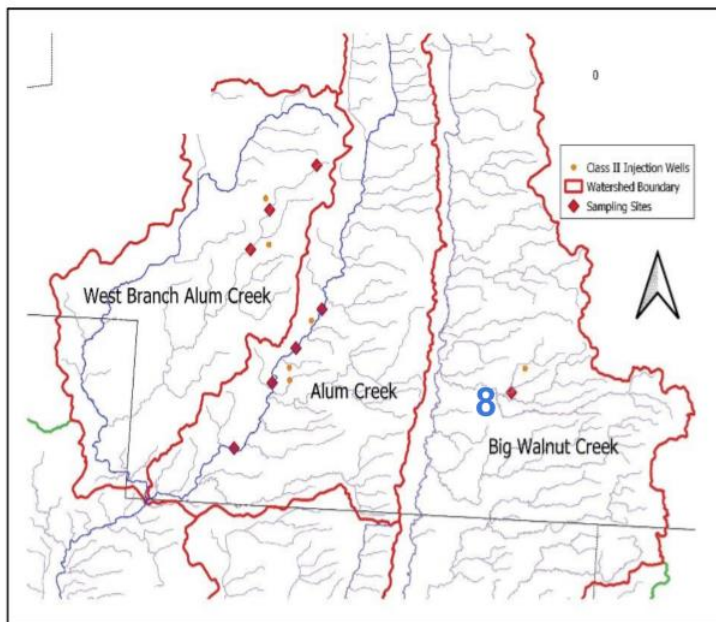
The graphs mostly follow each other very well and show little difference between the conductivity measured at the four sites on each corresponding date, except for one or two dates in February 2022.



Figure 7 Alum Creek water quality.

Plots show chloride (A), sulfate (B), iron (C), and methane (D) plotted with biweekly total dissolved solids at Alum Creek sites 4-7 from August 2021 to August 2022. If four measurements don't appear on a graph, that parameter was under the detection limit. The discontinuity in TDS data for Site 7 on 02/11/2022 was due to frozen conditions. At the Alum Creek sites, no measurements were above EPA Secondary Maximum Contaminant Levels (SMCL) in drinking water.

Drainages 3 and 4: Headwaters of Big Walnut and Little Walnut Creeks



The Big Walnut Creek watershed contains one injection well. A single site (Site 8) was monitored immediately downstream of the well.

Figure 8 Site map of Big Walnut Creek.

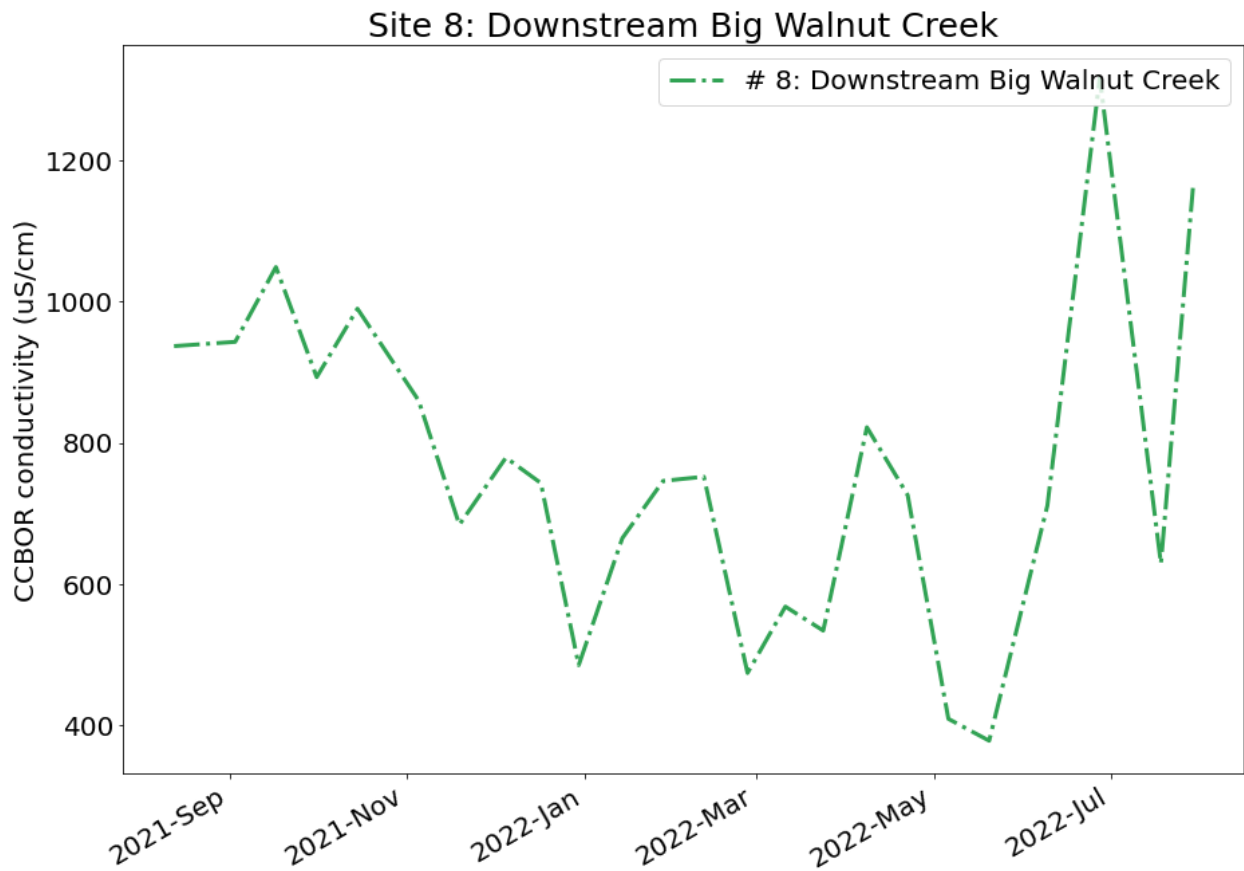
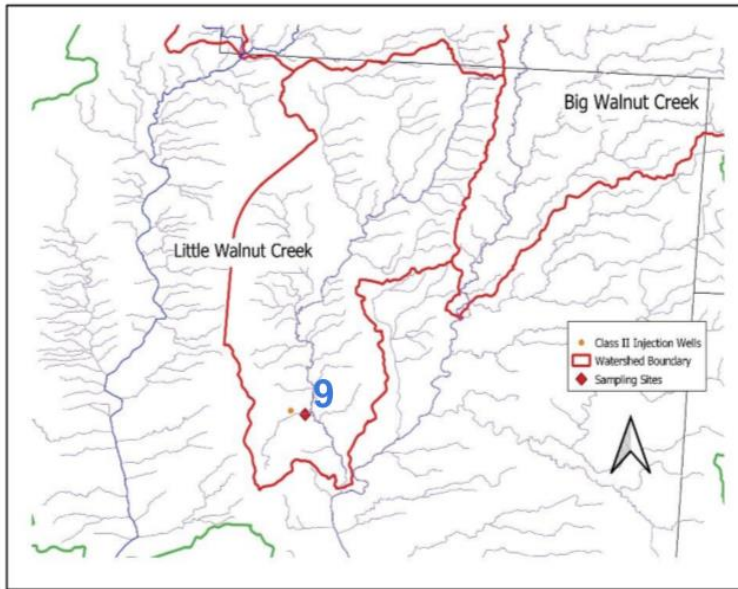


Figure 9 Conductivity at Downstream Big Walnut Creek.



