Supplementary Information for

Targeted Sampling Reveals Localized Brine Signals Without Evidence of Regional Water Quality Impacts from Unconventional Oil and Gas Development

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Text S1. Field Methods

At every site, the homeowner was first asked where the well/spring was located, and a visual inspection was conducted. For both spring and well water sources, a pressure tank (small, ~20-gallon tank that pressurizes the water before it enters the house pipes) was located where the water was piped into the house. These tanks often, but not always, have a normal hose spigot at their base. Depending on the water treatment systems, it was sometimes possible to physically bypass the treatments (route water around the system). Some springs are developed such that they have an overflow pipe to release extra water with a spring that is always flowing. Some houses have a Coyote tank system installed (proprietary system that pumps water from the well when water is available and the tank is not full and collects it in a large, ~1000-gallon tank so that the house draws from the reservoir).

Sampling points were chosen prior to any treatment systems and large holding tanks, or with treatments bypassed. Most often, a spigot was available at a pressure tank or between the house and the water source. When the inflow (where water is pumped from the well) into a Coyote tank was accessible and the well could be triggered to pump, the flow-through bucket was lowered to the inflow point. When sampling at a spring overflow pipe, samples were taken directly from flowing water with no traditional "purge" possible due to continuous flow. Stream samples were taken directly from the streams. If a property had multiple water sources, multiple samples were taken, as long as we concluded that the water sources were distinct from each other (e.g. a well and a spring on opposite sides of a hill).

When possible, water sources were purged to clear standing water in the well bore, pipes, etc. and ensure that fresh groundwater was sampled. At the beginning of purging and for every five minutes during purging, pH, dissolved oxygen, specific conductance, and temperature (in °C) were measured using a YSI ProDSS multiparameter digital water quality meter with pH/ORP (oxidation reduction potential), DO, conductivity and temperature sensors. The probe was submerged in the targeted water in a "flow-through" bucket (5-gallon bucket with a valve installed at the bottom that allows water to cycle while keeping sensors submerged for stability of readings). Water was purged until pH and temperature values stabilized within 5% over a 5-minute interval. At that point, samples were collected. The ProDSS was calibrated daily following the applicable sections in the YSI ProDSS Calibration Guide. A 2-point calibration was implemented for pH 7 and 10, recalibrating to pH 4 and 7 if necessary for very low pH waters. One-point calibrations were used for specific conductance (SC) at 1000 µS/cm and for DO using water-saturated air (100%).

The methane concentration in air was measured using a Bascom-Turner Gas-Rover. The Rover was calibrated prior to each trip with 2.5% methane gas mixture from Bascom Turner; calibration is stable for at least a week. The detection limit was established at 5ppm methane. The Gas-Rover sensor was held over flowing water during the purge and around the sampling area; the maximum reading was recorded. No Gas-Rover concentrations were taken at 6 field sites due to time constraints or device malfunction.

After sufficient purging, the first samples collected were for volatile organic compound (VOC) analysis. They were collected in 20mL amber glass screw top headspace vials until a reverse meniscus formed, at which point they were capped with PTFE-lined magnetic screw caps and checked to ensure they contained no gas headspace. Next, samples for major element anions, major element cations, trace metals, and strontium isotopes were collected in acid-washed LDPE bottles (15mL, 30mL, 60mL, and 60mL respectively). Samples for anions, cations, trace metals, and strontium isotopes were filtered using acid-washed syringes and 0.45-µ Nylon syringe filters. All filtered samples except anions were acidified with trace-metal grade nitric acid.

Samples for alkalinity were collected unfiltered and non-acidified in 250mL acid-washed LDPE bottles. These samples were titrated in the field (within 24 hours) to a pH of 4.2 [1] using a Thermo Scientific Orion field pH meter calibrated daily to pH 4 and 7 and a Hach digital titrator with 1.6N sulfuric acid cartridges and 100mL of sample [2].

Samples for dissolved inorganic carbon were collected in 125mL acid-washed LDPE bottles, submerged carefully in the flow-through bucket after purging was complete to avoid introducing bubbles into the bottle. Bottles were capped underwater, then inverted to check that there was no headspace.

IsoFlasks were filled for dissolved hydrocarbon gas analysis according to IsoTech's sampling protocol [3]. When sampling from a spring overflow pipe, the top of the IsoFlask connector tubing was held under water to achieve steady flow. When sampling from a stream or bailed sample, a set of connector tubing was adapted to connect to the 5-gallon bucket to maintain a steady flow.

After collection, samples were stored on ice until the field team returned to the laboratory, where anion samples were frozen until analysis while all others except IsoFlasks were stored in a refrigerator held at <40°F. Once sampled, IsoFlasks were stored unrefrigerated and kept flat, as directed by IsoTech.

Text S2. Blanks

Blanks were collected or analyzed for all analytes except dissolved inorganic carbon and hydrocarbon gases. The different types of blanks are summarized below.

Process blanks. One process blank per trip was collected for major element anion, major element cation, trace metal, strontium isotope, and alkalinity analyses. For these blanks, DI water from the Penn State Laboratory for Isotopes and Metals in the Environment (PSU LIME) laboratory was used. DI water was filtered and run through an ion exchange system to remove dissolved constituents. DI water was also taken into the field and was used for rinse water. This DI water was filtered and acidified as if it were a normal sample (or not acidified if analyzed for anions), then submitted for analysis as a process blank with the other samples, using the same bottles, technique, etc.

Trip blanks. One set of trip blanks per trip were taken for the BTEX analysis. In the PSU LIME laboratory prior to the trip, a set of cleaned vials were filled with ultra-high purity 0.03-micron filtered organic-free water. These vials were carried in the cooler with the samples during the day, stored in the refrigerator with the samples overnight, and submitted to the laboratory for analysis with each campaign's samples.

Text S3. Laboratory Analysis

Anion analysis. Fluoride, chloride, sulfate, and bromide were analyzed for all trips at the PSU LIME using a Dionex ICS-2100 Integrated IC System with an IonPac AS18 4×250 mm anion exchange column, an IonPac AG18 4×50 mm guard column, a Dionex Carbonate Removal Device 200-4mm, and a Dionex EGC III KOH RFIC Eluent Generator Cartridge using manual adjustments of baselines for peak overlap. Early in the project, when no carbonate removal device (CRD) was available in PSU LIME, relatively large carbonate peaks were sometimes observed. The lack of CRD did not affect NO_3 analysis because nitrate shows little to no overlap with carbonate. Samples for F, Cl, SO_4, and Br were held for analysis until a CRD became available.

To check the effects of longer holding times, larger volumes were sampled for Trips 3-7. This enabled analysis at an additional laboratory where a CRD was available (the Penn State Agricultural Analytical Laboratory (PSU AAL)). These concentrations, reported with precision and accuracy generally better than +1% and +10%, respectively, were completed at holding times <14 days. Following methods as described in the literature [4,5], inter-lab data were compared by ordinary linear regression for a data range likely to

have the same measurement error, i.e., a subset of at least 10 values selected randomly from within the range where most samples were measured (<1 mg/L (F), <50 mg/L (Cl), <65 mg/L (SO_4), <10 mg/L NO_3)). Only values >LOQ were included. Within 99.9% confidence, the intercepts and slopes did not differ from 0 and 1, respectively, for all anions except bromide.

Given the issues with the bromide analysis, and to analyze concentrations at lower levels than possible at either LIME or AAL (especially where sulfate concentrations create interference), we re-analyzed all of the samples between 4 and 9 months after sampling in the Kappe Engineering Laboratory at PSU. These results are reported herein instead of the original analyses for bromide. The analyses of Br at Kappe Engineering Laboratory were completed using a Thermo Fisher Integrion High Pressure Ion Chromatography (HPIC) system with a Dionex IonPac AS18 column and a Dionex carbonate removal device. Methodology for analysis is outlined in IonPac AS18 manual "Isocratic Separation of Anions in 12-Anion Standard". The method provided a flowrate and eluent concentration for the isolation of bromide from other ion peaks. The MDL and reproducibility for bromide are reported as 0.01 mg/L and +/- 3%.

Major element analysis. Major elements were measured at PSU LIME using a Thermo iCAP 7400 inductively coupled plasma atomic emission spectroscopy (ICP-AES) system with a 2.5 ppm lutetium (Lu) internal standard. Trace elements were measured at PSU LIME using a Thermo Scientific iCAP TQe Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and iCAP RQ ICP-MS New Wave 193 nm excimer laser.

Sr isotope analysis of the groundwater samples was completed in the Metal Isotopes Laboratory at PSU LIME. Prior to isotopic analysis, elemental concentration data from the ICPMS in LIME were used to determine the volume of sample required to attain 1 µg of Sr. This volume of sample was dried down and resuspended in 0.5mL of 8N HNO_3 for ion exchange chromatographic separation. Samples were purified chromatographically to isolate the Sr using Eichrom Sr Spec resin. After ion exchange purification, samples were dried down and resuspended in 2 µL of 2N HNO_3. One µL of the sample volume was loaded on a single zone-refined rhenium filament with $TaCl_5$ activator and phosphoric acid. Samples were then loaded onto the turret, with a maximum of 19 samples per reel and two filaments loaded with Sr standard SRM987. Measurement of Sr isotopic composition ($^{87}Sr/^{86}Sr$) were collected using the Thermo Scientific Triton Plus Thermal Ionization Mass Spectrometer (TIMS). Repeated analysis of the SRM987 standard resulted in an average $^{87}Sr/^{86}Sr$ value of 0.710268 with a standard deviation of 9.9×10^{-6} (n=13), well within the certified composition of 0.71034 ± 0.000260.

Dissolved inorganic carbon was analyzed using a Shimadzu TOC-L analyzer at the PSU SALinity with IsoTopeS (SALTS) Laboratory. Samples were filtered into dedicated 40mL vials to allow for two tests per sample.

BTEX was measured using headspace gas chromatography - mass spectrometry (GC MS/MS) (EPA method 5021A with application notes from Agilent, Inc.) using a GC MS/MS system at the Penn State University Energy and Environmental Sustainability Laboratory (PSU EESL). A Trace 1310 GC system (ThermoFisher Scientific SpA, Strand Rivoltana, Km4, 20090, Rodano Milan, Italy) was used that is connected to a TSQ 9000 – AEI tandem mass spectrometer (ThermoFisher Scientific, Milan, Italy) and is equipped with an Advanced Electron Impact (AEI) source. The data recorded were processed using Thermo ScientificTM Dionex ChromeleonTM 7.2.10 ES Chromatography Data System ™ Version Mus (24543) software. One drop of HCl was added to headspace vials 14 days after sampling if longer holding times were needed. Some samples from Trip 1 were not analyzed for BTEX due to a refrigerator malfunction (samples froze and bottles broke). Stream samples were not analyzed for Trip 6 due to budgetary constraints.

