

RESEARCH REPORT

Hydrocarbon Extraction and Risk to Groundwater in Pennsylvania: Part 2. An Analysis of Water Quality in the Oldest Hydrocarbon Basin in the United States

Jennifer Baka, Susan L. Brantley, Tao Wen, Nathaniel Warner,
Casey Pinto, Zachary Bitzer, Brandon Forsythe, Allison Fenske,
Jianfeng Su, Lara Williams, and Evelyn Mahugu

INCLUDES A COMMENTARY BY THE HEI ENERGY REVIEW COMMITTEE

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Research Report 233, Part 2

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ABOUT HEI ENERGY

The Health Effects Institute's Energy Research program (HEI Energy) was formed to identify and conduct high-priority research on potential population exposures and health effects from the development of oil and natural gas in the United States. Since 2022, HEI Energy has supported population-level exposure research in multiple oil and gas regions. This research followed an extensive planning process that included preparing reviews of the scientific literature, hosting multisector workshops to learn about research priorities, and developing an online curated database and spatial bibliography to advance both public and scientific understanding. The research scope of HEI Energy is expanding beyond oil and gas to other forms of energy development, with an overarching goal of providing impartial knowledge about the benefits and drawbacks associated with various technologies.

The peer-reviewed scientific research provided by HEI Energy contributes high-quality and credible science to the public debate about unconventional oil and natural gas development and provides needed support for decisions about how best to protect public health. To achieve this goal, HEI Energy has put into place a governance structure that mirrors the one successfully employed for nearly 40 years by its parent organization, the Health Effects Institute (HEI), with several critical features:

- Balanced funding from the US Environmental Protection Agency under a contract that funds HEI Energy exclusively and from the oil and natural gas industry, with other public and private organizations periodically providing support
- An independent Board of Directors consisting of leaders in science and policy who are committed to fostering the public-private partnership that is central to the organization
- A research program governed independently by individuals having no direct ties to or interests in sponsor organizations
- An HEI Energy Research Committee, consisting of internationally recognized experts in one or more subject areas relevant to the Committee's work, that conducts and reviews scientific research impartially and has been vetted to avoid conflicts of interest
- Research that undergoes rigorous peer review by the HEI Energy Review Committee, which is not involved in the selection and oversight of HEI Energy studies
- Staff and committees that participate in open and extensive stakeholder engagement before, during, and after research and communicate all results in the context of other relevant research

In addition, HEI Energy publicly shares all literature reviews and original research that it funds, along with summaries written for a general audience. Without advocating policy positions, it provides impartial science targeted to make better-informed decisions.

HEI Energy is funded separately from the Health Effects Institute's other research programs (www.healtheffects.org), with financial support from the US Environmental Protection Agency, the oil and gas industry, and private foundations.

ABOUT THIS REPORT

HEI Energy Research Report 233, *Hydrocarbon Extraction and Risk to Groundwater in Pennsylvania: Part 2. An Analysis of Water Quality in the Oldest Hydrocarbon Basin in the United States*, presents a research project funded by HEI Energy and conducted by Jennifer Baka and Susan L. Brantley (The Pennsylvania State University) and colleagues. The report contains three main sections:

The **HEI Statement**, prepared by staff at HEI Energy, is a brief, nontechnical summary of the study and its findings; it also briefly describes the HEI Energy Review Committee's comments on the study.

The **Investigators' Report**, prepared by Baka, Brantley, and their colleagues, describes the scientific background, aims, methods, results, and conclusions of the study.

The **Commentary**, prepared by members of the HEI Energy Review Committee with the assistance of HEI staff, places the study in a broader scientific context, points out its strengths and limitations, and discusses the remaining uncertainties and implications of the study's findings for public health and future research.

This report has gone through HEI Energy's rigorous review process. When an HEI Energy-funded study is completed, the investigators submit a draft final report presenting the background and results of the study. Outside technical reviewers first examine this draft report. The report and the reviewers' comments are then evaluated by members of the Review Committee, an independent panel of distinguished scientists who are not involved in selecting or overseeing HEI Energy studies. During the review process, the investigators have an opportunity to exchange comments with the Review Committee and, as necessary, to revise their report. The Commentary reflects the information provided in the final version of the report.

Although this report was produced with partial funding by the United States Environmental Protection Agency under Contract No. 68HERC19D0010 to the Health Effects Institute, it has not been subjected to the Agency's peer and administrative review and may not reflect the views of the Agency; thus, no official endorsement by the Agency should be inferred. This report also has not been reviewed by private party institutions, including those that support HEI Energy, and may not reflect the views or policies of these parties; thus, no endorsement by them should be inferred.

PREFACE

HEI's Research to Assess Community Exposures Associated with Unconventional Oil and Gas Development

INTRODUCTION

The scale and rate of onshore oil and natural gas development since the early 2000s differ markedly from earlier development, stemming from technological changes involving the increased use of hydraulic fracturing combined with horizontal drilling. While hydraulic fracturing has captured much public attention, this process alone is not new. Neither is horizontal drilling or the extraction of oil and gas from unconventional formations, such as tight (i.e., low permeability) sandstone and shale. What is new is the use of high-volume (millions of gallons of water per well), multistage hydraulic fracturing combined with horizontal drilling (thousands of feet in length).

This combination of technological innovations has influenced the scale of development and where development is feasible. With their extensive number of fracture stages along lengthy horizontal wells, today's unconventional oil and gas wells intersect more of the targeted oil- or gas-bearing rock than earlier vertical wells, which involves the following:

- Larger well pads with extensive amounts of equipment that are transported to and from the pad
- More raw materials that must be transported to the well pad for drilling, cementing, and hydraulically fracturing the target hydrocarbon-bearing formation to produce the oil or gas
- More liquid and solid waste from multiple wells drilled on one well pad that must be captured, transported, and treated, for reuse or ultimate disposal
- A longer period of industrial activity is required at a single well pad when multiple wells are developed on it and
- Increased truck traffic, changing demands on community infrastructure, and other possible community effects associated with population mobility.

Consequently, unconventional oil and gas development (UOGD) can be associated with a wide range of potential exposures to chemical and nonchemical agents. The rapid expansion of this development has given rise to concerns about potential effects on human health.

Current evidence indicates that people can be exposed to chemical agents (e.g., criteria and hazardous air pollutants, radioactive material, indicators of produced water, and odorous compounds) and nonchemical agents (e.g., noise, light, and vibration) released from UOGD processes. HEI Energy compiled this evidence in two extensive literature reviews (HEI Energy Research Committee 2019, 2020). But despite this literature and considering the recommendations of a wide variety of government, industry, and academic stakeholders at three HEI-hosted research planning workshops, HEI Energy concluded that important gaps remain in our understanding of who might be exposed, the full range of exposures, which processes lead to exposures, and how exposures vary over time and across regions. Specifically, few studies to date provide the information necessary for linking chemical or nonchemical agents from UOGD processes with exposed communities. In addition, the applicability of study results to UOGD operations, geographic areas, and populations beyond those investigated in the studies is not clear. Given the current state of knowledge, HEI issued complementary requests for applications in 2020 ([RFAs E20-1](#) and [E20-2](#)) to improve the understanding of human exposure to UOGD.

OBJECTIVES OF THE RFAs

HEI solicited studies that can document one or more complete exposure pathway(s), should one exist, between UOGD process(es) and a population(s) potentially exposed to UOGD chemical emissions to air, chemical releases to water, or noise. The research should inform future health studies and be designed in an efficient way to maximize understanding of the variability in potential human exposures under routine operating conditions, while also being capable of capturing exposures associated with accidental scenarios.

OBJECTIVES OF RFA E20-1

[RFA E20-1](#): Community Exposures Associated with Unconventional Oil and Natural Gas Development solicited studies that apply a combination of approaches

to quantify the spatial and temporal variability in human exposures to UOGD-generated atmospheric chemical concentrations and noise. To maximize the generalizability of the research, HEI encouraged research that couples established rigorous methods to measure air and noise exposure at multiple spatial scales with equally rigorous fate and transport modeling. The RFA had five major objectives:

1. Identify the UOGD processes that have resulted or might result in releases of chemicals or noise to outdoor air and the potential for human exposure resulting from such releases.
2. Quantify the magnitude, frequency, and duration of potential exposures to chemicals in outdoor air and to noise released from specific UOGD processes at multiple spatial and temporal scales.
3. Quantify the influence of various factors (e.g., varying meteorology, topography, operational characteristics, proximity to populations, and population behavior) on potential UOGD-related human exposures to characterize variability in exposures and enable the results of the research to be generalized to other conditions.
4. Estimate community exposures from UOGD sources across spatial and temporal scales relevant to a current or future assessment of potential health effects.
5. Distinguish potential UOGD exposures from other conventional oil and gas development and any other background source to the extent practicable.