The Little Walnut Creek watershed contains one injection well. A single site (Site 9) was monitored immediately downstream of the well.

Figure 10 Site map of Little Walnut Creek.

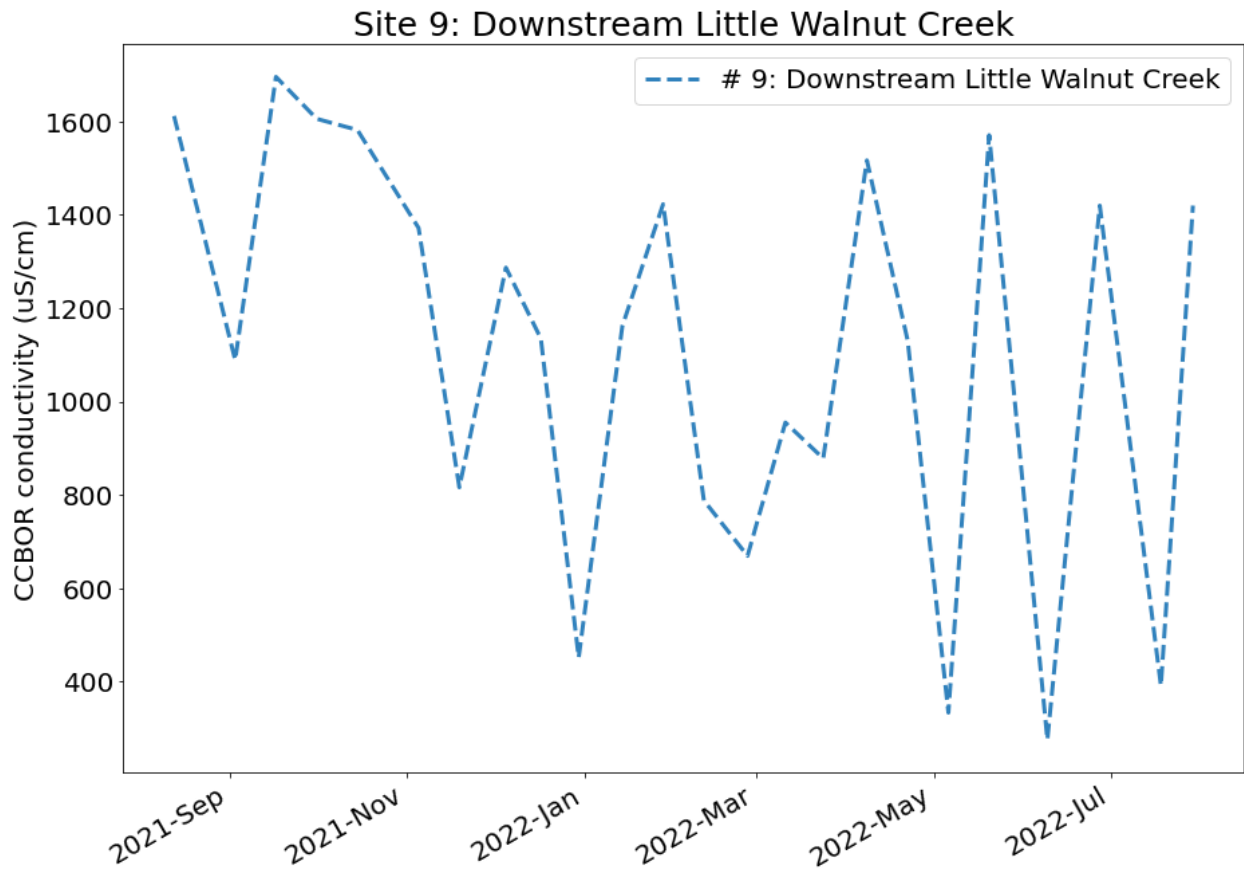
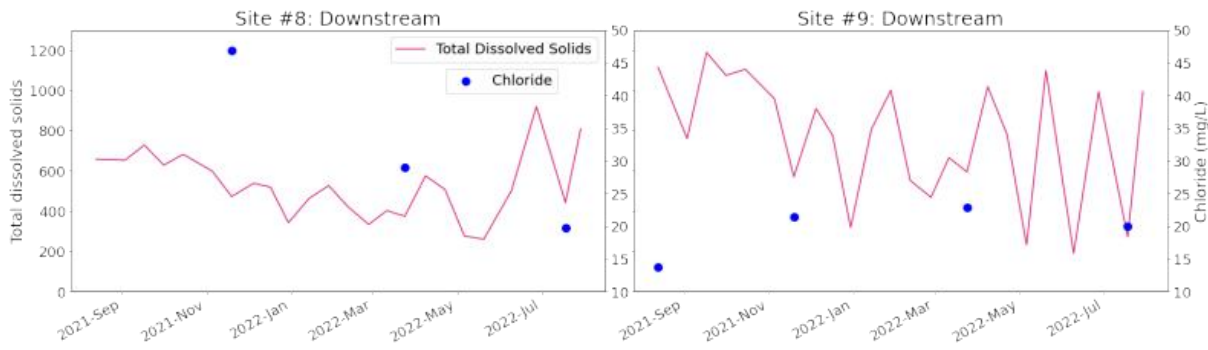
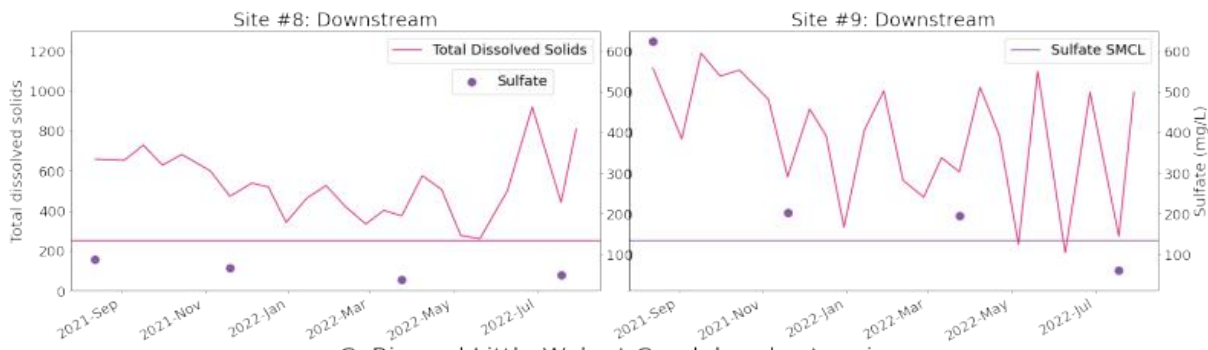


Figure 11 Conductivity at Little Walnut Creek.