Hydrocarbon gas concentrations were quantified by gas chromatography at IsoTech Laboratories, Inc [6]. Samples were analyzed for quantities of dissolved methane, ethane, and propane. Carbon and hydrogen isotopic compositions of gas components were also analyzed, where gas concentrations were high enough, by chromatographic separation followed by combustion and dual-inlet isotope ratio mass spectrometry [7]. Specifically, those with >1 mg/L of methane were subsequently analyzed for carbon isotope ratios of carbon-13 (^{13}C) to carbon-12 (^{12}C), called "delta-13-C" ($\delta^{13}C$) and hydrogen isotope ratios of deuterium (^{2}H or D) to hydrogen (^{1}H), called "delta-D" (δD) of the methane gas. Samples with >1 mg/L ethane were also analyzed for $\delta^{13}C$ of ethane when the budget allowed. Stream samples were not analyzed for hydrocarbon gases due to budgetary constraints.

Text S4. Quality Control

It is well known that detections of analytes can occur in blanks even when the analytes have not been added to the blank sample [8]. We therefore analyzed concentrations in process blanks for each trip of 25 species using ion chromatography, inductively coupled plasma atomic emission spectroscopy, or inductively coupled plasma mass spectrometry (F, Cl, SO_4, Br, NO_3, Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Si, Sr, Li, Be, Ni, Cu, As, Cd, Tl, Pb, U).

Of the 25 analytes, 12 inorganic species were detected at least once in a process blank over 7 trips. For seven of these (F, Cl, Ca, K, Mg, Na, Si), one to four spurious detections were noted but at much lower concentrations than measured in the lowest-concentration samples from the associated trips. Five of the analytes (NO_3, P, Li, Cu, Pb) were detected in the process blanks at concentrations above the lowest concentration in one or more of the associated trips. For sample concentrations that were less than or equal to the detected concentration in the process blank for the associated trip, we marked the concentration with an asterisk (*) in the results table.

Concentrations of one or more BTEX compounds were detected in trip blanks from all but one of the trips where trip blanks were collected: the maxima for these trip-blank values were 0.39 µg/L for benzene, 3.22 µg/L for toluene, 9.46 µg/L for ethylbenzene, and 12.5 µg/L for total xylenes. This indicates a low-level source of these compounds in the laboratory used for trip deployment. All of the sample concentrations were less than the maximum trip-blank value measured for total xylenes, while eight water samples showed concentrations within a factor of 2 of the maximum concentrations for BTEX in trip blanks. All BTEX concentrations in water samples were below the corresponding EPA MCLs [9].

Several quality control analyses were calculated following a U.S.G.S. protocol [10] with revisions suggested by Csuros [9]. Charge imbalance was calculated as ((sum of cation equivalents - sum of anion equivalents)/(sum of cation equivalents + sum of the anion equivalents))*100. Ninety-eight percent of samples were within ±10%, and all were within ±12%. Ion-to-SC ratios were calculated as (sum of cation milliequivalents or sum of anion milliequivalents)/(0.01*SC) with SC as µmhos/cm. Eighty-five percent of samples were within the accepted range of 0.92 - 1.24 for both ratios. TDS was calculated as 0.6*[alkalinity] + Na + K + Ca + Mg + Cl + SO_4 +SiO_3 + (NO_3-N) + F where all concentrations were expressed in mg/L. Sodium/potassium and TDS/SC ratios were within acceptable range (Na>K if K<10 mg/L and <0.81, respectively) for all samples with TDS in mg/L and SC in µmhos/cm. Only the upper bound of the TDS/SC ratio was tested because calculated TDS values can be lower than measured TDS by up to 20%.

Text S5. PADEP Record Review and Incident Characterization

Incident details and regulatory information for brownfield sites (In Pennsylvania, brownfield sites are former industrial or commercial properties whose reuse is complicated by potential contamination from hazardous substances but that are eligible for cleanup and redevelopment) within the Land Recycling

Program were obtained from the Pennsylvania Department of Environmental Protection (PADEP). These records are publicly accessible via informal file review requests.

We collected samples within buffer areas surrounding five brownfield locations in Washington County. We retrieved records for these sites from the PADEP Southwest office. Records available include notifications, inspection reports, notices of violations, enforcement orders, applications, permit review letters, sample results, remediation plans, approvals, denials, pollution prevention plans, and external correspondence. Review of these records confirmed that the actual spill locations were situated either directly on the well pad or along its immediate boundary. For four of these five sites, available data were limited to a small number of soil and surface water samples intended solely to characterize remediation efforts. No groundwater sample data were available in the PADEP reports for these four spills.

For spill A, as documented by the PADEP reports, on December 4, 2021, a washout failure of a buried dump line east of the 11H gas production unit (GPU) caused a release of produced fluid. EQT notified PADEP, shut in the well pad, and initiated repairs and interim remediation. Following a PADEP inspection on December 8 and issuance of a Notice of Violation, EQT conducted additional assessment activities. EQT subsequently discontinued use of buried dump lines, installed temporary and then permanent aboveground lines, and downsized the pad by removing the 11H GPU, associated equipment, and contaminated material. Analysis of fluid disposal records and gas-to-water ratios indicated that a slow leak may have been occurring from December 2020 to December 2021, resulting in an estimated release of 19,213–22,425 barrels of produced fluid, which EQT reported to PADEP. The Water Quality Monitoring Program was thus initiated, and a substantial groundwater sample dataset was collected over the installed monitoring wells.

The PADEP report also detailed additional investigative activities, including surface water and soil sampling, fracture trace analysis, structural geology surveys, and electrical imaging resistivity methods, to examine hydrogeologic conditions and delineate the extent of groundwater and surface water impacts. The well pad is situated within the Waynesburg Hills section of the Appalachian Plateaus physiographic province of western Pennsylvania, an area characterized by nearly horizontal beds of sedimentary rocks with gentle folds. The investigation area of spill A is underlain by the middle member of the Lower Permian-age Washington Formation, which consists of cyclic sequences of sandstone, shale, limestone, and coal; the underlying Waynesburg Formation exhibits similar lithologic characteristics. The aquifer system consists of a local (shallow) aquifer system present in areas of high relief that supplies most water wells, and a regional aquifer system found at greater depths that discharges into major river valleys. Primary porosity in the clastic bedrock units is extremely low because pore spaces have been filled with calcareous or siliceous cement. Consequently, groundwater movement is dictated by secondary porosity in the form of vertical and horizontal bedrock fractures, making the aquifer strongly heterogeneous and anisotropic. Stress-relief fracturing is the dominant cause of secondary permeability, with horizontal stress-relief fractures being more numerous in valleys due to greater erosion, while vertical stress-relief fractures are more prevalent in hilltop and hillside settings; the number of fractures generally decreases from valleys to hilltops and with increasing depth. Fracture trace analysis identified 51 potential linear features within the zone of influence, with the dominant fracture orientation trending north-northeast to south-southwest (0°-23°) and a secondary orientation trending north-northwest to south-southeast (155°-180°), both roughly perpendicular to the strike of bedding. Groundwater in the shallow and intermediate aquifers generally flows southeastward from the well pad, while groundwater in the deeper aquifer flows eastward. The resulting contaminant plume is irregular with elongated flow paths due to preferential groundwater flow along linear fracture zones. Vertical impacts appear limited to the lower member of the Washington Formation and the upper, middle, and lower members of the Waynesburg Formation: no impacts associated

with the slow leak were identified at monitoring well MW-11I, which is screened within the underlying Uniontown Formation, nor were impacts identified north or west of the Well Pad.

Text S6. Domestic Well Identification, Recruitment Methods and Community Engagement

As we intended to collect groundwater samples in the predefined hotspot, impoundment, spill, and control areas, homes with private wells in each of these categories meeting the criteria were identified using: 1) county tax parcel data[11,12]; 2) a database containing property records for all tax-paying properties in the USA[13]. Properties in that database are distinguished by category (i.e. business, residential) with the name and address of each property owner. Residences were also cross-referenced with the PA Groundwater Information System (PAGWIS) data to identify which parcels had groundwater wells when there were more than enough residential parcels in an area identified to allow for more targeted outreach.

We used the following methods to recruit participants from the house we identified:

a. mailed recruitment postcards to 336 households
b. worked with a local community group to advertise the study to their members and through their social media channels
c. worked with the Penn State Master Well Owner Network to advertise the study to their volunteers in Washington and Greene counties
d. worked with a Penn State Extension agent to conduct door knocking in our study areas
e. called ~45 homes in the hotspot (Figure 1 in main text) that were in the PAGWIS database
f. to maintain community engagement, conducted additional snowball sampling while in the field by recruiting neighbors, family members of homes already sampled in our areas of interest, and homeowners who expressed interest in our study, even if they were not located in our predefined treatment areas (goodwill samples categorized as “Others” in main text)
g. encouraged all signups to share the study information with their neighbors and on social media

No financial incentives were provided for participation; however, all participating homeowners received their water-quality results.

Homeowner’s informed consent was provided before sample collection, and no personal health information was collected during the process. All household identifiers (e.g., exact well coordinates) were removed from the study’s dataset. For community engagement purposes, we also returned all water-quality results to participating homeowners and hosted a community meeting to explain the findings, answer questions, and provide information about the study.