OBJECTIVES OF RFA E20-2

RFA E20-2: Community Exposures Associated with Unconventional Oil and Natural Gas Development solicited studies that involve the synthesis and modeling of existing data and original research to better understand the nature, extent, and frequency of potential exposures related to UOGD impacts on water quality. The RFA had four major objectives:

1. Determine the UOGD processes that have resulted or might result in releases to groundwater or surface water and potential for leading to human exposure.
2. Quantify the magnitude, frequency, and duration of potential exposures to chemicals in surface water or groundwater released from specific UOGD processes.
3. Quantify the influence of various factors (e.g., varying geology) on potential human exposures to maximize the generalizability of the research and inform decision-making.
4. Distinguish potential UOGD exposures from conventional oil and gas development and any other background sources to the extent practicable.

STUDIES FUNDED UNDER RFA E20-1

HEI Energy funded three research teams to collaborate on improving our understanding of community exposures associated with air quality and noise from UOGD. The collaboration, "TRACER Community Exposures and Releases (TRACER) from UOGD," (1) quantified acute and chronic human exposures in three regions of the United States and (2) developed a model that captures our collective understanding of UOGD emission sources, estimates their impacts on local and regional air quality, and can be updated as UOGD operations and UOGD governance change over time.

Measuring and Modeling Air Pollution and Noise Exposure Near Unconventional Oil and Gas Development in Colorado, Jeffrey L. Collett Jr., Colorado State University, USA

The research team assessed population exposures to chemicals and noise in air associated with specific UOGD processes over the UOGD life cycle at four well pads in the Colorado North Front Range, located within the Denver-Julesburg Basin. With the cooperation of well pad operators, the team conducted fixed-site air and noise monitoring and mobile air monitoring at multiple locations surrounding multiwell pads to connect specific UOGD processes with air monitoring results. These processes included well drilling, hydraulic fracturing, coiled tubing/millout operations, flow-back, and early production. The team obtained samples of drilling mud and compared emissions from different formulations. In addition to the monitoring program, they collaborated with Dr. Hildebrandt Ruiz to provide preproduction input data to the TRACER model and developed a preproduction emissions model designed for use by a variety of stakeholders to forecast HAPs and other VOC emissions from planned drilling and well completion operations and to assess whether efforts to reduce emissions achieve the desired goals. The team applied the model to simulate emissions and dispersion around specific well pads and estimate effects on local air quality, interpreting findings in the context of Colorado's regulatory setback distances separating UOGD from residences, schools, and other forms of development.

Assessing Source Contributions to Air Quality and Noise in Unconventional Oil Shale Plays, Meredith Franklin, University of Toronto, Canada

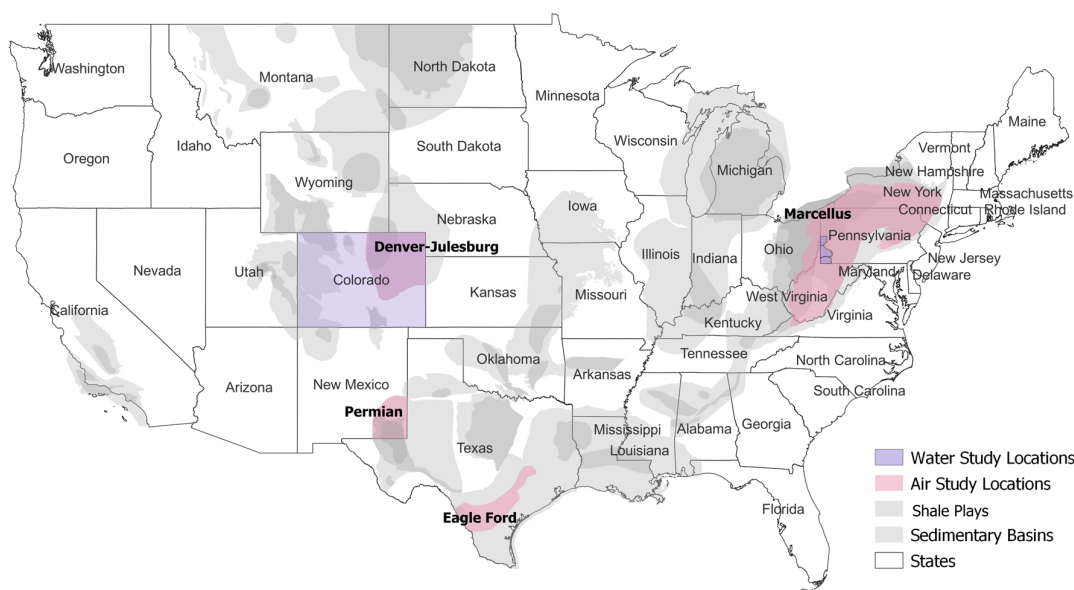
The research team assessed population exposures to ambient air pollution, radioactivity, and noise associated with UOGD. The team has coupled air, noise, and radioactivity measurements with meteorology and land use data to characterize UOGD sources of human exposure in the study regions: Permian Basin, Texas, and Eagle Ford Shale, Texas. To understand temporal variability in chemical concentrations in air, radioactivity, and noise levels, they conducted time-resolved fixed-site monitoring in the Permian Basin and leveraged ongoing fixed-site monitoring in the Denver-Julesburg basin. To understand spatial variability, they deployed passive samplers in both study regions. They linked monitoring data with satellite observations to characterize the location and magnitude of flaring.

Predictive, Source-Oriented Modeling and Measurements to Evaluate Community Exposures to Air Pollutants and Noise from Unconventional Oil and Gas Development, Lea Hildebrandt Ruiz, University of Texas at Austin, USA

The research team utilized a combination of measurement and modeling approaches in diverse study sites to assess the quality of an emission and dispersion modeling tool (TRACER model), which was advanced and refined from an existing model for methane emissions. The capabilities of the preexisting model were expanded from modeling emission and dispersion of methane from single UOGD well pads to assess community exposures. The expanded capability of the model included additional sources of emissions, regional scale modeling, a broad suite of pollutants of concern to human health, including secondary pollutants, and an assessment of the model for exposure assessment in future health studies. The original scope of work focused on the Eagle Ford Shale region in Texas; the project was later expanded to also include monitoring in the Permian Basin in New Mexico and modeling in the Marcellus Shale Region in the Northeastern United States, in close collaboration with the other two studies funded under this RFA.

Description of the Research Program

Three studies were funded under [RFA E20-1](#), and two studies were funded under [RFA E20-2](#) to cover the various RFA objectives; they are summarized below (**Preface Table**). The study locations stretch across several major oil and gas producing regions of the United States (**Preface Figure**).



Preface Figure. Map of RFA E20-1 and E20-2 study locations and associated plays and basins across the United States.

STUDIES FUNDED UNDER RFA E20-2

HEI funded two studies in Colorado and Pennsylvania to combine existing water quality data and modeling to assess community exposures associated with UOGD releases to water. Both studies provide frameworks for identifying areas of potential water contamination, apportioning the sources of contamination, and identifying exposure pathways that connect UOGD to community water sources.

Part 1: Using Geoscientific Analysis and Community Engagement to Analyze Exposures to Potential Groundwater Contamination Related to Hydrocarbon Extraction in Southwestern Pennsylvania, Jennifer Baka, Susan L. Brantley, and Lingzhou Xue,* The Pennsylvania State University, USA The research team assessed linkages between UOGD and potential water contamination in a tri-county region of Southwestern Pennsylvania with a long history of industrial activity. Using an existing database of greater than 28,000 groundwater samples, the team investigated whether they could distinguish constituents associated with UOGD from other regional sources of similar contaminants (e.g., conventional oil and gas development and coal mining). The research team used statistical analysis and a machine learning tool (nonnegative matrix factorization [NMF]) to isolate the influences of natural and anthropogenic processes on groundwater chemistry and identify potential linkages between UOGD and water contamination. The team hosted focus groups to elicit community concerns regarding UOGD, water contamination, and public health, and they considered what they learned in completing their assessment of potential community exposures associated with UOGD.

*Co-principal investigators.

Assessing the Effects of Unconventional Oil and Gas Development on Community Water Sources, Joseph Ryan, University of Colorado, USA The research team used existing data to assess the potential for community exposure to releases attributable to UOGD in ground and surface waters used as community water supplies. The team used monitoring data for water quality near oil and gas development, records of community water supplies, and records related to oil and gas operations in the Denver-Julesburg, Piceance, San Juan, and Raton Basins (e.g., well construction and integrity) to assess temporal and spatial correlations with water quality issues affecting communities. They identified chemicals of possible concern detected in the water quality dataset and coupled those with multi-phase subsurface fluid flow and transport models to predict the likelihood of complete transport pathways in the Denver-Julesburg Basin.