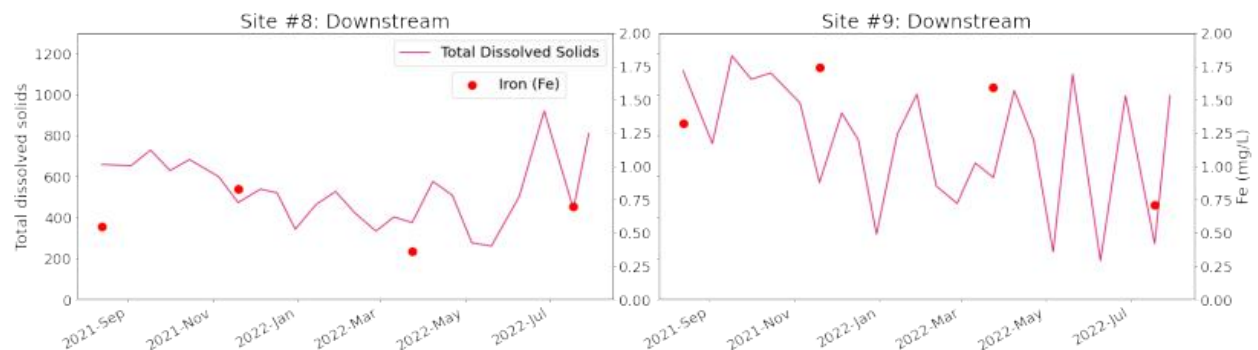
A. Big and Little Walnut Creek headwaters chloride



B. Big and Little Walnut Creek headwaters sulfate



C. Big and Little Walnut Creek headwaters iron



D. Big and Little Walnut Creek headwaters methane

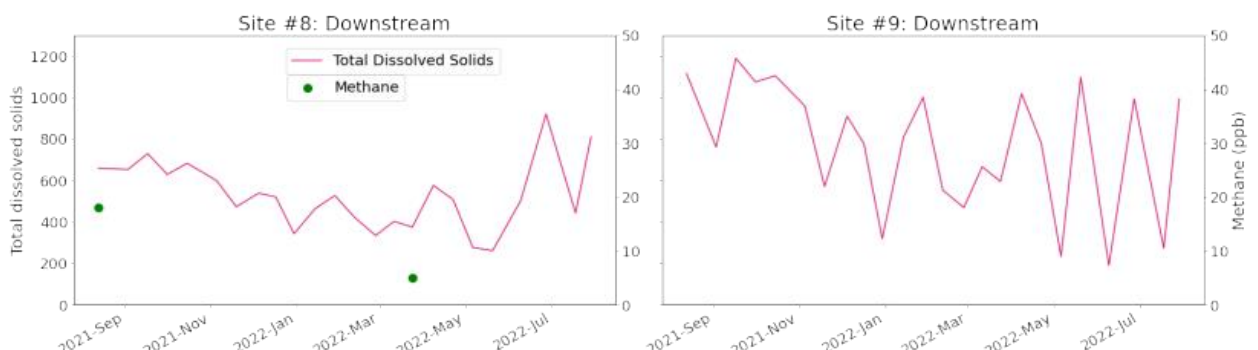


Figure 12 Big and Little Walnut Creek water quality.

Plots show chloride (A), sulfate (B), iron (C), and methane (D) plotted with biweekly total dissolved solids at Big Walnut (Site 8) and Little Walnut (Site 9) Creek headwaters from August 2021 to August 2022. On three occasions at the Little Walnut Creek Site (9), sulfate measurements exceeded the Secondary Maximum Contaminant Level (SMCL) for sulfate in drinking water (250 milligrams per liter) as established by the EPA.

Mass Ratio Analysis

In January 2023, Dr. Tetiana Cantlay at Duquesne University analyzed CCBOR's water quality samples from all 9 sites to test if there are any indications of contamination from conventional drilling, unconventional drilling, or mining activity. Dr. Cantlay and colleagues developed mass ratio analysis for the study of oil and gas development-related contamination as detailed in their 2020 publication in the *Journal of Environmental Science and Health*¹. Mass ratio analysis can look at the chemical fingerprints of containment sources (brines, acid mine drainage, fracking fluid flowback, or other potential contaminants). By testing over 1,000 contaminants and uncontaminated water samples, applications of this technique have shown that certain combinations of ratios (Mg/Na vs SO₄/Cl; SO₄/Cl vs Mg/Li) are diagnostic of specific contaminants in ground and surface water. A primer on mass ratio analysis for fingerprinting water contamination sources can be found in **Appendix B**.

Water samples from each of the sampling periods were analyzed for mass ratios and compared to diagnostic contaminants standards. Results from CCBOR's monitoring sites are in **Appendix A**.

¹ Cantlay, T., Bain, D. J., Curet, J., Jack, R. F., Dickson, B. C., Basu, P., & Stolz, J. F. (2020). Determining conventional and unconventional oil and gas well brines in natural sample II: Cation analyses with ICP-MS and ICP-OES. *Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances & Environmental Engineering*, 55(1), 11–23.

Conclusion and Recommendations

Summary.

The quarterly water quality measurements analyzed by CCBOR showed yearly variability, not unexpected in waterways affected by large-scale agricultural and residential use. There were individual measurements with measured sulfate and nitrate that exceeded the EPA drinking water standards at site 9 (Little Walnut Creek Headwaters, downstream of well #3404120160). Overall, there was no evidence of surface injection well leaks or spills within the study period of August 2021 to August 2022, which we expect would manifest as elevated levels of bromine, chlorine, and overall conductivity.

Mass ratio analysis plots (Figs 13 – 21) show the sampled data within regions indicative of acid mine drainage but on or near the border of regions indicative of conventional oil activities. For the conventional oil activity influence on water quality, this is not surprising, as the area has a long history of oil exploration and production. As for mine draining influence on water quality, it is curious that the samples plot inside regions indicative of acid mine drainage because there is no history of mining in the sampled areas. However, since the regions are determined by collections of data previously sampled, it could be the case that if more samples were taken – particularly in the Ohio shale region – the plotted areas for conventional oil activity might change and include the samples collected.

It is important to note that the geology changes over the length of the sampling area and different base flows to the streams from the different geologic formations may be responsible for changes in water chemistry.

We emphasize that the means available to our community group are likely insufficient to capture a leak or spill event, which may only be detectable for hours or days. Quarterly measurements are not enough, but the work of CCBOR provides a seasonal baseline to compare with future measurements. We urge the Columbus Division of Water to use the

data presented here to continue a high-frequency monitoring program of both surface and groundwater near all Class II injection well sites.

Key recommendations

1. **Continuous monitoring.** We only sampled bi-weekly and for a single year. If there was any surface leakage from injection wells or accidental spills from the injection process, the signal from injected fluids could have easily been missed and been flushed downstream in the Alum Creek or Hoover Reservoirs.
2. **Groundwater monitoring.** Due to the huge volumes of oil & gas waste injected into class II injection wells under high pressure, CCBOR is very concerned about groundwater contamination. The geology is rife with fissures and fault lines and there have been incidents where oil and gas brine injected into class II injection wells has affected production wells miles away and has even resurfaced.