SI Tables

Table S1. Summary of health standards for drinking water and violation instances

Analyte	US EPA Primary Standard[14]	US EPA Secondary Standard[15]	Analytical Detection Limit	Other Standards	# Sites Exceeding Standard
pH (range)		6.5-8.5	0-14		12
Fluoride	4 mg/L	2 mg/L	0.002 mg/L		0 (1)
Chloride		250 mg/L	0.01 mg/L		5
Sulfate		250 mg/L	0.06 mg/L		2
Bromide			0.01 mg/L	2 mg/L[16]	1
Nitrate	44 mg/L		0.03 mg/L		0
Aluminum		0.2 mg/L	0.01 mg/L		2
Barium	2 mg/L		0.005 mg/L		1
Iron		0.3 mg/L	0.005 mg/L		7
Manganese		0.05 mg/L	0.005 mg/L		19
Strontium			0.005 mg/L	4 mg/L[17]	0
Lithium			0.15 µg/L	10 µg/L[18] 60 µg/L[19]	46 3
Beryllium	4 µg/L		0.05 µg/L		0
Nickel			0.05 µg/L	100 µg/L[17]	0
Copper		1000 µg/L	0.05 µg/L	1300 µg/L[20]	0 (0)
Arsenic	10 µg/L		0.05 µg/L		0
Cadmium	5 µg/L		0.05 µg/L		0
Thallium	2 µg/L		0.25 µg/L		0
Lead			0.05 µg/L	15 µg/L[20]	0
Uranium	30 µg/L		0.05 µg/L		0
Methane				10 mg/L 28 mg/L[21]	2 1
Benzene	5 µg/L		0.04 µg/L		0
Toluene	1000 µg/L		0.04 µg/L		0
Ethylbenzene	700 µg/L		0.04 µg/L		0
Xylenes, total	10,000 µg/L		0.06 µg/L		0
Calc. TDS		500 mg/L			19

Table S2. Statistical summary of all groundwater samples, excluding four surface water samples, one rainwater sample, and two AMD-impacted samples

Analyte	Unit	n	Min	Max	Mean	Median	5th Percentile	25th Percentile	75th Percentile	95th Percentile	MCL/ SMCL	% Exceeding MCL/SMCL
DO	mg/L	90	0.278	9.92	3.955	2.975	0.336	0.669	7.167	9.103	-	-
SC	µS/cm	90	230	3485	782.881	658	428.635	556.25	816.75	1580.8	-	-
pH	pH	90	6.05	8.99	7.135	7.04	6.564	6.885	7.278	8.046	6.5-8.5	8.9% (8)
Alkalinity	mg CaCO3/L	79	43	668	272.746	265	170.13	224.5	304.5	443	-	-
Air [CH_4]	ppm, max	83	5	132	8.241	5	5	5	5	15.9	-	-
F	mg/L	90	0.04	3.52	0.281	0.114	0.057	0.088	0.186	1.331	2	1.1% (1)
Cl	mg/L	90	0.684	697	61.616	16.4	2.12	6.498	67.65	254.95	250	5.6% (5)
SO4	mg/L	90	0.06	225	40.313	32.6	9.493	23.525	44.15	95.975	250	0.0% (0)
Br	mg/L	89	0.014	5.813	0.127	0.034	0.021	0.027	0.054	0.166	2	1.1% (1)
NO3	mg/L	90	0.038	27.8	3.653	1.515	0.108	0.3	6.095	12.27	44	0.0% (0)
Al	mg/L	90	0.01	0.02	0.011	0.01	0.01	0.01	0.01	0.02	0.05-0.2	0.0% (0)
Ba	mg/L	90	0.04	2.05	0.17	0.13	0.05	0.082	0.16	0.31	2	1.1% (1)
Ca	mg/L	90	0.67	295	84.24	84.3	6.81	56.65	105.5	159.45	-	-
Fe	mg/L	90	0.005	2.12	0.058	0.005	0.005	0.005	0.005	0.196	0.3	4.4% (4)
K	mg/L	90	0.03	7.01	1.989	1.855	0.833	1.368	2.56	3.536	-	-
Mg	mg/L	90	0.31	53.7	16.02	14.85	2.228	10.325	20.375	31.265	-	-
Mn	mg/L	90	0.005	0.43	0.036	0.005	0.005	0.005	0.03	0.195	0.05	16.7% (15)
Na	mg/L	90	2.04	622	54.885	15.4	3.436	6.695	57.1	241.35	-	-
P	mg/L	90	0.01	0.29	0.028	0.02	0.01	0.01	0.02	0.07	-	-
Si	mg/L	90	1.05	9.62	5.571	5.32	3.474	4.772	6.212	8.402	-	-
Sr	mg/L	90	0.1	2.14	0.609	0.46	0.14	0.32	0.678	1.648	4	0.0% (0)
Li	µg/L	90	0.27	61.9	11.152	9.86	3.396	6.475	13.175	20.195	10	48.9% (44)
Be	µg/L	90	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	4	0.0% (0)
Ni	µg/L	90	0.05	2.19	0.378	0.275	0.06	0.162	0.46	1.126	100	0.0% (0)
Cu	µg/L	90	0.05	23.2	3.5	2.41	0.059	0.7	4.828	9.772	1000	0.0% (0)
As	µg/L	90	0.05	3.58	0.304	0.11	0.05	0.05	0.188	1.537	10	0.0% (0)
Cd	µg/L	90	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	5	0.0% (0)
Tl	µg/L	90	0.05	1.54	0.091	0.05	0.05	0.05	0.05	0.21	2	0.0% (0)
Pb	µg/L	90	0.05	1.59	0.271	0.185	0.05	0.07	0.358	0.694	15	0.0% (0)
U	µg/L	90	0.05	0.97	0.311	0.26	0.05	0.07	0.478	0.735	30	0.0% (0)
$^{87}Sr/^{86}Sr$	-	80	0.711	0.713	0.712	0.712	0.711	0.711	0.712	0.713	-	-
Benzene	µg/L	84	0.04	0.77	0.113	0.04	0.04	0.04	0.045	0.549	5	0.0% (0)
Toluene	µg/L	84	0.04	3.29	0.432	0.04	0.04	0.04	0.122	3.103	1000	0.0% (0)
Ethylbenzene	µg/L	84	0.04	9.49	1.263	0.04	0.04	0.04	0.11	9.21	700	0.0% (0)
m,p-Xylene	µg/L	84	0.08	0.954	0.105	0.08	0.08	0.08	0.08	0.15	10000	0.0% (0)
o-Xylene	µg/L	84	0.06	0.464	0.074	0.06	0.06	0.06	0.06	0.117	10000	0.0% (0)
Xylene(total)	µg/L	84	0.14	1.418	0.179	0.14	0.14	0.14	0.14	0.267	10000	0.0% (0)
Methane	mg/L	89	0	57	1.195	0.001	0	0	0.009	5.48	10	3.4% (3)
Ethane	mg/L	89	0	0.58	0.016	0	0	0	0	0.032	-	-
Propane	mg/L	89	0	0.005	0	0	0	0	0	0	-	-
$\delta^{13}C\text{-}C_1$	-	8	-77.2	-51.5	-66.5	-65.5	-76.1	-71.2	-64.1	-55.7	-	-
$\delta D\text{-}C_1$	-	8	-219.3	-153.9	-191.9	-196.6	-213.9	-202.7	-184.7	-161.2	-	-
$\delta^{13}C\text{-}C_2$	-	1	-35.2	-35.2	-35.2	-35.2	-35.2	-35.2	-35.2	-35.2	-	-

Table S3. Statistical summary of hotspot (HS) groundwater samples

Analyte	Unit	n	Min	Max	Mean	Median	5th Percentile	25th Percentile	75th Percentile	95th Percentile	MCL/ SMCL	% Exceeding MCL/SMCL
DO	mg/L	30	0.398	9.2	3.724	2.975	0.521	1.03	5.692	8.927	-	-
SC	µS/cm	30	447.6	2392	778.997	671.5	497.865	605.25	836	1219.9	-	-
pH	pH	30	6.37	7.87	7.047	6.99	6.572	6.885	7.198	7.566	6.5-8.5	3.3% (1)
Alkalinity	mg CaCO3/L	27	175	404	271.37	269	194.7	231	305.5	366.7	-	-
Air [CH_4]	ppm, max	28	5	16	5.679	5	5	5	5	9.3	-	-
F	mg/L	30	0.057	1.4	0.196	0.128	0.068	0.095	0.184	0.356	2	0.0% (0)
Cl	mg/L	30	1.45	568	68.906	16.9	3.644	8.645	88.05	228.85	250	6.7% (2)
SO4	mg/L	30	17.1	82.5	38.367	33.8	20.36	26.2	43.35	73.305	250	0.0% (0)
Br	mg/L	30	0.014	0.124	0.041	0.034	0.02	0.025	0.044	0.084	2	0.0% (0)
NO3	mg/L	30	0.143	26.8	4.841	2.905	0.166	0.876	6.55	14.25	44	0.0% (0)
Al	mg/L	30	0.01	0.02	0.011	0.01	0.01	0.01	0.01	0.015	0.05-0.2	0.0% (0)
Ba	mg/L	30	0.04	0.24	0.139	0.135	0.05	0.1	0.17	0.24	2	0.0% (0)
Ca	mg/L	30	33.8	219	92.54	88.45	40.945	60.6	116.75	159.45	-	-
Fe	mg/L	30	0.005	0.13	0.012	0.005	0.005	0.005	0.005	0.037	0.3	0.0% (0)
K	mg/L	30	0.03	3.59	2.198	2.325	1.128	1.625	2.685	3.375	-	-
Mg	mg/L	30	6.17	37.1	18.987	17.4	8.952	13.1	25	32.09	-	-
Mn	mg/L	30	0.005	0.43	0.041	0.005	0.005	0.005	0.01	0.266	0.05	13.3% (4)
Na	mg/L	30	3.4	193	41.17	21.6	4.358	5.873	62.725	120.855	-	-
P	mg/L	30	0.01	0.04	0.018	0.02	0.01	0.01	0.02	0.035	-	-
Si	mg/L	30	4.07	9.62	5.812	5.325	4.598	4.93	5.772	9.175	-	-
Sr	mg/L	30	0.24	2.14	0.697	0.49	0.254	0.39	0.9	1.624	4	0.0% (0)
Li	µg/L	30	4.79	38.03	12.009	11.85	4.854	6.698	13.975	27.12	10	53.3% (16)
Be	µg/L	30	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	4	0.0% (0)
Ni	µg/L	30	0.08	1.23	0.414	0.275	0.098	0.182	0.46	1.178	100	0.0% (0)
Cu	µg/L	30	0.05	23.2	3.882	2.8	0.151	1.188	4.842	10.9	1000	0.0% (0)
As	µg/L	30	0.05	2.62	0.262	0.14	0.05	0.055	0.262	0.546	10	0.0% (0)
Cd	µg/L	30	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	5	0.0% (0)
Tl	µg/L	30	0.05	0.21	0.062	0.05	0.05	0.05	0.05	0.132	2	0.0% (0)
Pb	µg/L	30	0.05	0.64	0.236	0.165	0.05	0.085	0.358	0.546	15	0.0% (0)
U	µg/L	30	0.05	0.94	0.36	0.365	0.05	0.173	0.538	0.68	30	0.0% (0)
$^{87}Sr/^{86}Sr$	-	29	0.711	0.712	0.712	0.712	0.711	0.711	0.712	0.712	-	-
Benzene	µg/L	29	0.04	0.74	0.099	0.04	0.04	0.04	0.04	0.45	5	0.0% (0)
Toluene	µg/L	29	0.04	3.13	0.29	0.04	0.04	0.04	0.04	2.132	1000	0.0% (0)
Ethylbenzene	µg/L	29	0.04	9.21	0.677	0.04	0.04	0.04	0.04	5.554	700	0.0% (0)
m,p-Xylene	µg/L	29	0.08	0.21	0.088	0.08	0.08	0.08	0.08	0.128	10000	0.0% (0)
o-Xylene	µg/L	29	0.06	0.28	0.072	0.06	0.06	0.06	0.06	0.118	10000	0.0% (0)
Xylene(total)	µg/L	29	0.14	0.36	0.16	0.14	0.14	0.14	0.14	0.3	10000	0.0% (0)
Methane	mg/L	30	0	0.041	0.005	0.001	0	0	0.004	0.024	10	0.0% (0)
Ethane	mg/L	30	0	0.009	0	0	0	0	0	0	-	-
Propane	mg/L	30	0	0.003	0	0	0	0	0	0	-	-
$\delta^{13}C\text{-}C_1$	-	0	-	-	-	-	-	-	-	-	-	-
$\delta D\text{-}C_1$	-	0	-	-	-	-	-	-	-	-	-	-
$\delta^{13}C\text{-}C_2$	-	0	-	-	-	-	-	-	-	-	-	-