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- HEI Energy Research Committee. 2019. Potential Human Health Effects Associated with Unconventional Oil and Gas Development: A Systematic Review of the Epidemiology Literature. Special Report 1. Boston, MA: Health Effects Institute. Available: <https://www.heienergy.org/system/files/he-energy-epi-lit-review.pdf>.
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Preface Table. Key Characteristics of HEI's Research to Assess Community Exposures Associated with Unconventional Oil and Gas Development

Principal Investigator	Location	Study Period	Study Population	Main Pollutants in Air or Water	Monitoring Data	Exposure Assessment
RFA E20-1: Community Exposures Associated with Unconventional Oil and Gas Development — Air Quality and Noise						
Collett	Northern Front Range, Colorado (part of the Denver-Julesburg basin)	2022–2024	All subpopulations in the study location	VOCs, methane, PM _{2.5} , NO _x , A- and C-weighted noise	Fenceline fixed-site and mobile	TRACER emissions model and local air quality modeling
Franklin	Carlsbad-Loving, New Mexico (part of the Permian basin), Eagle Ford Shale region, Texas	2022–2024	All subpopulations in the study location	VOCs, methane, PM _{2.5} , NO _x , A- and C-weighted noise, ozone, H ₂ S, radioactivity (alpha)	Regional fixed-site (NM) and passive (TX)	Non-negative matrix factorization for source apportionment
Hildebrandt Ruiz	Eagle Ford Shale region, Texas, Permian Basin, New Mexico, and Marcellus Shale Region	2022–2024	All subpopulations in the study location	VOCs, methane, PM ₁ , NO _x , A- and C-weighted noise, ozone, H ₂ S, black carbon	Fixed-site (TX) and mobile (TX and NM)	TRACER emissions model and local and regional air quality modeling
RFA E20-2: Community Exposures Associated with Unconventional Oil and Gas Development — Water Quality						
Baka, Brantley, and Xue	Beaver, Greene, and Washington Counties in Southwestern Pennsylvania	2022–2024	All subpopulations in the study location	VOCs, metals	Existing state-level data	Machine learning and statistical modeling
Ryan	State of Colorado	2022–2024	All subpopulations in the study location	VOCs, metals	Existing state-level data	Chemical transport model and statistical tests

HEI STATEMENT

Synopsis of Research Report 233, Part 2

Water Quality in the Oldest Hydrocarbon Basin in the United States

BACKGROUND

The onset of unconventional oil and gas development (UOGD)* through hydraulic fracturing in the early 2000s has led to a substantial increase in oil and gas production in the United States, and concurrently, concerns about effects on human health from exposure to water potentially contaminated from UOGD. This concern is particularly acute in rural areas where many residents rely on private groundwater wells for drinking water.

Research on water quality changes from accidental UOGD releases is challenging as any contamination of the soil and groundwater typically requires substantial effort and resources to determine the extent and severity of effects on groundwater. Furthermore, it is difficult to distinguish UOGD-related contamination from other natural or anthropogenic sources, particularly in areas with a history of conventional oil and gas or coal extraction, because associated contaminants are often the same.

In Part 1 of their study, funded under ([RFA E20-2](#)) Community Exposures Associated with Unconventional Oil and Natural Gas Development, Baka, Brantley, and colleagues at The Pennsylvania State University used statistical analyses and machine learning to identify links between various UOGD sources and potential groundwater contamination. They also used focus groups to understand community concerns regarding UOGD. Based on publicly available water quality data primarily collected before 2014, they found areas of elevated salts that may indicate localized areas of potential groundwater contamination, and they reported that residents in Southwestern Pennsylvania were principally concerned about health effects of UOGD related to water quality, waste disposal, and radioactive contaminants.

As a follow-on, in Part 2 of the study, the investigators sought to evaluate the groundwater quality in these areas and address

What This Study Adds

- Part 1 of the study, based on decade-old water quality data, identified elevated salts as a potential indicator of groundwater contamination related to unconventional oil and gas development (UOGD) in areas of Pennsylvania. It also documented community concerns about potential radiation exposures and water quality impacts from UOGD waste management.
- In Part 2, this study provides more recent water quality data from surveys conducted in areas where evidence gathered in Part 1 suggested that groundwater may have been contaminated by UOGD.
- The investigators collected 97 water samples from private groundwater wells, springs, and streams near oil and gas activities, as well as control sites, and analyzed them for 41 chemicals associated with UOGD and human health. They also used multiple statistical analyses and chemical fingerprinting to identify impacts from UOGD versus other sources.
- The investigators found that few analytes exceeded drinking water standards, and exceedances were limited to secondary standards, which are based on aesthetic qualities rather than health effects. Overall, based on multiple lines of evidence, the investigators found no conclusive evidence of UOGD-related impacts in private groundwater wells, noting that geological, geographical, and land use variation across the relatively small number of sample sites may also explain their observations.
- This study contributes to the broader understanding of groundwater and drinking water quality in areas proximate to UOGD and adds valuable data that may help distinguish localized UOGD-related impacts to groundwater from broader regional effects of historical energy extraction or geology. The study also directly addressed community concerns by investigating whether private drinking water wells were contaminated by UOGD.

This Statement, prepared by HEI Energy, summarizes a research project funded by HEI Energy and conducted by co-principal investigators Jennifer Baka and Susan L. Brantley (The Pennsylvania State University) and their colleagues. Research Report 233, Part 2 contains the detailed Investigators' Report and a Commentary on the study prepared by the HEI Energy Review Committee.

*A list of abbreviations and other terms appears at the end of this report.

community concerns about potential contamination in privately owned drinking water sources. Thus, they conducted water quality surveys in areas where evidence suggested that groundwater may have been contaminated by UOGD.

APPROACH

Baka, Brantley, and colleagues conducted several sampling campaigns during 2024. They collected 97 water samples from private groundwater wells, springs, and streams in select “treatment” and “control” areas. These samples were collected to address two questions:

1. Do these groundwater wells contain contaminants associated with UOGD that pose human health concerns?
2. Do groundwater wells previously identified as being at elevated risk of UOGD contamination show evidence of actual impact?

The treatment areas, many of which overlap, were defined as those within 2–3 km of locations of interest:

- Those that had increased chloride concentrations near one or more UOG wells (“hotspots”).
- Impoundments that stored oil and gas wastewater (also known as “produced water”) that were directed by the Pennsylvania Department of Environmental Protection to either close or store only fresh water (“impoundments”).
- Areas near produced water spills that had occurred in Southwestern Pennsylvania between 2022 and 2024 (“spills”). The team also included 12 UOGD-related brownfield sites in the “spills” area. Finally, control sites were located between 5 and 7 km from the central points of impoundment and hotspot areas and more than 5 km from spills.

Within the hotspot, impoundment, spills, and control areas, the team recruited 68 homes to approach to sample private groundwater wells. The team also included “goodwill” sample sites that did not meet criteria but were sampled to generate interest and goodwill in the study.

The investigators analyzed all samples for 41 chemical analytes, which are more likely to be elevated if UOGD contamination had occurred, with a focus on those that are of concern to human health. To estimate potential health concerns, they compared the results to the US EPA Primary and Secondary Drinking Water Standards. When these standards were not available, they used other health-based benchmarks or guidance established or proposed by federal agencies.

They also employed several different analyses to tease out any potential impacts from UOGD specifically

from those of other sources. These included statistical comparisons of samples from “treatment” sites with control sites, geospatial analyses to analyze whether concentrations were higher closer to UOGD operations, and isotope analyses and element ratios, which can serve as chemical fingerprints, to interpret the origin of analytes.

KEY RESULTS

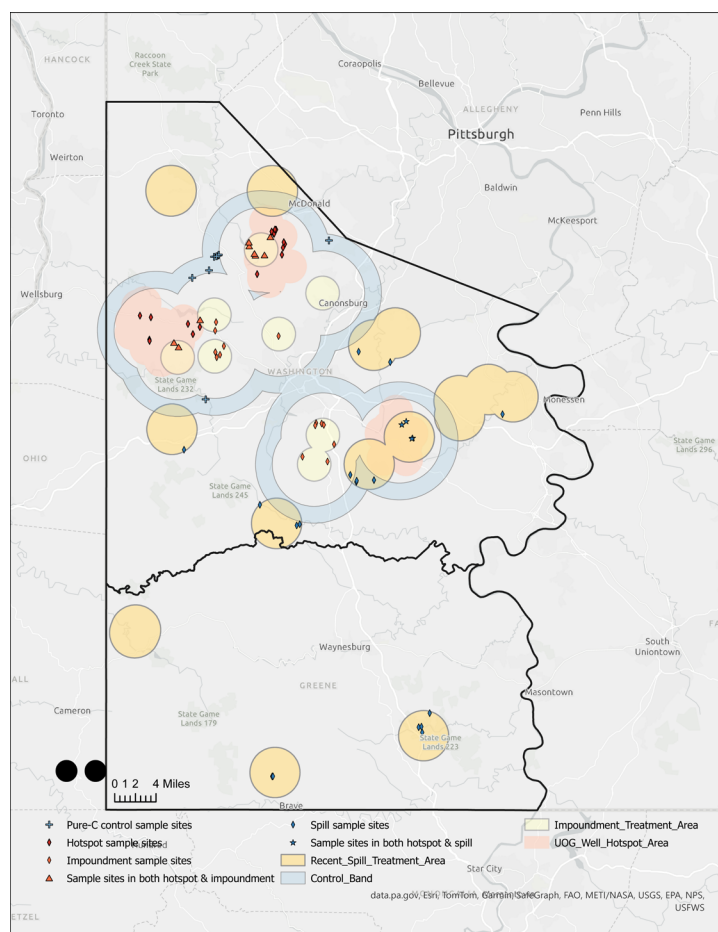
Between May and November 2024, the investigators conducted seven field campaigns, collecting 97 water samples (79 groundwater wells, 14 springs, and four streams) from 91 residential properties and three public sites. Of these, 62 samples came from hotspots, impoundments, and spill sites, some overlapping (**Statement Figure**), distributed among the three types, with eight from control areas and 27 classified as goodwill samples.