Appendix A: Mass ratio analysis

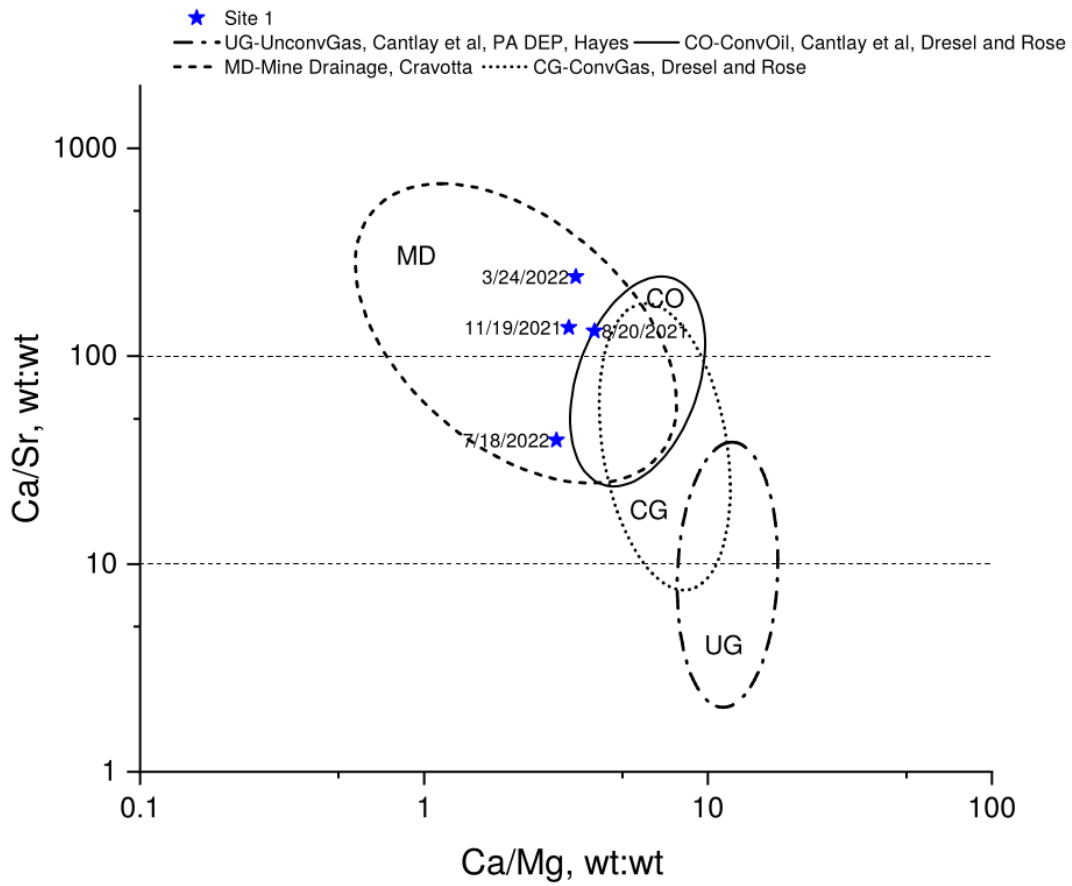


Figure 13 Mass ratio analysis of Site 1

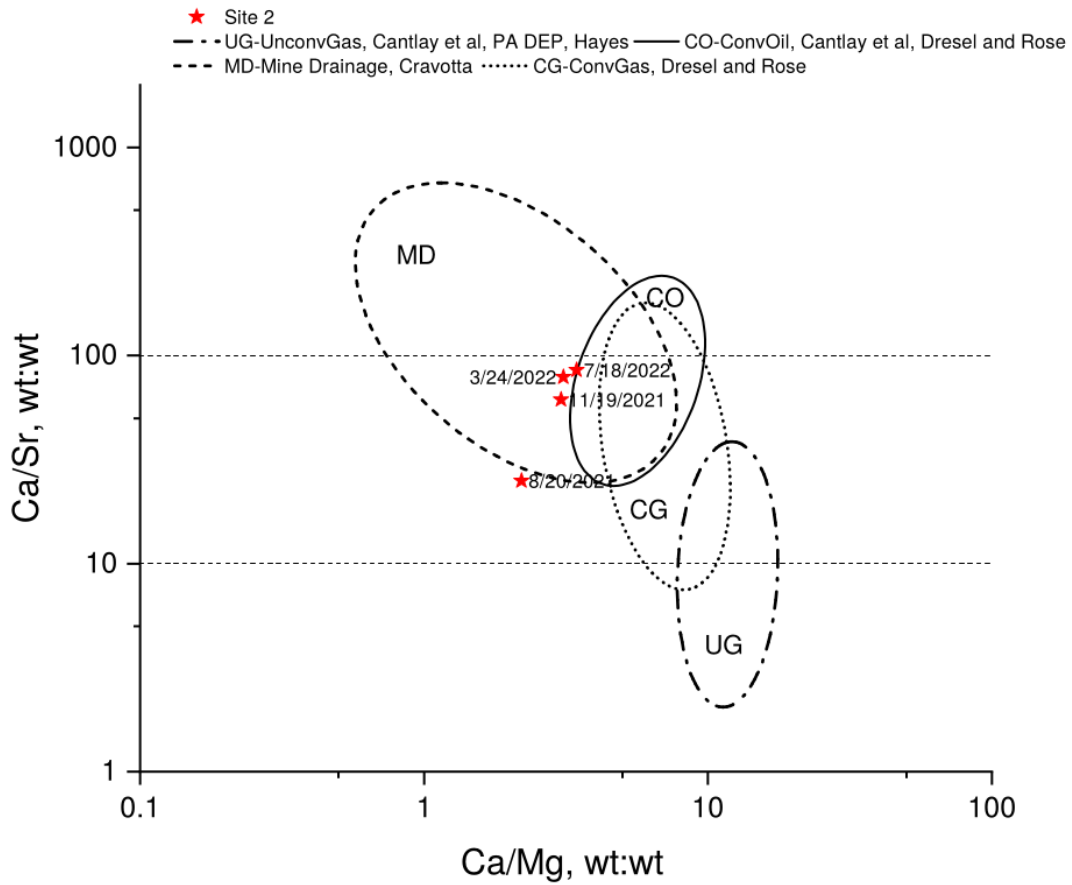


Figure 14 Mass ratio analysis of Site 2

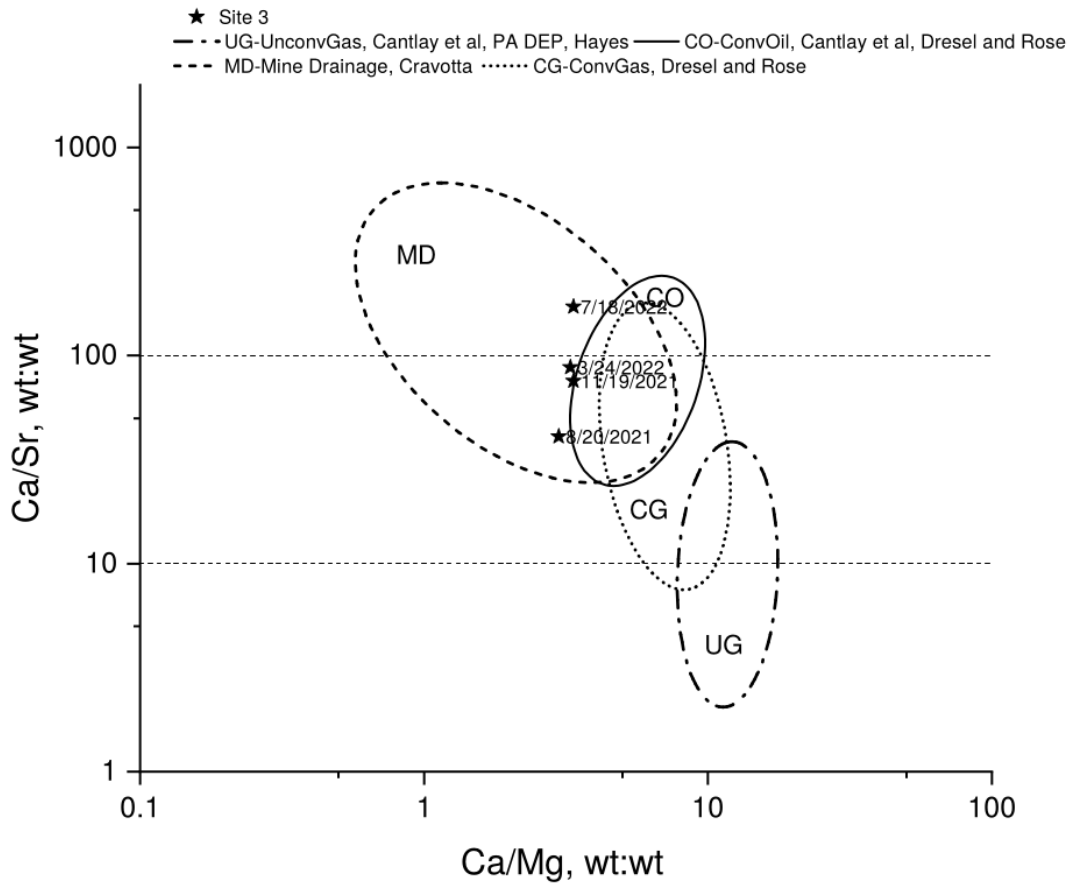


Figure 15 Mass ratio analysis of Site 3

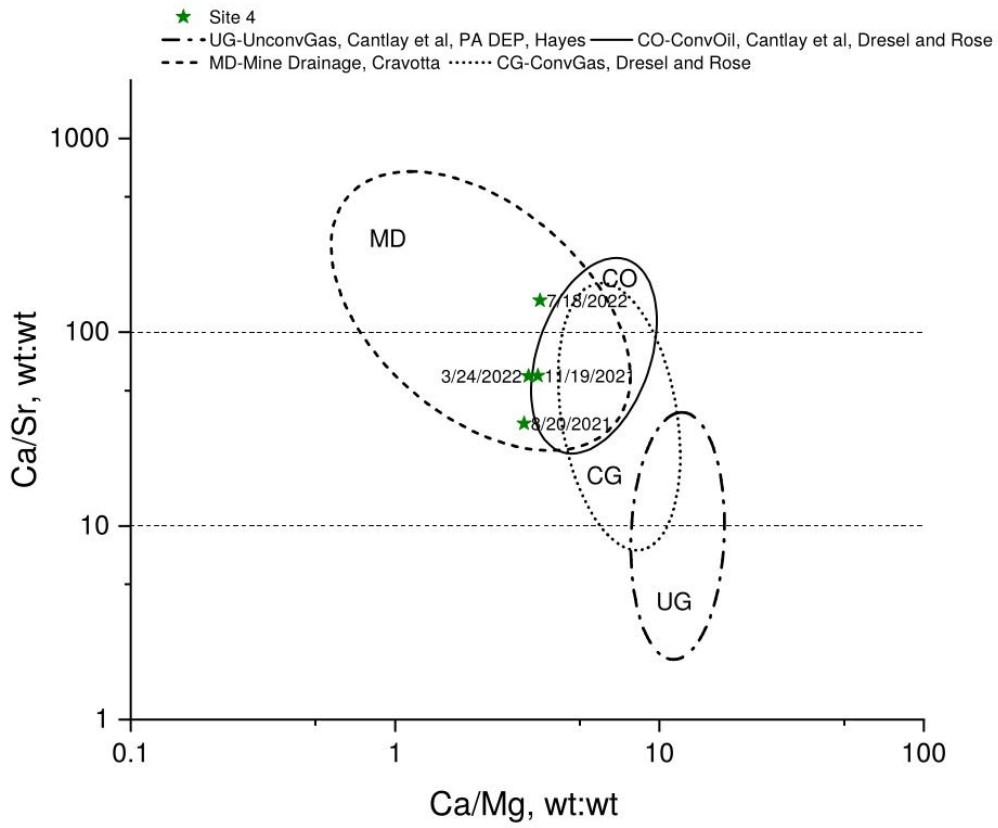


Figure 16 Mass ratio analysis of Site 4

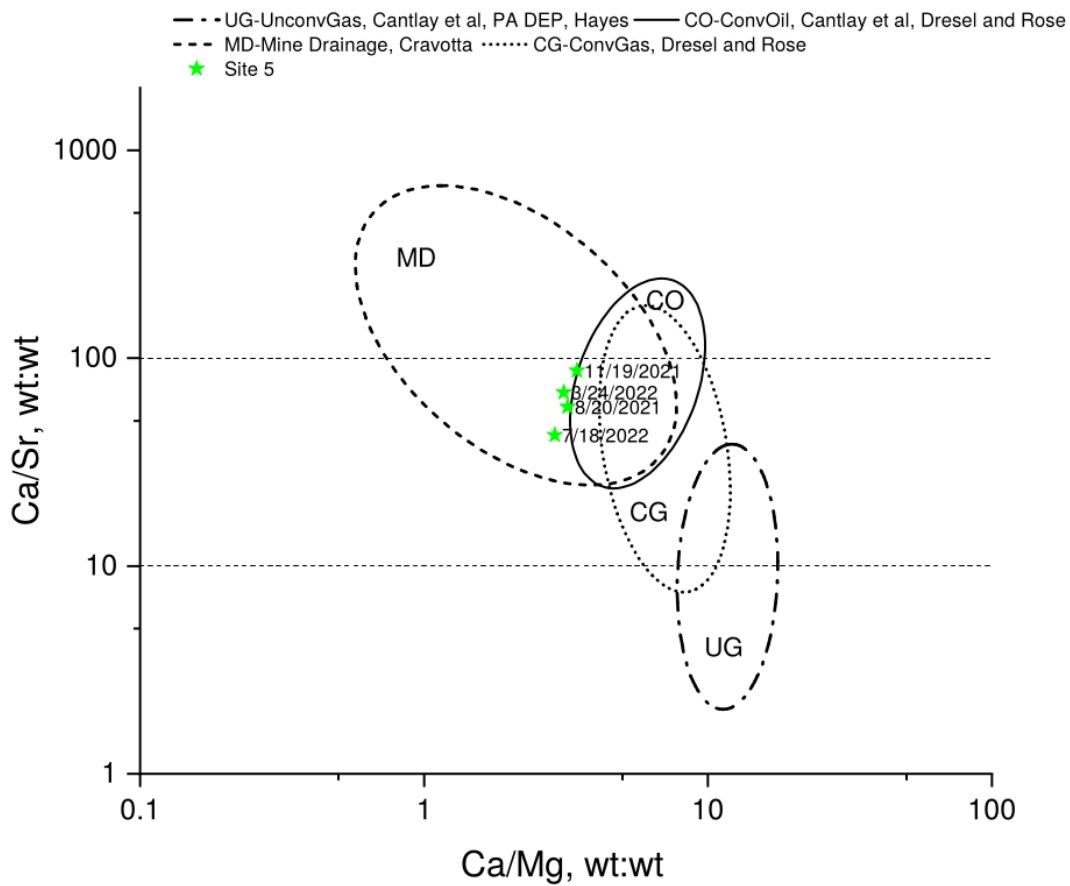


Figure 17 Mass ratio analysis of Site 5

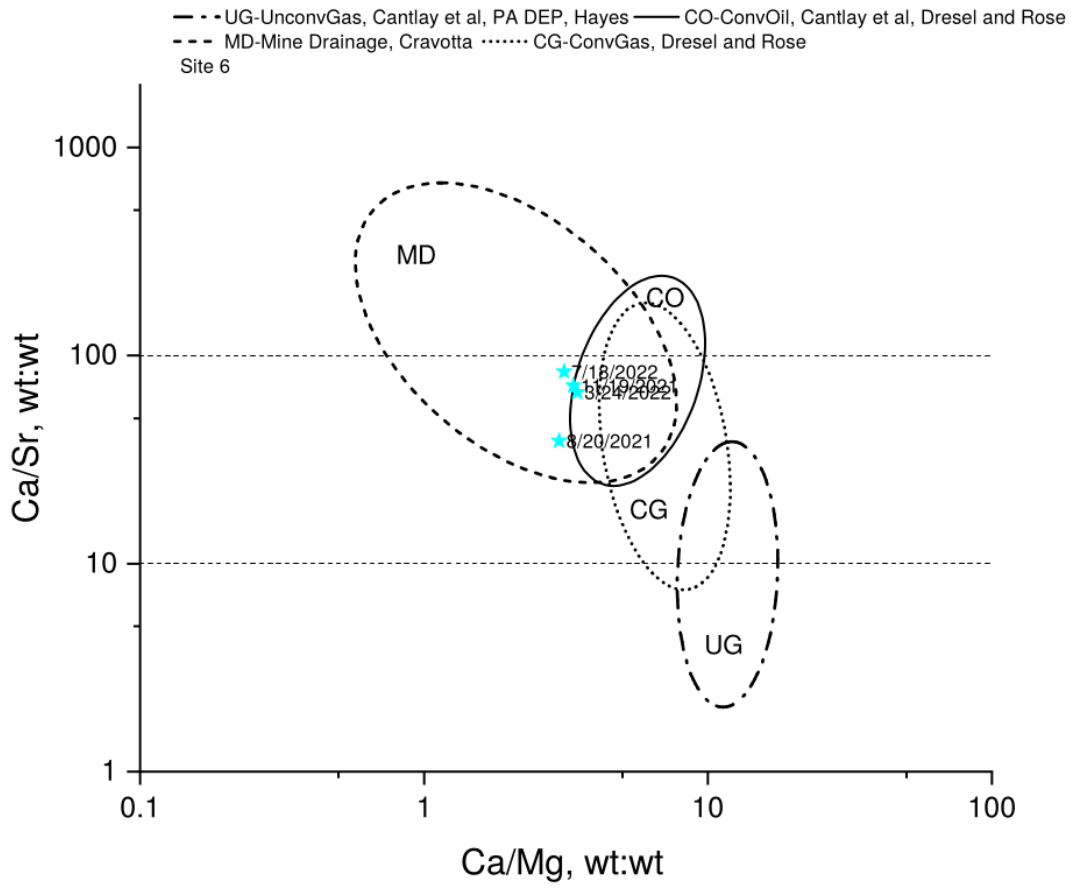


Figure 18 Mass ratio analysis of Site 6

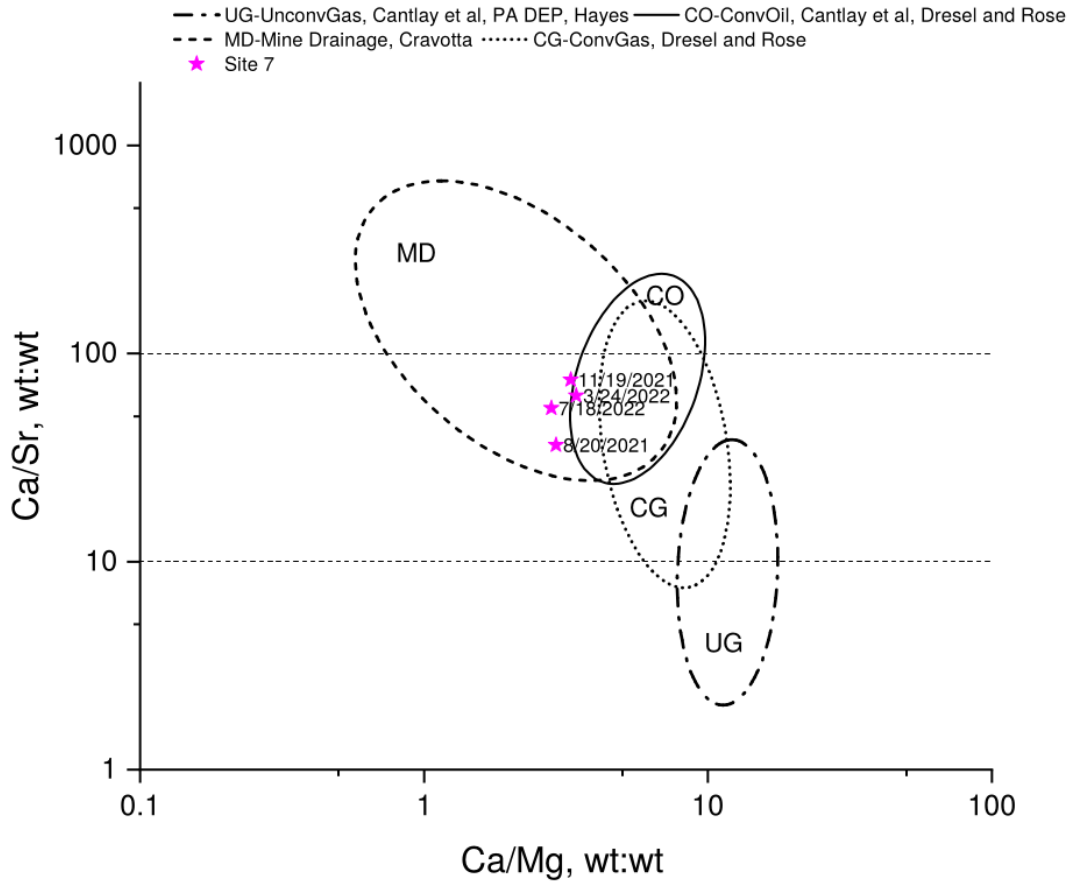


Figure 19 Mass ratio analysis of Site 7

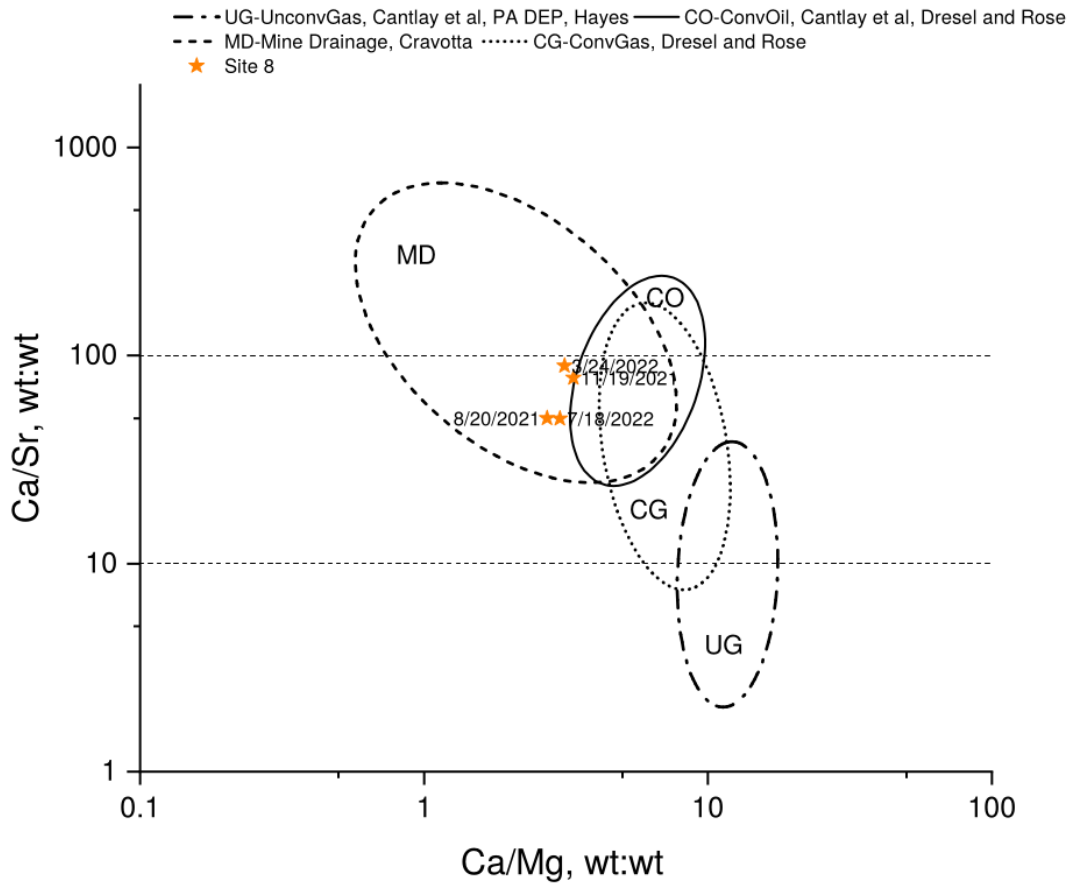


Figure 20 Mass ratio analysis of Site 8