Table S4. Statistical summary of impoundment (I) groundwater samples

Analyte	Unit	n	Min	Max	Mean	Median	5th Percentile	25th Percentile	75th Percentile	95th Percentile	MCL/ SMCL	% Exceeding MCL/SMCL
DO	mg/L	24	0.297	9.81	2.328	0.862	0.341	0.41	2.21	8.446	-	-
SC	µS/cm	24	406.9	1539	717.162	663.5	534.55	613.25	723.25	976.55	-	-
pH	pH	24	6.27	7.98	7.132	7.035	6.693	6.948	7.252	7.921	6.5-8.5	4.2% (1)
Alkalinity	mg CaCO3/L	21	178	404	285.381	288	182	268	307	404	-	-
Air [CH_4]	ppm, max	22	5	5	5	5	5	5	5	5	-	-
F	mg/L	24	0.042	1.4	0.256	0.116	0.058	0.096	0.155	1.091	2	0.0% (0)
Cl	mg/L	24	2.03	307	41.998	17.4	4.225	8.855	43.55	126.05	250	4.2% (1)
SO4	mg/L	24	6.61	195	38.721	31.3	15.06	21.4	41.875	71.445	250	0.0% (0)
Br	mg/L	24	0.02	0.187	0.052	0.034	0.02	0.026	0.062	0.129	2	0.0% (0)
NO3	mg/L	24	0.092	26.8	3.542	0.404	0.101	0.202	3.555	15.025	44	0.0% (0)
Al	mg/L	24	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.05-0.2	0.0% (0)
Ba	mg/L	24	0.06	0.43	0.153	0.135	0.06	0.108	0.182	0.24	2	0.0% (0)
Ca	mg/L	24	13.3	214	89.238	91.3	27.385	72.375	106.25	127	-	-
Fe	mg/L	24	0.005	0.45	0.05	0.005	0.005	0.005	0.018	0.232	0.3	4.2% (1)
K	mg/L	24	0.06	3.76	1.885	1.77	0.3	1.465	2.335	3.236	-	-
Mg	mg/L	24	2.86	35.7	14.971	14.15	4.085	10.04	18.8	30.62	-	-
Mn	mg/L	24	0.005	0.43	0.059	0.01	0.005	0.005	0.062	0.258	0.05	29.2% (7)
Na	mg/L	24	2.61	192	38.797	11.47	4.359	6.528	57.925	136.2	-	-
P	mg/L	24	0.01	0.04	0.017	0.015	0.01	0.01	0.02	0.038	-	-
Si	mg/L	24	2.92	9.62	5.996	5.48	4.406	5.118	7.138	8.264	-	-
Sr	mg/L	24	0.14	2.14	0.701	0.505	0.212	0.39	0.948	1.823	4	0.0% (0)
Li	µg/L	24	3.27	20.6	10.972	11.65	3.696	7.9	13.375	17.84	10	62.5% (15)
Be	µg/L	24	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	4	0.0% (0)
Ni	µg/L	24	0.08	1.11	0.293	0.21	0.086	0.14	0.29	0.94	100	0.0% (0)
Cu	µg/L	24	0.09	5.41	1.829	1.205	0.102	0.328	2.755	4.994	1000	0.0% (0)
As	µg/L	24	0.05	0.53	0.138	0.115	0.05	0.05	0.18	0.262	10	0.0% (0)
Cd	µg/L	24	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	5	0.0% (0)
Tl	µg/L	24	0.05	0.21	0.078	0.05	0.05	0.05	0.053	0.195	2	0.0% (0)
Pb	µg/L	24	0.05	1.59	0.397	0.31	0.053	0.195	0.44	1.194	15	0.0% (0)
U	µg/L	24	0.05	0.94	0.258	0.19	0.05	0.057	0.36	0.625	30	0.0% (0)
$^{87}Sr/^{86}Sr$	-	24	0.711	0.713	0.712	0.712	0.711	0.711	0.712	0.713	-	-
Benzene	µg/L	23	0.04	0.77	0.245	0.04	0.04	0.04	0.48	0.739	5	0.0% (0)
Toluene	µg/L	23	0.04	3.29	1.025	0.1	0.04	0.04	2.92	3.197	1000	0.0% (0)
Ethylbenzene	µg/L	23	0.04	9.49	3.27	0.11	0.04	0.04	9.135	9.379	700	0.0% (0)
m,p-Xylene	µg/L	23	0.08	0.41	0.1	0.08	0.08	0.08	0.08	0.138	10000	0.0% (0)
o-Xylene	µg/L	23	0.06	0.28	0.078	0.06	0.06	0.06	0.06	0.145	10000	0.0% (0)
Xylene(total)	µg/L	23	0.14	0.56	0.178	0.14	0.14	0.14	0.14	0.348	10000	0.0% (0)
Methane	mg/L	24	0	4.7	0.245	0.001	0	0	0.009	0.853	10	0.0% (0)
Ethane	mg/L	24	0	0.019	0.001	0	0	0	0	0	-	-
Propane	mg/L	24	0	0	0	0	0	0	0	0	-	-
$\delta^{13}C\text{-}C_1$	-	2	-77.16	-74.26	-75.71	-75.71	-77.015	-76.435	-74.985	-74.405	-	-
$\delta D\text{-}C_1$	-	2	-204	-202.3	-203.15	-203.15	-203.915	-203.575	-202.725	-202.385	-	-
$\delta^{13}C\text{-}C_2$	-	0	-	-	-	-	-	-	-	-	-	-

Table S5. Statistical summary of spill (S) groundwater samples

Analyte	Unit	n	Min	Max	Mean	Median	5th Percentile	25th Percentile	75th Percentile	95th Percentile	MCL/ SMCL	% Exceeding MCL/SMCL
DO	mg/L	14	0.325	7.26	3.322	3.31	0.329	0.426	6.325	7.013	-	-
SC	µS/cm	14	431	3485	864.521	603	472.795	550.25	682.25	2269.5	-	-
pH	pH	14	6.05	8.97	7.097	7.04	6.492	6.872	7.165	7.969	6.5-8.5	14.3% (2)
Alkalinity	mg CaCO3/L	13	88	541	288.692	263	128.8	225	319	532.6	-	-
Air [CH_4]	ppm, max	12	5	63	11.667	5	5	5	10.25	37.15	-	-
F	mg/L	14	0.057	3.52	0.476	0.108	0.065	0.084	0.276	2.161	2	7.1% (1)
Cl	mg/L	14	3.55	697	78.019	18.35	3.881	5.568	25.75	354.45	250	7.1% (1)
SO4	mg/L	14	1.1	110	36.194	28.3	6.456	21.55	45.725	85.365	250	0.0% (0)
Br	mg/L	14	0.015	5.813	0.451	0.032	0.02	0.028	0.034	2.116	2	7.1% (1)
NO3	mg/L	14	0.038	10.7	2.927	1.495	0.08	0.32	5.315	8.633	44	0.0% (0)
Al	mg/L	14	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.05-0.2	0.0% (0)
Ba	mg/L	14	0.05	2.05	0.309	0.14	0.063	0.092	0.168	1.244	2	7.1% (1)
Ca	mg/L	14	0.67	106	59.155	72.75	12.91	38.9	75.95	91.245	-	-
Fe	mg/L	14	0.005	0.86	0.068	0.005	0.005	0.005	0.005	0.314	0.3	7.1% (1)
K	mg/L	14	1.16	7.01	2.583	2.25	1.186	1.505	2.652	5.846	-	-
Mg	mg/L	14	0.31	28.5	15.47	12.05	5.588	9.995	23.875	26.615	-	-
Mn	mg/L	14	0.005	0.2	0.033	0.01	0.005	0.005	0.032	0.128	0.05	21.4% (3)
Na	mg/L	14	4.77	622	89.652	17.85	5.823	14.325	46.6	432.85	-	-
P	mg/L	14	0.01	0.07	0.03	0.02	0.016	0.02	0.028	0.07	-	-
Si	mg/L	14	3.42	8.46	5.287	5.265	3.452	4.455	5.86	7.413	-	-
Sr	mg/L	14	0.1	2.1	0.589	0.505	0.198	0.3	0.655	1.248	4	0.0% (0)
Li	µg/L	14	3.07	61.9	11.472	7.73	3.902	5.62	9.688	30.18	10	21.4% (3)
Be	µg/L	14	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	4	0.0% (0)
Ni	µg/L	14	0.1	2.19	0.5	0.35	0.132	0.268	0.498	1.273	100	0.0% (0)
Cu	µg/L	14	0.05	23.2	6.386	4.16	0.414	2.115	6.25	22.55	1000	0.0% (0)
As	µg/L	14	0.05	1.78	0.221	0.095	0.05	0.053	0.16	0.753	10	0.0% (0)
Cd	µg/L	14	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	5	0.0% (0)
Tl	µg/L	14	0.05	0.21	0.062	0.05	0.05	0.05	0.05	0.112	2	0.0% (0)
Pb	µg/L	14	0.05	0.55	0.189	0.14	0.05	0.112	0.262	0.374	15	0.0% (0)
U	µg/L	14	0.05	0.78	0.312	0.26	0.05	0.078	0.4	0.708	30	0.0% (0)
$^{87}Sr/^{86}Sr$	-	5	0.711	0.713	0.712	0.712	0.711	0.712	0.713	0.713	-	-
Benzene	µg/L	14	0.04	0.217	0.069	0.04	0.04	0.04	0.055	0.18	5	0.0% (0)
Toluene	µg/L	14	0.04	1.562	0.176	0.04	0.04	0.04	0.085	0.696	1000	0.0% (0)
Ethylbenzene	µg/L	14	0.04	0.259	0.072	0.04	0.04	0.04	0.092	0.175	700	0.0% (0)
m,p-Xylene	µg/L	14	0.08	0.954	0.159	0.08	0.08	0.08	0.11	0.47	10000	0.0% (0)
o-Xylene	µg/L	14	0.06	0.464	0.098	0.06	0.06	0.06	0.075	0.247	10000	0.0% (0)
Xylene(total)	µg/L	14	0.14	1.418	0.257	0.14	0.14	0.14	0.175	0.717	10000	0.0% (0)
Methane	mg/L	14	0	57	4.209	0.012	0	0.001	0.112	20.925	10	7.1% (1)
Ethane	mg/L	14	0	0.58	0.042	0	0	0	0	0.204	-	-
Propane	mg/L	14	0	0	0	0	0	0	0	0	-	-
$\delta^{13}C\text{-}C_1$	-	2	-65.87	-65.2	-65.535	-65.535	-65.836	-65.702	-65.368	-65.234	-	-
$\delta D\text{-}C_1$	-	2	-219.3	-153.9	-186.6	-186.6	-216.03	-202.95	-170.25	-157.17	-	-
$\delta^{13}C\text{-}C_2$	-	0	-	-	-	-	-	-	-	-	-	-