None of the samples exceeded health-based, US EPA Primary Drinking Water Standards, although one sample equaled the primary standard for barium. Some samples exceeded Secondary Drinking Water Standards (aesthetics-based) for aluminum, iron, manganese, total dissolved solids, or chloride. However, those are some of the most common elements in Pennsylvania bedrock. BTEX compounds (benzene, toluene, ethylbenzene, and xylene), which are commonly associated with oil and natural gas, and radium compounds, which are naturally occurring in the Marcellus shale, did not exceed drinking water standards in any sample.

Thirty-three samples exceeded the US EPA proposed water standard for radon (values above which could indicate risk from exposure to radon in indoor air), and 46 exceeded the US EPA health-based screening level for lithium. Three samples exceeded US Department of Interior action levels for further investigation for dissolved methane in water, which indicates a potential need for venting, monitoring, or mitigation to prevent gas buildup.

In each case where the team found analytes above standards or guidelines, they provided a letter describing the specific findings and potential mitigation resources and called the homeowners.

After accounting for suspected contamination from agriculture and potential artifacts in the statistical analyses, the investigators found that only radium concentrations were statistically higher in groundwater wells within hotspots and impoundments as compared to control sites. However, none of the samples exceeded the maximum contaminant levels established for radium in drinking water, and the investigators note that radium concentrations were within the typical range for principal aquifers in the United States.



Statement Figure. Map of the study treatment and control areas and sample locations in Washington and Greene Counties, Pennsylvania. Source: Investigators' Report Figure 1.

Other analytes showed higher concentrations closer to impoundments and spills, but the data were variable. It is possible that these analytes could be related to produced water leaks from impoundment sites or spills at well pads. When the team considered additional lines of evidence, including isotopic analyses of geochemical tracers and methane, they could not conclusively identify UOGD as the source. Instead, they note that the observed variations may reflect differences in local geology or land use.

INTERPRETATION AND CONCLUSIONS

In Part 2 of the study, Baka, Brantley, and colleagues examined whether groundwater presumed to be at higher risk of UOGD contamination showed evidence of such impacts. In so doing, they also directly addressed community concerns about whether UOGD activities were adversely affecting local water quality in private groundwater wells. The investigations found that few analytes exceeded drinking water standards, and exceedances were primarily limited to secondary

standards, which are based on aesthetic qualities rather than health effects. Across all sampled sites, the team found no conclusive evidence of UOGD-related contamination in private groundwater wells based on multiple lines of evidence.

In its independent review of the study, the HEI Energy Review Committee identified the study's rigorous analytical approach as a key strength, noting that it focused on a well-considered subset of water quality analytes relevant to both potential UOGD-related contamination and associated health effects.

The Committee also recognized the value of the community-centered approach, which accommodated community requests for increased and transparent water sampling. Each participant received a letter with individual water quality analysis results, with additional information and resources in the cases where the investigators found analytes above standards or guidelines. The Committee appreciated the strong, consistent communication with the community.

The Committee recognizes that a study of this size and scope cannot conduct every analysis or obtain every type of data. The inherent complexity of subsurface groundwater flow, limited information on private well construction, or unevenly distributed controls may all complicate the ability to delineate the potential groundwater contamination. While cited by the investigators as limitations in the lack of discussion of the potential effect of these limitations on the findings was a notable omission.

The Committee also noted that some key findings are presented without context to understand the implications of such results, such as samples with lithium concentrations that exceeded their health-based screening level. The Committee also questioned why the investigators suggest that future analyses of the blood and hair of residents could be used to discern the potential effects of contamination. Given the findings of this study, such an intervention seems unwarranted and unsupported.

In summary, this study contributes to the broader understanding of water quality in areas proximate to UOGD and adds valuable data that may help distinguish localized impacts of UOGD on drinking water from broader regional effects, including legacy energy extraction or underlying geological conditions.

Hydrocarbon Extraction and Risk to Groundwater in Pennsylvania: Part 2. An Analysis of Water Quality in the Oldest Hydrocarbon Basin in the United States

Jennifer Baka^{1*}, Susan L. Brantley^{1*}, Tao Wen², Nathaniel Warner¹, Casey Pinto¹, Zachary Bitzer¹, Brandon Forsythe¹, Allison Fenske¹, Jianfeng Su², Lara Williams¹, and Evelyn Mahugu¹

¹The Pennsylvania State University, University Park, Pennsylvania, USA; ²Syracuse University, Syracuse, New York, USA

ABSTRACT

Introduction This study examines the relationship between groundwater contamination and unconventional oil and gas development (UOGD)[†] in Southwestern Pennsylvania (SWPA), one of the most intensively drilled portions of the Marcellus Shale basin. Water samples were gathered from 97 private groundwater wells, springs, and streams to evaluate potential UOGD-related contamination for groundwater near (1) chloride hotspots, identified in previous research, (2) UOGD wastewater impoundments that were removed by state regulatory authorities, and (3) well pad spills and brownfield cleanup sites.

Methods Geochemical and radiation analyses were conducted on the water samples to test for the presence of various dissolved constituents, including salts, heavy metals, dissolved gases, and radioactive species. A household survey and literature review were simultaneously conducted to (1) better understand household demographics, well characteristics, and land use practices of sampled homes; and (2) explore for potential public health risks from exposure to analytes found to be above safe drinking water thresholds in our water sampling analysis. Statistical analyses and regression modeling were conducted to compare median values between treatment and control sites and to evaluate relationships between analyte concentrations and distance from unconventional oil and gas (UOG) wells, hotspots, impoundments, and spill sites.

This Investigators' Report is one part of Health Effects Institute Research Report 233, Part 2, which also includes a Commentary by the HEI Energy Review Committee and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Dr. Jennifer Baka, Department of Geography, 302 Walker Building, University Park, PA 16802; email: jeb525@psu.edu. No potential conflicts of interest were reported by the authors.

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*Co-principal investigators.

[†]A list of abbreviations and other terms appears at the end of this report.

Results In our study area, none of the BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) were observed at concentrations above public health limits, and no samples exceeded US Environmental Protection Agency (EPA) limits for beryllium, nickel, copper, arsenic, cadmium, thallium, lead, or uranium. Thirty-three sites exceeded the EPA's proposed standards for radon. Twenty samples exceeded EPA secondary drinking water standards, which primarily address aesthetic concerns, rather than those related to health, for aluminum (0.2 mg/L), iron (0.3 mg/L), and/or manganese (0.05 mg/L). One or two samples had high dissolved aluminum and iron concentrations, as well as a relatively high dissolved methane concentration, and could be evidence of particulates mobilized in the presence of natural gas bubbles. Four samples exceeded drinking water standards for dissolved methane. Isotopic analysis indicates that strontium from the saltiest samples may have derived from the Marcellus Shale, but comparisons of strontium/chloride ratios from these samples differ from those commonly found there. The isotopic signature of the dissolved methane in the samples is consistent with a primarily biogenic origin or a mixture of gas of biogenic and thermogenic origin.

We observed higher concentrations of some constituents that could be associated with UOG contamination (e.g., chloride, radium, radon) in treatment areas compared with controls. However, after applying a procedure to control false positive discoveries among the 41 analytes analyzed, only radium in the hotspot and impoundment treatment sets had higher concentrations than those in the controls. We observed that concentrations of strontium increase with proximity to impoundments (in two of four statistical tests performed), and that concentrations of sodium (in three of four statistical tests), barium (one of four), and methane (two of four) increased with proximity to spill sites. These results could indicate that strontium, sodium, barium, and methane contamination are related to UOGD but not to leakage from UOG wells within hotspots.