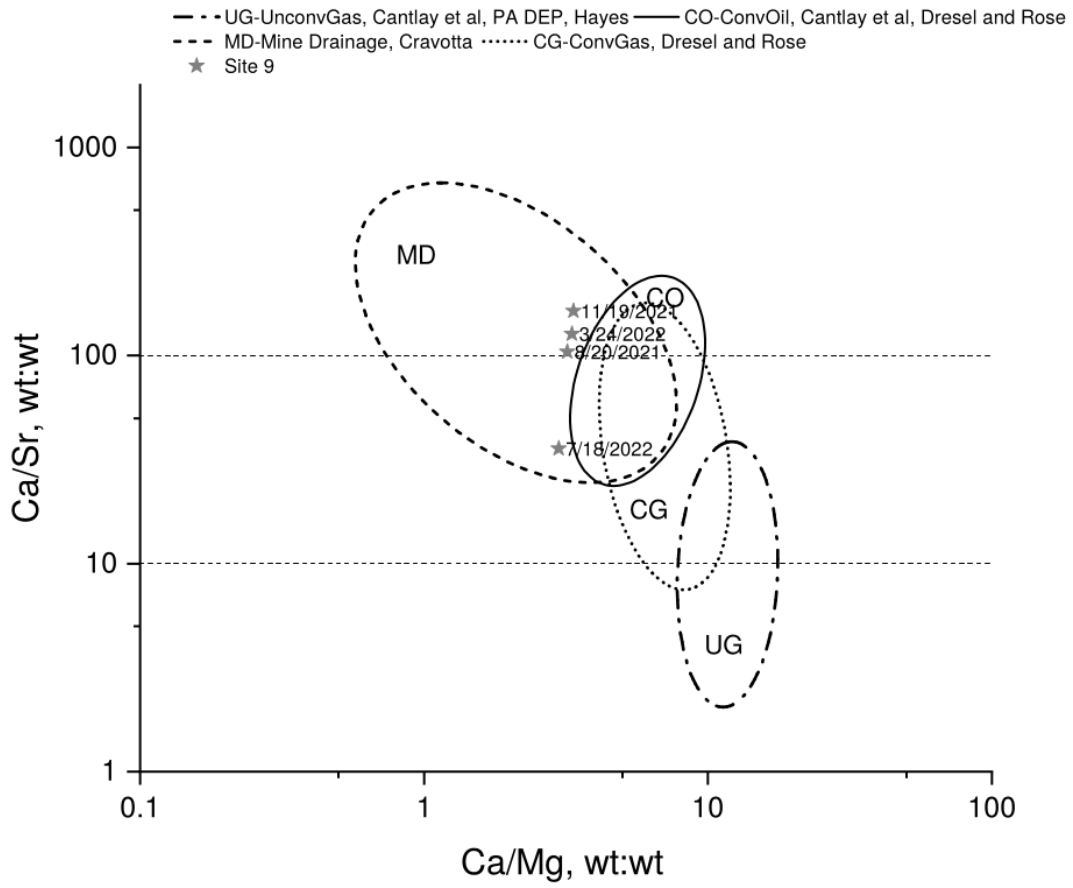


Figure 21 Mass ratio analysis of Site 9

Appendix B: Mass ratio analysis primer

Abbreviations

MRA	Mass ratio analysis
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
AMD	Acid mine drainage
MCL	Maximum contaminant level

What is mass ratio analysis?

Put simply, mass ratio analysis (MRA) looks at relative abundances of various ions like calcium (Ca), magnesium (Mg), or sulfate (SO₄) in a given sample. Different water sources naturally have different ratios of these ions because of the soils/rocks with which they have contact. Contaminants like fracking fluids, acid mine drainage, and brines may have very different ratios of these same ions. Flowback and produced water generated during hydraulic fracturing of unconventional oil and gas formations contain a suite of cations (mostly metal ions with positive charges) that are usually in a high salt matrix (e.g., NaCl). These differences in ion ratios can be exploited to differentiate between uncontaminated water and contaminated water.

How is mass ratio analysis performed?

Mass ratio analysis requires the quantitative measurement of individual chemical species, typically as ions (charged atoms or molecules). Often in the field of water quality, ions are measured using ICP-OES (inductively coupled plasma-optical emission spectroscopy) or ICP-MS (inductively coupled plasma-mass spectrometry).

ICP-MS and ICP-OES are similar, and both use inductively coupled plasma (essentially very hot, charged gas). Both of these instruments measure how much of certain ions (i.e., the amount of Na or Ca) are in samples, but they operate on different principles and are best suited for different types of target ions. In ICP-OES, the plasma produces excited atoms or ions that emit electromagnetic radiation (light) at wavelengths characteristic of a particular element. The light's intensity is then measured with photomultiplier tubes that can "see" the specific wavelength(s) for each element. Simply put, those intensities are then used to determine how much of an element is present in the sample.