Table S6. Statistical summary of control (C) groundwater samples

Analyte	Unit	n	Min	Max	Mean	Median	5th Percentile	25th Percentile	75th Percentile	95th Percentile	MCL/ SMCL	% Exceeding MCL/SMCL
DO	mg/L	8	0.345	9.92	4.703	4.153	0.345	0.578	9.008	9.619	-	-
SC	µS/cm	8	468.9	970	638.362	572	479.435	539.5	697.5	915.05	-	-
pH	pH	8	6.67	8.1	7.232	7.155	6.761	7.012	7.388	7.869	6.5-8.5	0.0% (0)
Alkalinity	mg CaCO3/L	8	189	370	277.65	273.6	204.4	253.25	310	350.05	-	-
Air [CH_4]	ppm, max	5	5	132	32.6	5	5	5	16	108.8	-	-
F	mg/L	8	0.068	0.999	0.258	0.15	0.074	0.097	0.239	0.748	2	0.0% (0)
Cl	mg/L	8	1.59	108	21.804	7.29	2.724	6.075	14.055	80.805	250	0.0% (0)
SO4	mg/L	8	0.077	48.7	29.972	29.8	7.295	21	44.55	47.51	250	0.0% (0)
Br	mg/L	8	0.022	0.262	0.066	0.029	0.023	0.027	0.06	0.199	2	0.0% (0)
NO3-NO3	mg/L	8	0.147	2.06	1.073	1.205	0.158	0.274	1.66	2.004	44	0.0% (0)
Al	mg/L	8	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.05-0.2	0.0% (0)
Ba	mg/L	8	0.06	1.03	0.222	0.11	0.064	0.078	0.155	0.729	2	0.0% (0)
Ca	mg/L	8	8.35	108	78.469	95.35	21.738	56.725	107	107.65	-	-
Fe	mg/L	8	0.005	2.12	0.269	0.005	0.005	0.005	0.005	1.38	0.3	12.5% (1)
K	mg/L	8	0.95	2.59	1.6	1.425	0.96	1.122	2.08	2.464	-	-
Mg	mg/L	8	3.1	19.9	13.69	13.7	5.487	10.205	19.375	19.795	-	-
Mn	mg/L	8	0.005	0.15	0.032	0.008	0.005	0.005	0.03	0.118	0.05	25.0% (2)
Na	mg/L	8	3.48	191	37.169	10.75	3.529	3.868	34.35	138.85	-	-
P	mg/L	8	0.01	0.17	0.042	0.025	0.014	0.02	0.032	0.124	-	-
Si	mg/L	8	4.2	8.96	5.58	4.855	4.221	4.56	6.042	8.34	-	-
Sr	mg/L	8	0.27	1.77	0.639	0.385	0.288	0.342	0.663	1.542	4	0.0% (0)
Li	µg/L	8	3.72	16.7	9.214	7.625	4.27	6.16	11.875	16.35	10	37.5% (3)
Be	µg/L	8	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	4	0.0% (0)
Ni	µg/L	8	0.05	0.54	0.279	0.27	0.089	0.175	0.355	0.501	100	0.0% (0)
Cu	µg/L	8	0.05	5.61	1.842	1.445	0.057	0.235	2.472	4.976	1000	0.0% (0)
As	µg/L	8	0.05	3.58	1.161	0.095	0.05	0.05	2.312	3.528	10	0.0% (0)
Cd	µg/L	8	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	5	0.0% (0)
Tl	µg/L	8	0.05	0.38	0.13	0.05	0.05	0.05	0.158	0.352	2	0.0% (0)
Pb	µg/L	8	0.05	0.36	0.166	0.055	0.05	0.05	0.352	0.36	15	0.0% (0)
U	µg/L	8	0.05	0.52	0.195	0.18	0.05	0.05	0.262	0.432	30	0.0% (0)
$^{87}Sr/^{86}Sr$	-	8	0.711	0.712	0.712	0.712	0.711	0.711	0.712	0.712	-	-
Benzene	µg/L	8	0.04	0.14	0.053	0.04	0.04	0.04	0.04	0.105	5	0.0% (0)
Toluene	µg/L	8	0.04	2.86	0.419	0.04	0.04	0.04	0.128	1.922	1000	0.0% (0)
Ethylbenzene	µg/L	8	0.04	9.21	2.342	0.075	0.04	0.04	2.37	9.189	700	0.0% (0)
m,p-Xylene	µg/L	8	0.08	0.15	0.094	0.08	0.08	0.08	0.09	0.139	10000	0.0% (0)
o-Xylene	µg/L	8	0.06	0.1	0.065	0.06	0.06	0.06	0.06	0.086	10000	0.0% (0)
Xylene(total)	µg/L	8	0.14	0.25	0.159	0.14	0.14	0.14	0.15	0.225	10000	0.0% (0)
Methane	mg/L	8	0	13	1.628	0.001	0	0	0.006	8.456	10	12.5% (1)
Ethane	mg/L	8	0	0.44	0.055	0	0	0	0	0.286	-	-
Propane	mg/L	8	0	0	0	0	0	0	0	0	-	-
$\delta^{13}C\text{-}C_1$	-	1	-51.5	-51.5	-51.5	-51.5	-51.5	-51.5	-51.5	-51.5	-	-
$\delta D\text{-}C_1$	-	1	-174.7	-174.7	-174.7	-174.7	-174.7	-174.7	-174.7	-174.7	-	-
$\delta^{13}C\text{-}C_2$	-	1	-35.2	-35.2	-35.2	-35.2	-35.2	-35.2	-35.2	-35.2	-	-

Table S7. One-sided test results of Wilcoxon-Mann-Whitney rank sum (WMW) test and Brunner-Munzel (BM) tests for all data (springs and wells)

Compared Dataset	Significant difference	WMW	BM
HS vs. C	HS > C	NO_3, K, U	Cl, NO_3, K, U
	HS < C	P, Ethylbenzene	P
I vs. C	I > C	Cl, Pb	Pb, Benzene
	I < C	P	P
S vs. C	S > C	K, Cu	K, Cu
	S < C	-	-

Table S8. One-sided test results of Wilcoxon-Mann-Whitney rank sum (WMW) test and Brunner-Munzel (BM) tests for well data only

Compared Dataset	Significant difference	WMW	BM
HS vs. C	HS > C	Cl, K, Mg	Cl, K, Mg
	HS < C	P, Ethylbenzene	P, Ethylbenzene
I vs. C	I > C	Cl, Pb	Pb
	I < C	P	P
S vs. C	S > C	K, Cu	K, Cu
	S < C	-	-

Table S9. One-sided test results of Brunner-Munzel (BM) tests for comparison between newly collected groundwater samples (2024 SWPA) and SN dataset in Washington County

Compared Dataset	Significant difference	BM
2024 SWPA (WA) vs. SN (WA)	2024 SWPA > SN	As, Cd, Ca, Pb, Li, Mg, K, Na, Cl, SC, Sr, Ba
	2024 SWPA < SN	Br, Fe, Mn, SO4, Methane, Ethane, Propane, Benzene, Toluene, Ethylbenzene, Xylene

Table S10. One-sided test results of Wilcoxon-Mann-Whitney rank sum (WMW) test and Brunner-Munzel (BM) tests for comparison between valley and ridge (springs and wells)

Compared Dataset	Significant difference	WMW	BM
Valley vs. Ridge	Valley > Ridge	Ba, methane	Ba, methane
	Valley < Ridge	SC, SO4, Ca, Li, Ni	SC, SO4, Al, Ca, Li, Ni

Table S11. Brine-related analyte concentrations for Sample_003, SN samples within 1 km, and PADEP samples within 1.3 km

Analyte	Sample_003	Closest SN Sample[1]	Nearby SN Samples[2] (Min)	Nearby SN Samples[2] (Median)	Nearby SN Samples[2] (Max)	Nearby PADEP Samples[2] (Min)	Nearby PADEP Samples[2] (Median)	Nearby PADEP Samples[2] (Max)
SC (µS/cm)	501	462	93.5	542	1360	168	1145	25500
Na (mg/L)	6.39	6.22	1.4	14.3	287	-	-	-
Cl (mg/L)	12.5	17.8	2.5	7	112	2.46	32.7	920
Ba (mg/L)	0.16	0.123	0.025	0.088	0.182	0.01	0.362	13.9
SO4 (mg/L)	25.3	32	2	40.65	380	-	-	-
Sr (mg/L)	0.4	0.433	0.037	0.454	1.52	0.051	1.05	76.4
Br (mg/L)	0.023	-	0.2	0.2	0.28	0.072	0.362	102
Fe (mg/L)	0.005	0.025	0.01	0.13	14.4	0.185	0.185	18.5
Methane (mg/L)	0.001	2.5	0.002	2.5	6.91	-	-	-

[1]SN sample collected within 8.56 m on 2013-11-15. Given the small distance, we treated sample_003 and the nearest SN sample from the same sampling site

[2]SN samples collected <1km from Sample_003 and PADEP samples collected <1.3km from Sample_003