Conclusions Overall, we observed very few instances of contamination above established or proposed drinking water standards. The only statistically significant difference between treatment and control sites (after controlling for potential false-positive discoveries) was radium in hotspots and impoundments; however, the radium concentrations we

observed fall within the typical range reported for principal aquifers across the United States. Radium is a known carcinogen linked to lung and bone cancer. We found some analytes increased in concentration near impoundments (strontium) and spills (barium, methane, and sodium). Strontium and barium have been associated with health risks in the literature, including gastrointestinal disturbances, muscular weakness, elevated blood pressure, and adverse kidney effects for barium, and impaired bone growth in children, anemia, and cancer for strontium. However, isotopic analysis of strontium and methane did not provide conclusive evidence that UOGD contamination was the source of these analytes in groundwater. Geological, geographical, and land use variety across the study area could also explain or contribute to the observed correlations, especially considering the small number of sites sampled.

INTRODUCTION

Previous work investigating water quality in the northern Appalachian Basin in Pennsylvania, and specifically in areas south of Pittsburgh, has revealed evidence consistent with relatively infrequent groundwater contamination problems (e.g., salts, metals, methane) localized to certain geologically problematic areas or shale-gas wells that could be locations of ongoing contamination.¹ In previous work funded by the Health Effects Institute Energy, we concluded that, if the slight increases in concentrations of salt species near a small subset of unconventional oil and gas (UOG) wells are attributable to unconventional oil and gas development (UOGD), the most likely cause is infiltration into groundwater from spills or impoundment leaks.² The dataset used to make this inference had largely been collected earlier than 2014; more recent data were generally not available to test whether the putative contamination is ongoing.

To test for current evidence of water contamination and to address community concerns about the need for water testing in proximity to UOGD, discussed in our first project report, this study extends this work by (1) gathering and chemically analyzing water samples from private wells, springs, and streams in select “treatment” and “control” areas, described further below; (2) conducting a resident survey to assess potential exposures if evidence of contamination is found; and (3) conducting a literature review to determine possible health risks resulting from exposure to any contaminants identified in the water sampling analysis. We focus our study on areas in Southwestern Pennsylvania (SWPA) in proximity to (1) chloride “hotspots” identified by Shaheen and colleagues (2022),¹ and (2) sites near wastewater impoundments or sites near where spills or leaks apparently occurred. Shaheen and colleagues identified these two types of locations² as the most likely potential sources for groundwater contamination in the area.

Our research questions:

1. Do groundwater samples from within geostatistically identified hotspots in Shaheen and colleagues¹ show evidence

of current contamination for analytes potentially related to UOGD?

2. Do groundwater samples near now-removed impoundments in SWPA (identified by regulatory agencies as having potentially contaminated groundwater) show current evidence of contamination?
3. Do groundwater samples near recent well pad spills show contamination?

SPECIFIC AIMS

The project aims were the following:

1. Identify and recruit homes with groundwater wells in the areas of interest
2. Plan and conduct field work, including administering the household survey and taking water samples
3. Analyze the combined geochemical, radiological, and survey data
4. Disseminate results to individual participants, in community meetings, and through publications

STUDY DESIGN AND METHODS

SITE IDENTIFICATION

The research team selected four types of sites in SWPA for water sampling: (1) sites near impoundments (impoundments identified as possibly problematic by the state environmental regulator, the Pennsylvania Department of Environmental Protection [PADEP]),³ (2) sites within hotspots (potentially problematic areas identified as hotspots in Shaheen and colleagues),¹ (3) sites near recent spills and brownfield sites, and (4) control sites. The goal of this project was to investigate the lasting impacts of spills and wastewater leakage on groundwater. Our hypothesis, informed by the first phase of our research,⁶³ was that the most plausible pathway is surface spills or leakage. Therefore, we did not target other pathways in our project design and planning phase.

Homes with private wells in each of these categories that met the criteria described below were identified using county tax parcel data^{4,5} and a database containing property records for all tax-paying properties in the United States.⁶ 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 Pennsylvania Groundwater Information System (PAGWIS) data⁷ 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 (noting that PAGWIS data are incomplete and do not include all wells).

IMPOUNDMENT IDENTIFICATION

We identified impoundment sites for sampling as those located within 2 km of impoundments that were remanded by the PADEP and shut down or instructed to store only fresh water.⁸ A 2-km radius was selected, consistent with previous modeling⁹ and field-based studies¹⁰ that found that potential groundwater impairment caused by UOGD would be most probable within this radius. The locations of impoundments were determined by matching the impoundment names to well pads of the same name. We then used well pad locations for these impoundments as the centroid of the area targeted for impoundment sampling.

Hotspot Identification

We identified areas in Washington County in SWPA in proximity to hotspots identified by Shaheen and colleagues.¹ These hotspots are locations where groundwater chemistry shows evidence that chloride, an analyte released into water when salty UOGD wastewater is spilled or leaked, increases in concentration near one or more UOG wells. As hotspots are not point features, we identified UOG well locations from the PADEP SPUD Data Report⁸ within the areal extent of the hotspots identified in Shaheen and colleagues.¹ We then used all UOG well locations within the hotspot extent to define an outer perimeter that was 2 km from every well. A 2-km radius was selected based on previous modeling⁹ and field-based studies¹⁰ that found that potential groundwater impairment caused by UOGD would be most probable within this radius.

Spill and Brownfield Site Identification

Our intent in finding “spill sites” was to find groundwater sampling locations near a spill that had occurred within the 3 years before the sampling. A 3-year window was selected because lasting impacts from spills were observed in previous work in Pennsylvania in this range.² In addition, previous studies conducted in other geological and geographic settings (e.g., Texas) have suggested that impacts on groundwater quality from oil and gas production can persist for years if the contamination source and/or pathway is not eliminated.^{11–13}

We initially targeted three spills at two well pads in Greene County in SWPA that had occurred in 2022 and 2023 as potential locations for sampling.^{14,15} Given the low population density and PAGWIS water well density in Greene County, we expanded the buffer to a 3-km radius for the spill sites. Despite extensive outreach and recruitment, we were only able to recruit two homes within this radius. To increase the potential sampling possibilities near spills, we also (1) located springs and streams on public lands within 3 km of the spill sites, and (2) included UOG-related brownfield sites in Washington County as another type of spill-related location.

We identified these latter sites using records from the PADEP Land Recycling Program,¹⁶ which encourages voluntary cleanup and reuse of contaminated industrial and

commercial sites by providing uniform cleanup standards, liability relief, review and time limits, and potential financial assistance. We screened the in-progress brownfield sites in the southwestern region for site names listed under a major UOG company name (e.g., Range, CNX, EQT). We identified 12 brownfield locations in Washington County as potentially related to UOGD. We identified homes within 3 km of these UOGD-related brownfield sites for recruitment. During one of the later sampling campaigns, a new spill occurred on September 11, 2024, in southern Greene County (39.76133, -80.28292).¹⁷ We worked with a local community group to reach out to its members in the area, yielding three signups within 3 km of the spill. According to the PADEP’s inspection report, the spill was under control and quickly addressed through remediation, and no violations had been reported in the nearby drinking water supplies. While the spill was unlikely to affect groundwater within a few months of sampling, our sampling results provide a baseline for future studies near this spill.

Control Site Identification

We identified control sites (labeled as pure-C control throughout this report) as samples derived from sites within a band between 5 and 7 km from the centroids of impoundments and hotspots and more than 5 km from the identified recent spill sites. We selected a 5- to 7-km radius with the objective of obtaining groundwater samples unlikely to be affected by UOGD-related contamination while maintaining proximity to the treatment sites for comparative assessment, given findings from previous research that indicated impacts would be most likely within a 2-km radius.^{9,10}

RECRUITMENT METHODS

We used the following methods to recruit participants:

- Mailed recruitment postcards (Additional Materials 1) to 336 households.
- Worked with a local community group to advertise the study to its members and through its social media channels.
- Worked with the Penn State Master Well Owner Network to advertise the study to its volunteers in Washington and Greene counties.
- Worked with a Penn State Extension agent to conduct door-knocking in our study areas (~10 hours over 2 days of his outreach recruited).
- Called ~45 homes in the northeastern hotspot (**Figure 1**) that were in the PAGWIS database.
- Conducted additional snowball sampling while in the field by recruiting neighbors and family members of homes already sampled in our areas of interest.
- Encouraged all signups to share the study information with their neighbors and on social media.