In ICP-MS, the plasma is used to separate the sample into individual atoms (a process called atomization). Then the plasma ionizes these atoms, allowing them to be detected by the mass spectrometer. A mass spectrometer is an instrument that measures the mass-to-charge ratio of ions. There are many kinds of mass spectrometers, but the outcome is similar across them all: you wind up with a mass spectrum, which is a plot of the mass-to-charge ratio (on the x axis) versus intensity (correlated to abundance, on the y axis). Both approaches can simultaneously analyze multiple ions in one sample.

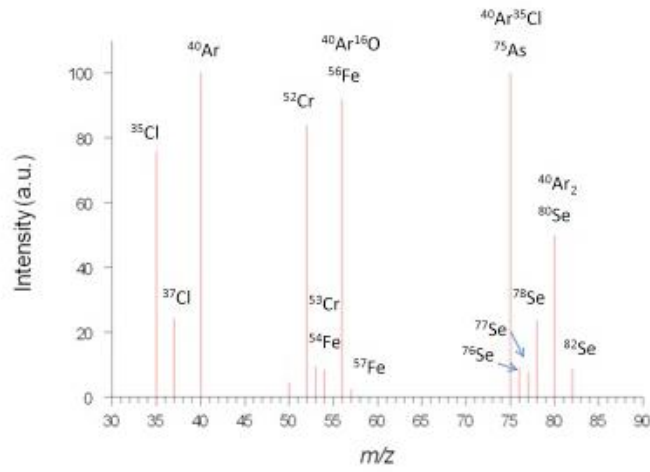


Figure 22 An example mass spectrum.

In Figure 22 above, we show an example mass spectrum that could be used in mass ratio analysis. On the x axis is the mass-to-charge ratio of the detected ions, including isotopes (differently weighted versions) of iron (Fe), chromium (Cr), and argon (Ar). On the y axis is the intensity of the detected ion in arbitrary units (a.u.), an expression of the relative electric charge imparted on the mass spectrometer’s detector by ion.

Why is it useful for water quality measurements?

Mass ratio analysis can look at the chemical fingerprints of containment sources (brines, acid mine drainage, fracking fluid flowback, or other potential contaminants). By testing over 1,000 contaminants and uncontaminated water samples, researchers have shown that certain combinations of ratios (Mg/Na vs SO₄/Cl; SO₄/Cl vs Mg/Li) are diagnostic of specific contaminants in ground and surface water. This is detailed in their 2020 publication (see summary below). Oil brines are different from gas brines and mine drainage. Crucially, this is not about overall abundance of specific ions, although MCL’s are important for compliance, but the relative abundance of the different ions compared to

each other. The goal is to diagnose contamination and its source.

What does a plot of a mass ratio analysis look like?

If you're used to looking at plots like times series water quality data results, at first a mass ratio analysis plot looks strange. The comparison is between two mass ratios, for example Ca/Mg versus Ca/Sr. To get this comparison you'd divide the measured amount of Mg ions in the samples (from your mass spectrometry results) over the amount of Na ions, and likewise for the SO₄ and Cl pair. You'd then plot one ratio on the x axis and one of the y (see Figure 2 below for the mass ratio analysis of CCBOR Site 1 for Ca/Mg versus Ca/Sr). It's not important which ratio goes to which axis, because all that's cared about is the comparison. Likewise, there are no units because we're dealing with ratios.

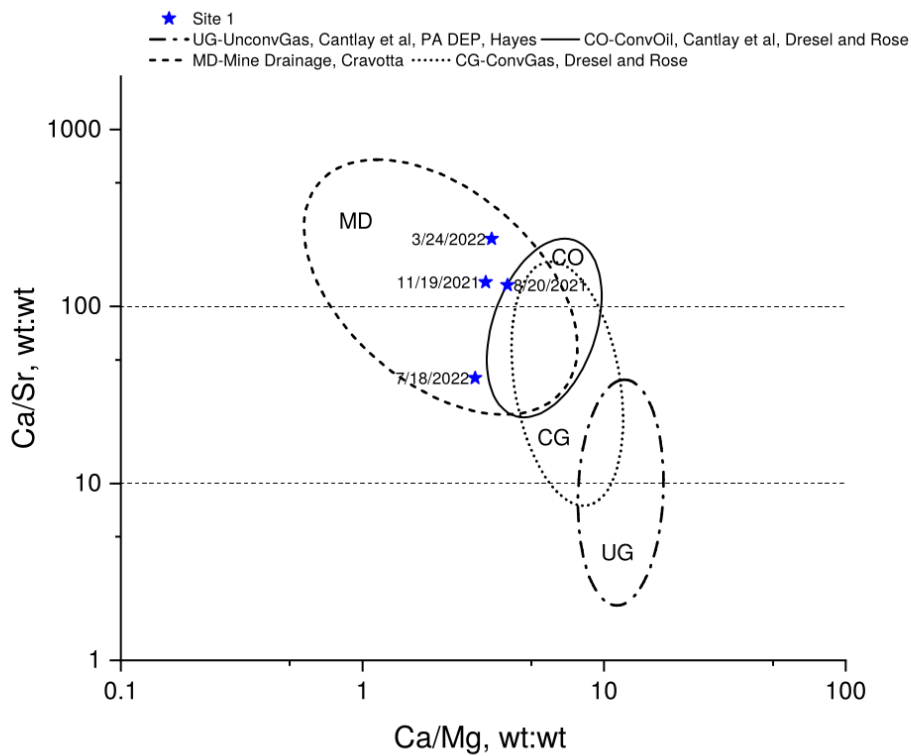


Figure 23 Ca/Mg versus Ca/Sr mass ratio analysis of CCBOR Site 1.

In Figure 23 (above), mass ratios are plotted in weight:weight (wt:wt) units and on a logarithmic scale. Measured ranges of contaminant standards in mass ratio space are plotted in solid or dashed lines for unconventional gas brine (UG), conventional oil brine (CO), mine drainage (MD), and conventional gas brine (CG) with relevant publication citations for those measurements indicated. CCBOR sample results are displayed as blue starts with their sampling date indicated.

Because the numerical range of ratios is so large, the plots are in logarithmic scale to keep the display compact and human-readable. By making repeated measurements of several contaminant standards, researchers have established ranges in mass ratio space that indicate conventional oil brines or mine drainage. Plotting sample results, as shown in Figure 1 with CCBOR's Site 1 samples, with these ranges can help determine if surface or groundwater is chemically similar to any of these contaminants. Visually, you can use plots like that above to see in which, if any, diagnostic contaminant range a sample may fall within.

What are the key takeaways of Cantlay et al., 2020?

This research paper is about analyzing the chemical composition of production fluids associated with natural gas and oil development.

- Anions (ions with negative charges, like Cl^- and SO_4^{2-}) and cations (like Na^+ and Sr^{2+}) were measured in 1,177 samples using the two types of mass spectrometers mentioned above, ICP-MS and ICP-OES.
- Different mass ratios including Ca/Sr and Ba/Sr were assessed to differentiate between brines from conventional wells; unconventional oil & gas wells or impoundments; mine drainage treatment pond water; and various groundwater and surface waters samples.
- The comparison of Mg/Sr ratios against Li concentrations provided clear separation among different types of samples. Correlations like Ca/Mg versus Ca/Sr were also shown to be useful in distinguishing between conventional & unconventional oils & gas fluid sources.

References

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