Table S12. Brine-related analyte concentrations for Sample_013-3 and SN samples within 1 km

Analyte	Sample 013-3	Closest SN Sample[1]	Nearby Samples[2] (Min)	Nearby Samples[2] (Median)	Nearby Samples [2] (Max)
SC (µS/cm)	495.3	549	40.9	542.95	905
Na (mg/L)	4.77	50.3	1.59	10.215	129
Cl (mg/L)	3.55	5	2.6	5	36.8
Ba (mg/L)	0.17	0.104	0.019	0.094	0.183
SO4 (mg/L)	26.2	41.4	5	38.9	229
Sr (mg/L)	0.26	0.56	0.026	0.561	0.973
Br (mg/L)	0.024	-	0.2	0.2	0.2
Fe (mg/L)	0.005	0.188	0.02	0.144	3.6
Methane (mg/L)	0.014	2.5	0.002	2.5	2.5

[1]SN sample collected within 632 m on 2013-11-15

[2]SN samples collected <1km from Sample_013-3

Table S13. Brine-related analyte concentrations for Sample_042 and SN samples within 1 km

Analyte	Sample_042	Closest SN Sample[1]	Nearby Samples[2] (Min)	Nearby Samples[2] (Median)	Nearby Samples[2] (Max)
SC (µS/cm)	671	533	174.5	542.95	652
Na (mg/L)	76.3	7.63	4.1	15.15	80.3
Cl (mg/L)	16.2	7.65	2.6	5	22.9
Ba (mg/L)	0.16	0.099	0.08	0.099	0.183
SO4 (mg/L)	32.9	35.2	14.9	36.6	60
Sr (mg/L)	0.46	0.583	0.183	0.709	1.14
Br (mg/L)	0.027	-	0.2	0.2	0.2
Fe (mg/L)	0.005	0.034	0.01	0.086	2.1
Methane (mg/L)	0.027	2.5	0.002	2.5	2.5

[1]SN sample collected within 500 m on 2013-11-15

[2]SN samples collected <1km from Sample_042

Table S14. Brine-related analyte concentrations for Sample_082 and SN samples within 1 km

Analyte	Sample 082	Closest SN Sample[1]	Nearby Samples[2] (Min)	Nearby Samples[2] (Median)	Nearby Samples[2] (Max)
SC (µS/cm)	3485	2027	349	785	4369
Na (mg/L)	622	423.43	8.227	31.434	423.43
Cl (mg/L)	697	318.9	5	11	318.9
Ba (mg/L)	2.05	1.251	0.02	0.074	1.251
SO4 (mg/L)	9.68	19	19	96	575
Sr (mg/L)	2.1	1.257	0.201	0.877	2.103
Br (mg/L)	5.813	-	-	-	-
Fe (mg/L)	0.005	0.99	0.01	0.049	0.99
Methane (mg/L)	0.14	2.5	2.5	2.5	2.5

[1]SN sample collected within 6.75 m on 2011-05-11. Given the small distance, we treated sample_082 and the nearest SN sample from the same sampling site

[2]SN samples collected <1km from Sample_082

Table S15. Brine-related analyte concentrations for Sample_090 and SN samples within 1 km

Analyte	Sample_090	Closest SN Sample[1]	Nearby Samples[2] (Min)	Nearby Samples[2] (Median)	Nearby Samples[2] (Max)
SC (µS/cm)	551	1885.7	166.1	708.75	6500
Na (mg/L)	47.3	462	0.5	50.8	1560
Cl (mg/L)	80.7	244	5	34	1950
Ba (mg/L)	0.07	0.413	0.005	0.203	5.14
SO4 (mg/L)	47.8	5	5	20.75	188
Sr (mg/L)	0.25	0.319	0.01	0.388	6.51
Br (mg/L)	0.034	-	-	-	-
Fe (mg/L)	0.02	0.01	0.01	0.1	189
Methane (mg/L)	0.003	51.1	2.5	2.5	78.2

[1]SN sample collected within 2.89 m on 2012-10-18.

[2]SN samples collected <1km from Sample_090

Table S16. Brine-related analyte concentrations for Sample_083 and SN samples within 1 km

Analyte	Sample_083	Closest SN Sample[1]	Nearby Samples[2] (Min)	Nearby Samples[2] (Median)	Nearby Samples[2] (Max)
SC (µS/cm)	621	466	101.8	482.2	833.8
Na (mg/L)	33.1	3.93	1.85	4.235	118
Cl (mg/L)	23.8	10	5	14.5	149
Ba (mg/L)	0.09	0.067	0.035	0.084	0.318
SO4 (mg/L)	110	37.5	10.3	28.1	92.5
Sr (mg/L)	0.27	0.221	0.052	0.244	0.672
Br (mg/L)	0.059	-	0.1	1.39	2.68
Fe (mg/L)	0.005	0.06	0.02	0.224	16.4
Methane (mg/L)	0	0.23	0.23	0.23	0.23

[1]SN sample collected within 678 m on 2016-01-27.

[2]SN samples collected <1km from Sample_083

Table S17. Fixed effects regression coefficients for groundwater analytes versus distance to the closest spill (km), excluding Sample_082. Covariates include TPI, season, and proximity (within 1 km) to COG wells, mines, and roads (* denote p<0.05)

Analyte	Spill without 082	COG_1km	Mine_1km	Road_1km	TPI	Season
SC	-0.01	-0.074	0.011	0.129	-0.212*	-0.082
Na	**-0.104***	-0.379	-0.018	0.129	-0.285	-0.261
Cl	-0.053	0.033	0.04	0.321	-0.379	-0.413
Ba	**-0.008***	0.033	-0.054*	0.031	0.015	-0.051
SO4	0.087*	0.122	0.534*	-0.221	-0.25	0.251
Sr	-0.001	0.039	-0.005	-0.026	-0.031	0.047
Br	-0.001	-0.011	0.011	0.002	-0.003	-0.024
Fe	**-0.012***	0.041	-0.09*	0.067*	-0.034	-0.023
Methane	**-0.068***	-0.041	-0.264	0.322*	-0.139	-0.165

SI Figures

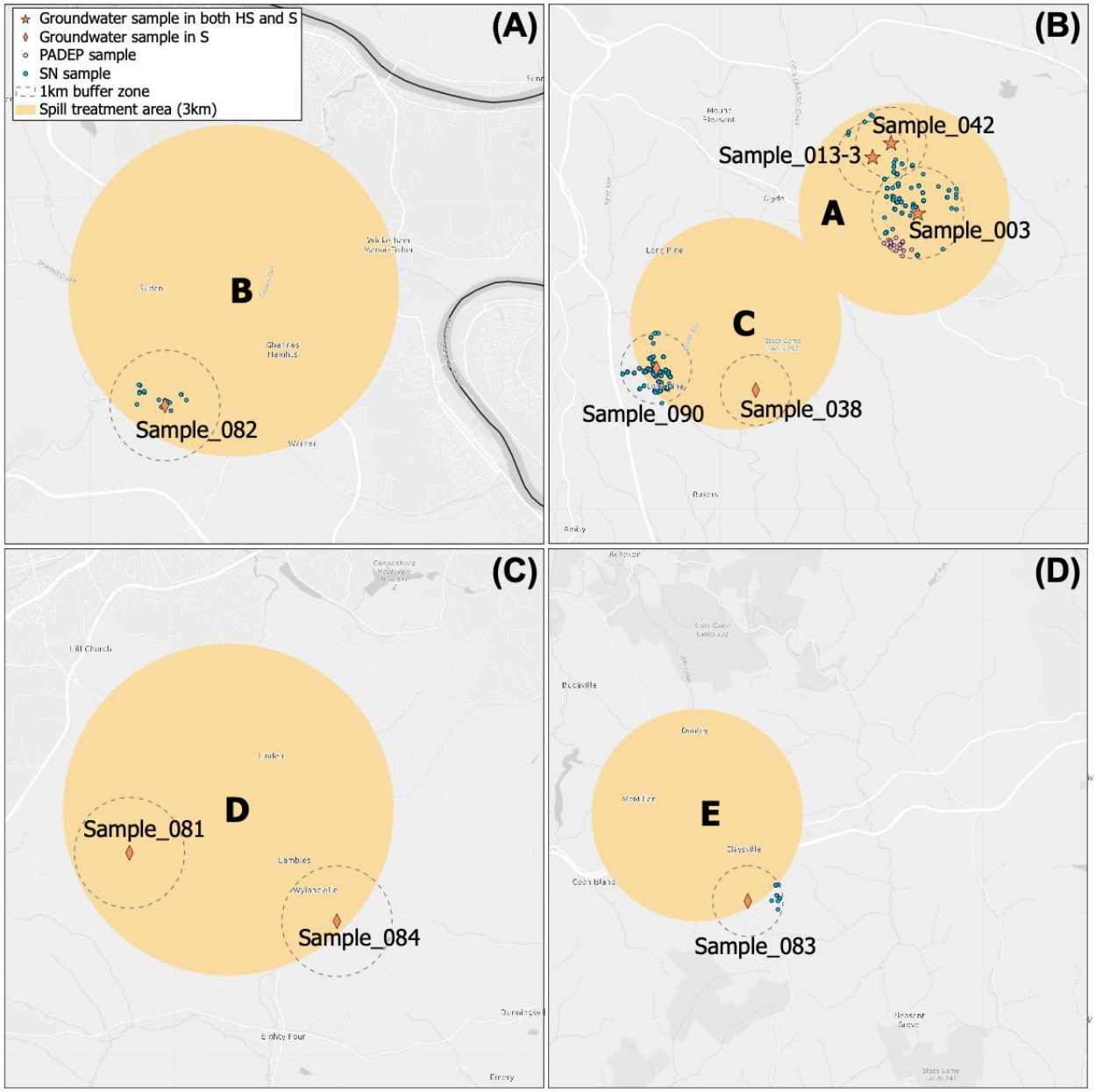

Figure S1. Spatial distribution of Shale Network (SN) and PADEP groundwater samples within 1 km (SN) and 1.3 km (PADEP) of six 2024 SWPA groundwater samples located in treatment areas associated with four of the five selected brownfield sites. The five brownfield sites, all located on oil and gas well pads, were investigated for local spill impacts and are marked with letters A–E. In each panel, the diameter of the brown circle is 3 km.