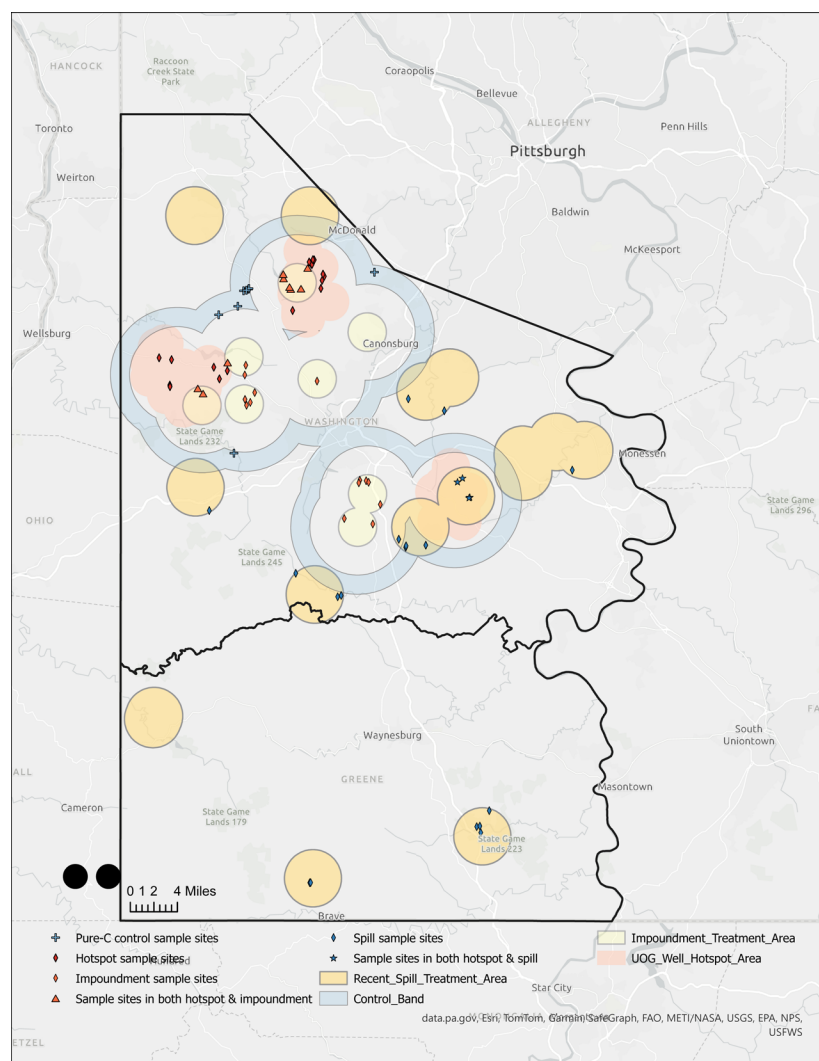


Figure 1. Map of the study areas in Washington and Greene counties, Pennsylvania. Target sampling areas and sites for impoundments, hotspots, recent spills (including brownfield sites), and control zones are color-coded. The study included three documented spills in Greene County within a 3-year window; an additional 12 brownfield sites were identified through the Pennsylvania Department of Environmental Protection Land Recycling Program.

These approaches yielded a total of 68 signups at impoundment, hotspot, and control sites that we sampled. Twenty-seven additional houses were sampled in areas that were not in our treatment and control areas to generate interest in the study and build community goodwill, even though they were not located in the areas of interest. Of these 27 goodwill sites, seven were in a hydrologic vulnerability zone identified as being potentially vulnerable to contamination from UOGD by Soriano, Deziel, and Saiers.⁹

As the sampling period progressed through the summer, we discussed water levels with each homeowner so they

⁹The 94 properties consist of 91 residential properties and three public land parcels with streams. One residential property also had a spring. Four residential properties had more than one well or spring.

could decide if our purging protocol might run the well dry. Several potential participants declined to participate because of this concern.

In total, we collected 97 samples from 94 different properties* over seven field campaigns (also referred to herein as “trips”) from May to November 2024. Additionally, we gathered one process blank and took one set of trip blanks for the BTEX (benzene, toluene, ethylbenzene, and xylenes) analyses during each field campaign. The breakdown of samples by type and category is listed in **Table 1**.

Figure 1 shows the final treatment (impoundment, hotspot, spill sites) and control (pure-C) areas and the sampling locations.

WATER SAMPLING METHODS

At each house, we gathered ~20 liters of water for samples and measured six parameters (**Table 2**) in the field following processes detailed in Appendix A. Water samples were tested for the following analytes (note that the table also includes methane analysis in ambient air).

SUMMARY OF CHEMICAL ANALYSES

We used handheld probes to measure pH, temperature, dissolved oxygen (DO), and specific conductance (SC). We measured alkalinity by sulfuric acid titration.

We analyzed chloride (Cl), fluoride (F), bromide (Br), sulfate (SO₄), and nitrate (NO₃) on all trips using ion chromatography (details in Appendix A). We measured major elements using inductively coupled plasma atomic emission spectroscopy (ICP-AES). We measured trace elements using an inductively coupled plasma mass spectrometer (ICP-MS).

We analyzed strontium (Sr) isotopes using thermal ionization mass spectrometry (TIMS) and dissolved inorganic carbon using a total organic carbon analyzer. We analyzed radium using a gamma-ray spectrometer. In most cases, we selected these analytes because previous statistical analysis of possible groundwater contamination from UOGD identified these species as the ones most likely to be elevated, if contamination had occurred.¹⁸ As the goal of this study was to compare concentration levels with established or proposed health standards, we did not include analytes that may be elevated near UOGD contamination but do not have established or proposed health standards, such as boron.

We measured dissolved radon-222 activity in the field at the time of home water sampling using a DurrIDGE RAD-7 with an H₂O attachment. We field-filtered radium-228 and

Table 1. Sampling Breakdown by Category

Site Type	I	HS	I + HS ^a	(S) ^b	S + HS	Pure-C	Other ^c	Total ^d
# Wells	20	23	8	16 ^e	2	7	23	79
# Springs	4	7	2	1	1	1	4	14
# Streams	0	1	0	4	1	0	0	4
Total	24	31	10	21	4	8	27	97

^aThese are homes located in both impoundment (I) and hotspot (HS) areas (Figure 1, overlap of pink and yellow).

^bFour of the sites sampled were around recent spills (S) in Greene County, and 16 were around brownfield sites in Washington County. Of the brownfield sites, four were also in a hotspot zone (S + HS column).

^cOther includes two groups: (1) homes that registered early in the study recruitment effort or were “snowball” samples in the field that fall outside our treatment and control (pure-C) areas, which we refer to as “goodwill samples” because they were sampled to build community support for the study; or (2) homes that were sampled in the control band that were ultimately <5 km from a spill (brownfield) site and so not included in the pure-C group.

^dSome water sources sampled fell within multiple areas of interest and must not be double-counted. Twenty-four sources were sampled around impoundments and 31 around hotspots, of which 10 were near both features (I and HS), for $24 + 31 - 10 = 45$ unique sources. Eight sources were sampled in the pure-C area. Twenty-one sources were sampled near spills, of which four were in both spill and hotspot areas, for an additional $21 - 4 = 17$ unique sources. The 27 “goodwill” sources had no overlap with other areas, yielding a total of $45 + 8 + 17 + 27 = 97$ unique sources sampled.

^eAmong the 16 well water S samples, one was identified as primarily influenced by rainwater, according to geochemical data and communication with the homeowner. Two well samples were considered significantly affected by nearby acid mine drainage sites, given their proximity to these sites in the DEP database and their geochemical characteristics. These three samples were excluded from our data analysis.

Table 2. Analytes Tested in the Field and in the Geochemical Laboratories

Parameter Group	Analytes
Field parameters	pH, temperature, dissolved oxygen, specific conductance, alkalinity, and methane concentration in air
Anions	Chloride, fluoride, bromide, sulfate, nitrate
Major elements ^a	Aluminum, barium, calcium, iron, potassium, magnesium, manganese, sodium, phosphorus, silicon, strontium
Trace elements	Lithium, beryllium, nickel, copper, arsenic, cadmium, thallium, lead, uranium
Dissolved carbon compounds	Methane, ethane, propane, dissolved inorganic carbon
Isotopes of dissolved species	Strontium (^{87/86} Sr), methane ($\delta^{13}\text{C}$, δD), ethane ($\delta^{13}\text{C}$)
Radionuclides	Radon, radium, gross alpha
Volatile organic compounds	Benzene, toluene, ethylbenzene, xylenes

^aThese elements include the major rock-forming elements.

radium-226 onto manganese oxide-coated fiber filters and then measured on a Canberra germanium detector following incubation for >21 days. We measured total alpha disintegrations using a PerkinElmer Tri-Carb Liquid Scintillation Analyzer.

We measured BTEX compounds using headspace gas chromatography-mass spectrometry/mass spectrometry (GC-MS/MS). We did not analyze some samples for BTEX compounds from trip 1 because of sample bottle breakage or from trips 6 and 7 because of budgetary constraints.

We analyzed methane in ambient air using a Bascom-Turner Gas-Rover. We quantified dissolved concentrations of three hydrocarbon gases (methane, ethane, and propane) by GC at IsoTech Laboratories. We also analyzed carbon and hydrogen isotopic compositions of gas components when gas concentrations were high enough by chromatographic separation followed by combustion and dual-inlet isotope ratio mass spectrometry when the budget allowed. We did not analyze stream samples for hydrocarbon gases because of budgetary constraints. Additional details of chemical analyses are in Appendix A.

RESEARCH ROADMAP

Aims and Research Conducted	Methods Description
Aim 1: Identify and recruit homes - Identify homes with groundwater wells in “treatment” and “control” areas in SWPA - Conduct targeted outreach to recruit homes	Study Design and Methods
Aim 2: Plan and conduct fieldwork - Design a household survey - Identify fieldwork dates - Schedule homes - Conduct fieldwork, which includes taking water samples and administering the household survey	Study Design and Methods
Aim 3: Perform data analysis - Perform geochemical water sampling analysis - Perform radiation water sampling analysis - Perform household survey analysis	Data Analysis
Aim 4: Disseminate results - Share individual results with participants - Conduct community meetings to share aggregate study results - Prepare manuscripts for publication	Additional Materials 4

SURVEY DESIGN

The survey for this project (Additional Materials 2) was based on the survey used in the 2022 Yale study¹⁹ and tailored to our research aims, specifically the objective of soliciting possible exposure pathways. The survey contained three sections: (1) a main household survey; (2) well characteristics; and (3) resident demographics. The main household survey collected information about home and water use characteristics, including the age of the home, length of occupation, water filtration systems, sources of water, and main uses of water. The well characteristics questions gathered information on depth, date of development/drilling, and water testing frequency for each well or spring on the property. The resident demographic questions gathered information on the age, occupation, educational attainment, and place of work/school for each household resident. Research team members administered surveys in the field on an iPad using RedCap survey software. Team members reviewed survey responses upon returning from the field to ensure accuracy. They did not attempt to verify the accuracy of certain survey responses, such as well depth and home age, as the purpose of the survey was to gather the perspectives of the property owners. Survey data were stored on a password-protected PSU OneDrive account.

Institutional Review Board (IRB) approval was obtained from the Pennsylvania State Office of Research Protections to

conduct the survey (STUDY00017918). We obtained verbal informed consent before administering the survey using an IRB-Approved Consent Form (Additional Materials 3), and a paper copy of the form was provided and explained to the participants at the time of the survey.

LITERATURE REVIEW

We conducted this narrative literature review by searching PubMed and Google Scholar and using articles to identify additional resources. The primary focus was on key metals and metalloids of interest, including arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), strontium (Sr), thallium (Tl), lead (Pb), radium (Ra), radon (Rn), and uranium (U). Several factors guided the literature review, which primarily concentrated on publications that identified areas with contaminated drinking water, groundwater, or surface water from heavy metals and provided an analysis of the human health effects of the index cases living in the area or close to the primary area of water contamination. Additionally, there were no restrictions on the dates of literature publication or country of exposure, as it is likely that toxicity from select contaminants would not change over time. The initial review was focused on human health; however, when data were limited on human exposure and health effects for contaminants, we broadened the search to include mice and rat studies as well as case reports.

Exclusions included non-English literature, occupational exposure studies, risk assessments, and any study that did not assess the human or potential human health effects of such exposure.

DATA ANALYSIS

WATER CHEMISTRY ANALYSIS

There are no state-level groundwater standards for private wells in Pennsylvania. We compared analytes with US Environmental Protection Agency (EPA) primary and secondary standards — maximum contaminant levels (MCLs) and secondary maximum contaminant levels (SMCLs) — or, in the absence of EPA standards, other government standards, as detailed in **Table 3**.

EPA MCLs, listed under the Safe Drinking Water Act (see citations in **Table 3**), are legally enforceable limits in public drinking water systems. The process to establish MCLs involves a risk assessment of health effects from contaminants but also the cost of treatment to create a balance between public health protection and practical implementation. EPA maximum contaminant level goals (MCLGs) are unenforceable benchmarks that are based solely on health risks and are intended to protect sensitive populations. For carcinogens, for example, these MCLG values are zero and much lower than MCLs.

When EPA had not established an MCL, we examined other government benchmarks used to protect human health, including regulatory thresholds defined under the EPA Lead and Copper Rule, which was established to protect sensitive populations. EPA also proposed a Br standard to avoid the formation of carcinogenic disinfection byproducts during chlorination. The US Geological Survey (USGS) proposed values for lithium, whereas the US Department of the Interior, Office of Surface Mining, proposed guidance for methane to avoid explosions (see citations in **Table 3**).

Statistical Analyses

The data analysis for water chemistry in this project consists of two major parts: (1) statistical analysis and (2) geospatial analysis. We replaced below-detection values with their corresponding detection limits for statistical and geospatial analyses. Many of the data distributions are not normal or have varying numbers of censored data values. We therefore used statistical or geostatistical tests to account for those characteristics as described below.^{20–23}

Statistical analysis, the primary focus of this study, provides a straightforward approach to testing the hypotheses. We divided the sample dataset into subsets depending on the sites of interest, with abbreviations provided in parentheses for future reference: (1) samples within hotspots, (2) samples within UOG impoundment zones, (3) samples within recent spill areas, and (4) samples within the pure-C control zone. Sites 1 through 3 are referred to collectively as treatment sites.

The research team calculated basic statistics for each chemical analyte for the full dataset ($n = 90$; 76 wells and 14 springs) as well as for the defined subsets. The full dataset excludes four stream samples, one rainwater sample, and two acid mine drainage (AMD) affected wells (**Table 1**). These statistics include the number of measurements (n), the minimum and maximum concentrations, the mean and median concentrations, and the concentrations at the 5th, 25th, 75th, and 95th percentiles. Additionally, we established threshold values in accordance with the MCL²⁴ and SMCL²⁵ defined in EPA regulations, along with health-based screening levels provided by EPA and the USGS.²⁶ We then determined the percentage and number of samples exceeding these thresholds. For further details, refer to **Table D-1** in **Appendix D**. We excluded stream samples from the statistical and geospatial analyses because surface water chemistry is influenced by different hydrologic and exposure processes than private wells and springs, and the primary study questions focused on groundwater used by households.

We conducted statistical comparisons between each treatment group and pure-C control for all the analytes. Note: Radon, radium-226, radium-228, and combined radium (226+228) were all tested as independent variables. Comparisons were completed with nonparametric tests — specifically, the Wilcoxon-Mann-Whitney (WMW) rank sum test and the Brunner-Munzel (BM) test. The WMW test is applicable when sample variances are similar because of its strength in detecting differences in central tendency under homoscedastic conditions. Conversely, the BM test is applicable when variances differ significantly because of its robustness to heteroscedasticity. When a large number of tied values are present — as can happen when measurements predominantly fall below the detection limit (DL), as occurred for aluminum, beryllium, and cadmium in this study — the BM test may not perform as intended, whereas the WMW test is generally more reliable under these conditions. Both tests have proven robust in handling skewed distributions, small group sizes, and a high proportion of analyte concentrations below the DL.²⁷

We used the pure-C control sites to establish the regional baseline profile for groundwater quality. The following comparisons were performed: hotspot versus pure-C, impoundment versus pure-C, and spill versus pure-C.

One-sided tests were performed to test the following null hypotheses (note: the comparison of distributions is often interpreted as the comparison of medians):

- a. The median of dataset A $\geq$ the median of dataset B
- b. The median of dataset A $\leq$ the median of dataset B

If $P < 0.05$ for either test, then $A < B$ (null hypothesis a) or $A > B$ (null hypothesis b).

We used one-sided nonparametric tests (WMW and BM) because our hypothesis was directional: that groundwater in treatment areas (e.g., hotspots, impoundments, spills) would exhibit higher concentrations of analytes indicative of UOGD

Table 3. Summary of Health Standards for Drinking Water and Instances of Exceedance for Geochemistry and Radiation Analyses

Analyte	EPA Primary Standard Super ²⁴	EPA Secondary Standard ²⁵	Analytical Detection Limit ^b	Other Standards	# Sites Exceeding Primary (Secondary) or Other 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 ³⁴	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 ³⁵	0
Lithium			0.15 µg/L	10 µg/L ²⁶ 60 µg/L ³⁰	46 3
Beryllium	4 µg/L		0.05 µg/L		0
Nickel			0.05 µg/L	100 µg/L ³⁵	0
Copper		1,000 µg/L	0.05 µg/L	1,300 µg/L ³⁶	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 ³⁶	0
Uranium	30 µg/L		0.05 µg/L		0
Radium-226+228	5 pCi/L		0.007 pCi/L		0
Radium-226			0.0024 pCi/L	27 pCi/L ⁶⁴	0
Radium-228			0.005 pCi/L	2.7 pCi/L ⁶⁴	0
Gross alpha	15 pCi/L		26 pCi/L		0
Radon			6 pCi/L	300 pCi/L 4,000 pCi/L ^{35,a}	33 0
Methane				10 mg/L 28 mg/L ³⁷	2 1
Benzene	5 µg/L		0.04 µg/L		0
Toluene	1,000 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

Calc. TDS = calculated total dissolved solids; EPA = US Environmental Protection Agency.