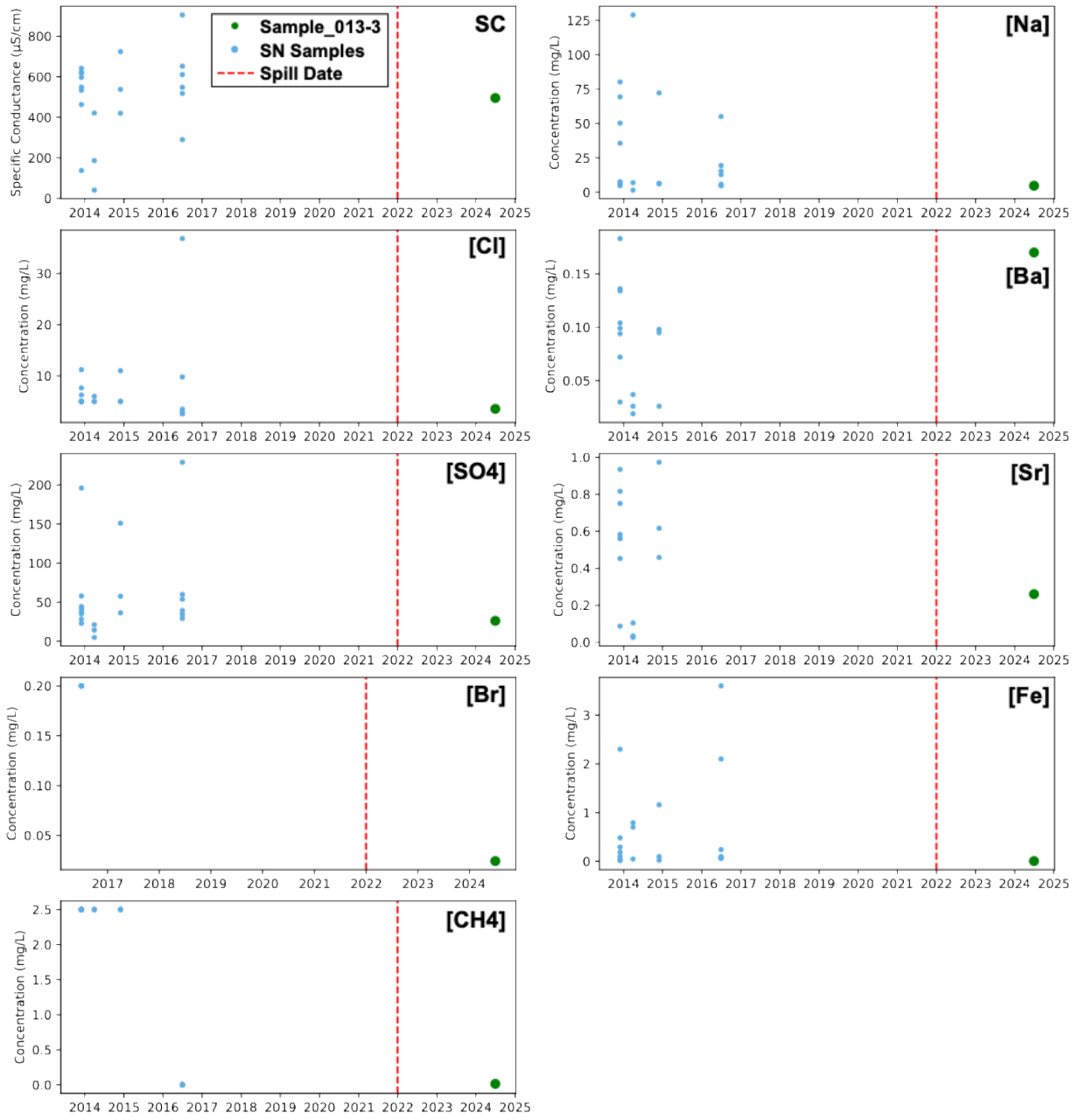

Figure S2. Scatter plots of brine-related species concentration vs. time (year) for Sample_013-3 (collected near spill A) and SN dataset samples (within 1km).

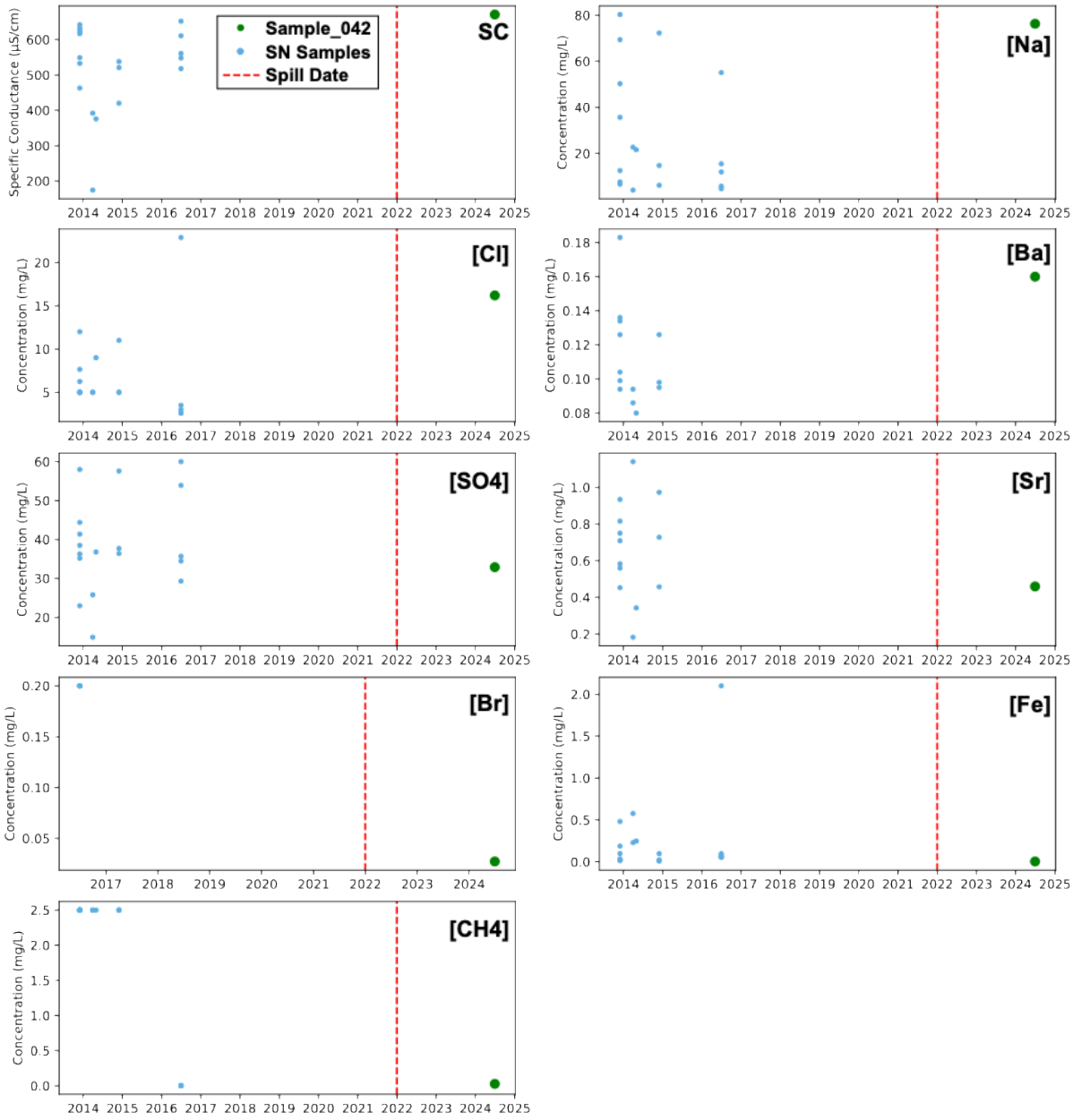

Figure S3. Scatter plots of brine-related species concentration vs. time (year) for Sample_042 (collected near spill A) and SN dataset samples (within 1km).

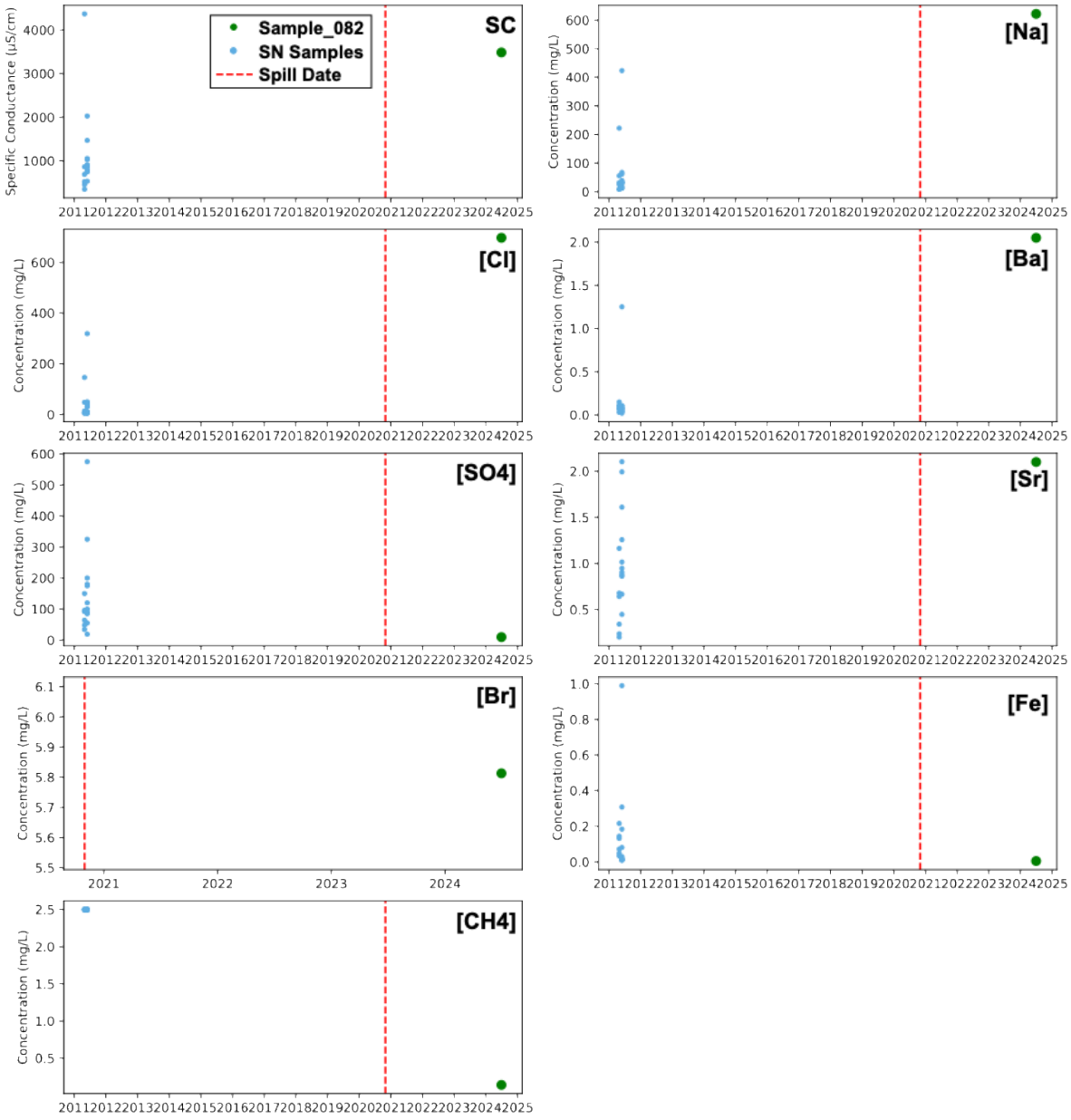

Figure S4. Scatter plots of brine-related species concentration vs. time (year) for Sample_082 (collected near spill B) and SN dataset samples (within 1km).

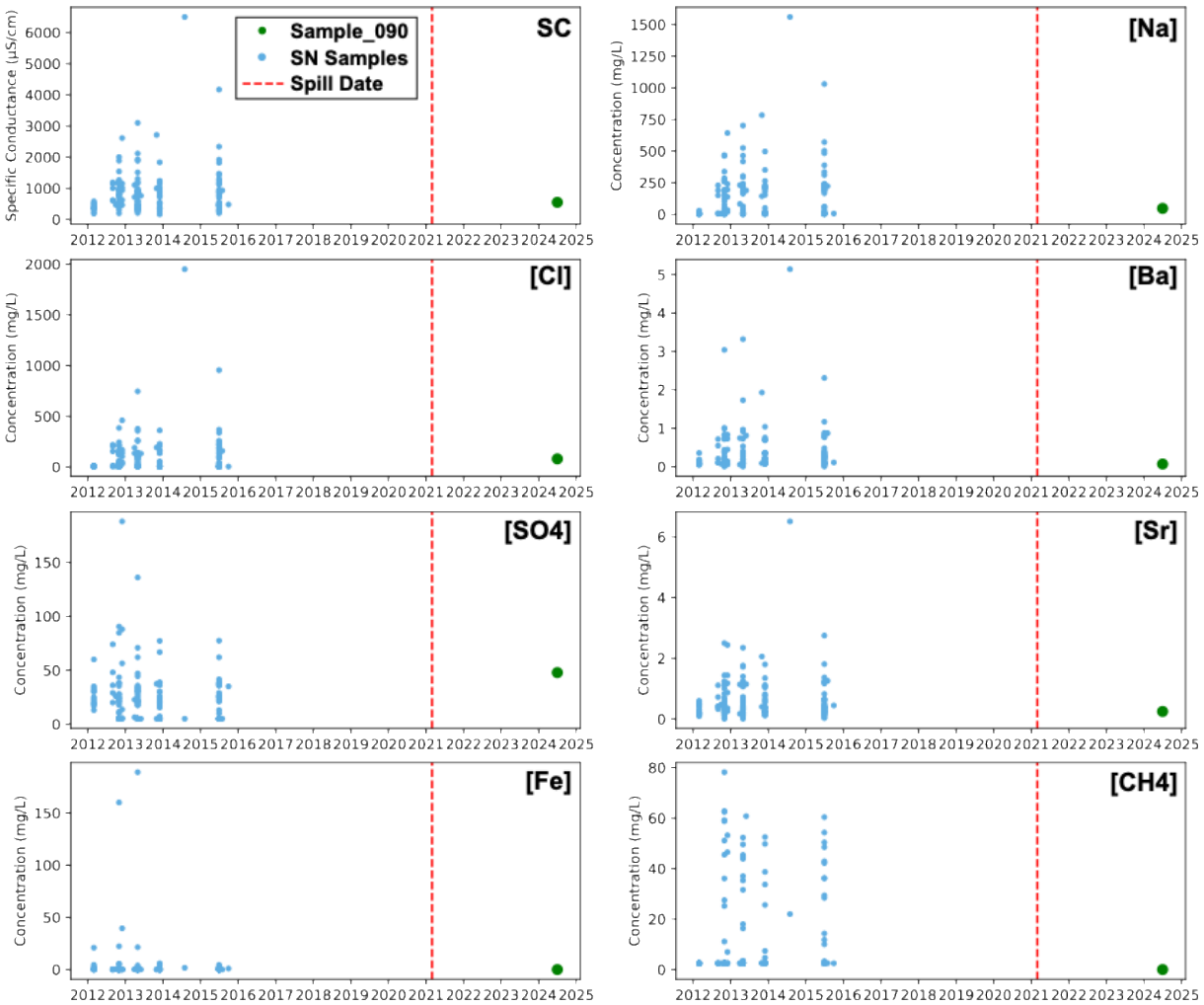

Figure S5. Scatter plots of brine-related species concentration vs. time (year) for Sample_090 (collected near spill C) and SN dataset samples (within 1km).

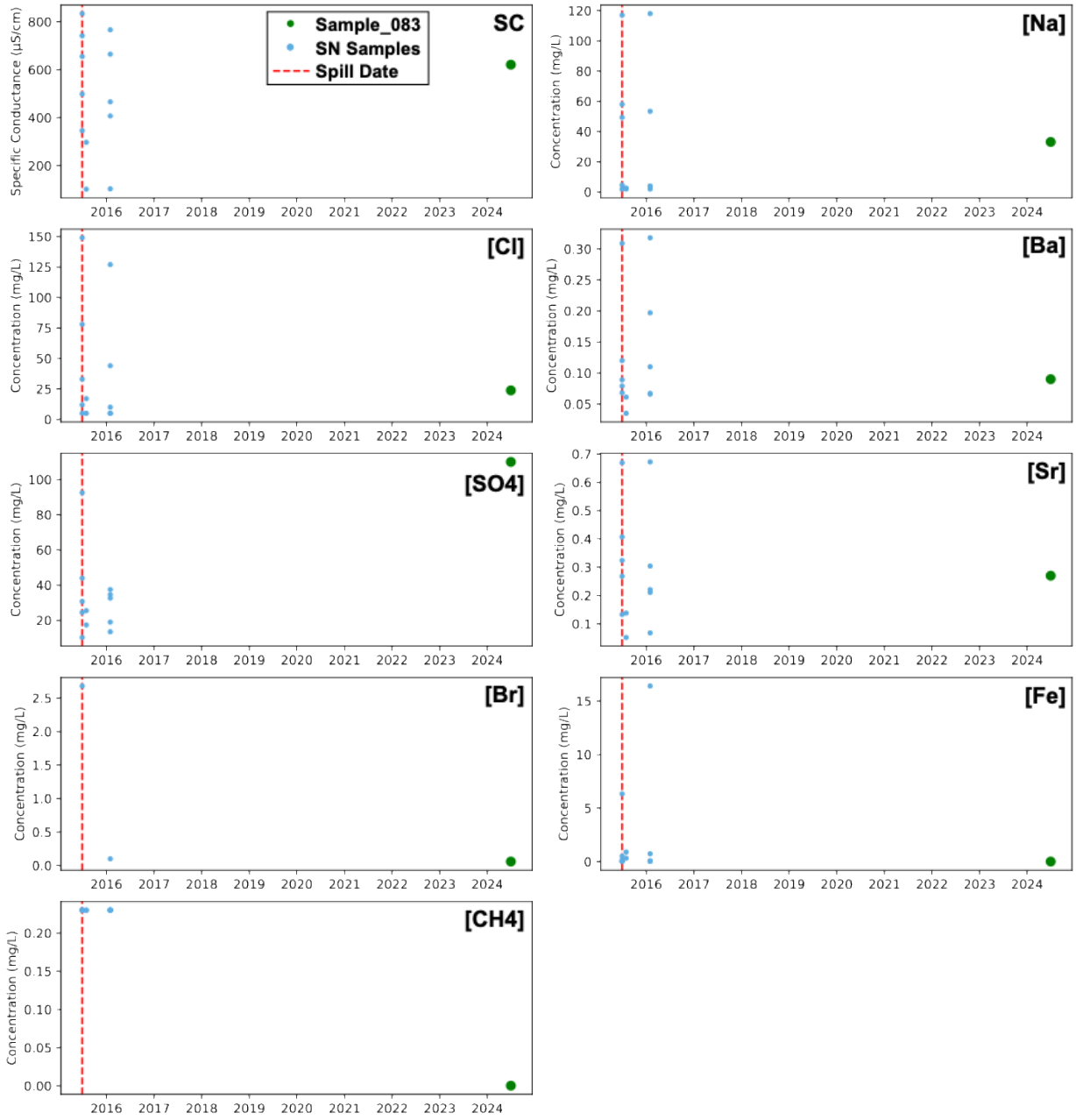

Figure S6. Scatter plots of brine-related species concentration vs. time (year) for Sample_083 (collected near spill E) and SN dataset samples (within 1km).

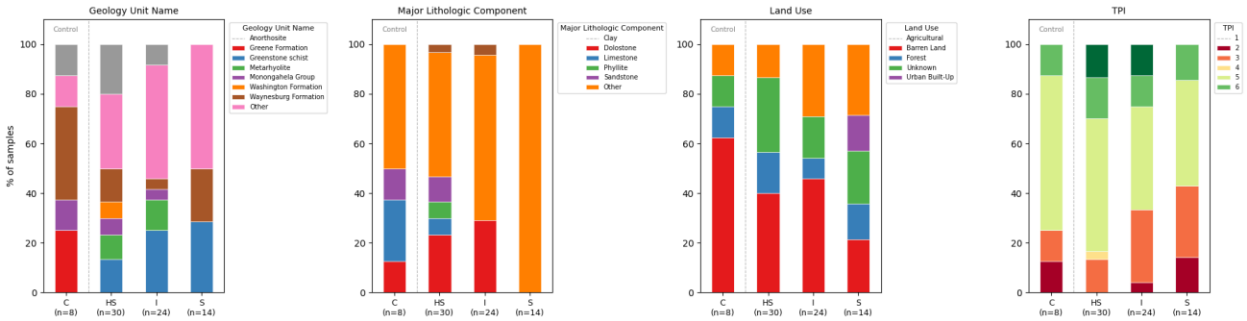

Figure S7. Distributions of geologic units, major lithologic components, land-use classes, and topographic position index (TPI) categories across control, hotspot, impoundment, and spill samples.