^aTwo different types of standards have been proposed. See discussion regarding radon in the Results section above.^bThese detection limits are provided by laboratory analysis reports.

contamination compared with pure-C controls. Concentrations lower than controls would not indicate contamination, and, therefore, a two-sided test would unnecessarily dilute statistical power. Nonetheless, for transparency, we report instances for which analyte concentrations in treatment sites were lower than in controls.

Given that each of these one-sided tests is expected to yield a false discovery of difference 5% of the time for each of the 41 analytes (excluding pH, alkalinity, air CH₄, 87Sr/86Sr, delta-13-C1, delta-13-C2, delta-D), we expect to observe multiple false discoveries. Thus, we also used the Benjamini-Hochberg procedure (also called the false discovery rate [FDR] procedure) to control the expected proportion of false discoveries. We used FDR = 0.1, meaning that we accepted up to 10% false positives. The procedure ranks the *P* values from our tests in ascending order and compares each to a rank-dependent threshold $(i/m) \times 0.1$, where *i* is the rank and *m* = 41 is the number of tests. Analytes with *P* values below this threshold were retained as significantly different, with no more than 10% expected to be false positives.

Geospatial Analysis

We used ordinary least squares (OLS) linear regression to examine the correlations between concentrations of brine-related species and the geodesic distance from each sample to the closest UOG wells within hotspots, impoundments, and recent spills. We calculated all distances using ArcGIS Pro and publicly available datasets (e.g., oil/gas location, spill location, recorded coordinates of water sampling sites). OLS is the method most used to determine linear correlation between independent and dependent variables. OLS minimizes the sum of squared differences between observed and predicted values, assigning all error to the dependent variable.²⁸ In addition, Spearman, Kendall's tau, and Theil-Sen (ATS)^{20–22} slopes were also calculated for the same sets of variable pairs. The Spearman rank correlation coefficient is a nonparametric indicator of statistical dependence for rankings of a variable assuming a monotonic relationship. This coefficient is used for distributions that are not necessarily normal and may have many censored values. Kendall's tau is a nonparametric test statistic calculated using a rank test and is used for distributions that are not necessarily normal and may have a large number of censored values (including chemical analyses that may have multiple reporting limits). The ATS slope estimator is another nonparametric method that yields ATS slopes as a robust estimate of the median slope by considering pairwise differences. ATS slopes are less sensitive to outliers and skewed distributions than OLS regression.^{20–22}

Correlations were considered statistically significant if they yielded a *P* value lower than 0.05. Negative correlations indicate that SC or the analyte concentrations ([*analyte*]) decrease as site distance increases (square brackets refer to dissolved concentration). The following species were selected for geospatial analysis: SC, chloride [Cl], sodium [Na], sulfate [SO₄], barium [Ba], strontium [Sr], bromide [Br], iron [Fe], methane [CH₄], and radon [Rn]. Specific conductance (SC),

chloride [Cl], and sodium [Na] are indicators of groundwater salinity and serve as proxies for assessing the effect of salt, a major component of UOG waste waters. Iron and sulfate were chosen because they are redox-sensitive and have sometimes been used to predict contamination related to UOGD.²⁹ SC, [Cl], [Ba], [Sr], [Br], methane, and radon are typically enriched in UOG-produced waters, making them valuable tracers for identifying deep formation brine, methane leakage, and potential UOG-related contamination.^{1,27} Geodetic distances between water samples and other features of interest (e.g., nearest spill) were calculated using the “Near” function in ArcGIS Pro (in units of kilometers), with WGS (World Geodetic System) 1984 as the designated geographic coordinate system.

SURVEY ANALYSIS

Descriptive statistics were compiled to examine the age of residents, number of occupants, education levels, income levels, age of the home, time lived in the home, main drinking water sources, well depth, well age, land use practices, and distance from UOGD wells (as reported by participants). Minimum, maximum, mean, and median values were assessed for these variables as appropriate.

RESULTS

FIELD MEASUREMENTS

Across all samples, including goodwill samples, sites assumed to be influenced by AMD, and the rainwater site (*n* = 97), water pH ranged from 3.15 to 8.99, with 88% of waters within the EPA-recommended range of 6.5–8.5. Seven sites exhibited pH < 6.5, and five exhibited pH > 8.5. The sets of wells and springs (ground waters) each showed an average pH of ~7, whereas streams (surface waters) averaged ~8. Temperature ranged from 11.5°C to 21.4°C, with well water on average coldest (~14°C), springs intermediate (~16°C), and streams warmest (~19°C). Specific conductance ranged from 25.3 to 3,490 µS/cm (microSiemens per centimeter). Most waters were <1,200 µS/cm, with seven higher outliers. Alkalinity ranged from 10 to 668 mg/L, expressed as calcium carbonate (CaCO₃), with the highest average alkalinity detected in groundwater wells (~280 mg CaCO₃/L), followed by springs (~240 mg CaCO₃/L) and streams (~190 mg CaCO₃/L).

Methane was detected in ambient air at concentrations >5 ppm for 15% of all (*n* = 97) sites, with the highest air reading at 132 ppm. Dissolved methane was detected in water samples at 70% of all (*n* = 97) sites (DL = 0.0002 ppm methane).

LABORATORY ANALYSES OF WATER CHEMISTRY

A statistical summary of the dataset for chemistry of groundwater wells (*n* = 76; excluding two AMD-affected samples and one rain-affected sample) and springs (*n* = 14) are collated in Table D-1 in Appendix D.

PUBLIC HEALTH LIMITS

Of all ($n = 97$) samples, the pH of 12 samples was outside the range suggested by EPA for drinking water (6.5 to 8.5). Two of these samples had very low pH (3.15 and 4.04) and very high aluminum ($[Al] > 0.2$ mg/L) and SO_4 (> 250 mg/L). These characteristics are common in waters affected by AMD resulting from coal mining, which is historically prevalent in the local area. As mentioned previously, we therefore removed these samples from the dataset and did not consider them further with respect to indications of potential UOGD contamination. Several of the other samples with out-of-range pH had characteristics of hard water derived from calcite-containing aquifers and were not deemed of concern to public health. Calculated values for total dissolved solids (TDS) for 19 samples were > 500 mg/L, exceeding the EPA-recommended SMCL for aesthetic qualities of drinking water.

With respect to trace elements and major element anions and cations, water chemistry was generally protective of human health. Five sites exceeded the EPA SMCL of 250 mg/L for chloride, and two exceeded the SMCL of 250 mg/L for sulfate; the high sulfate samples are those mentioned above that were identified as likely affected by AMD (Table 3). One site with high chloride also equaled or exceeded the EPA MCL for barium (2 mg/L; concentration in the sample was 2.05 mg/L, within analytical error of the MCL) and the SMCL of 2 mg/L for fluoride and bromide, with concentrations of 3.52 mg/L and 5.81 mg/L, respectively. Otherwise, all sites exceeded limits for only one anion.

Two major element cations, manganese (Mn) and iron (Fe), sometimes exhibited concentrations above EPA SMCLs, with 19 and seven sites, respectively, exceeding these thresholds. These secondary limits are based largely on aesthetic considerations. Lithium (Li) concentrations at 46 sites were higher than the EPA provisional peer-reviewed toxicity value of 10 μ g/L.²⁶ Of these samples, three exceeded the drinking water-only benchmark proposed by the USGS of 60 μ g/L.³⁰ All other trace metals (Be, Ni, Cu, As, Tl, Cd, Pb, and U) were only measured at concentrations below health and other EPA recommendations. Trace metal Be was detected (> 0.05 μ g/L) at two sites, Ni at 93, Cu at 92, As at 68, Tl at 19, Cd at 1, Pb at 73, and U at 75. Four copper detections and 13 lead detections may be spurious for the same reason mentioned above for lithium.

Regarding organic constituents, BTEX concentrations were all below the relevant health standards (Table 3). Sample values ranged from less than detection ($< DL$) to 0.77 μ g/L for benzene, $< DL$ to 3.29 μ g/L for toluene, $< DL$ to 9.49 μ g/L for ethylbenzene, and $< DL$ to 1.42 μ g/L for total xylenes. Dissolved methane concentrations were also generally very low, with only eight sites showing > 1 mg/L. Methane concentrations at three sites, however, were > 10 mg/L, the US Department of Interior (DOI) action level, with one of those sites showing > 28 mg/L, the DOI immediate action level. These warning and action levels refer to health concerns related to degassing and accumulation in enclosed spaces where methane poses an ignition and explosion risk.^{31,32}

RADON

Radon samples were collected for 89 sample locations. Samples were only collected from wells and springs (radon samples were not collected from stream locations). No radon samples were collected during trip 7. A spring from trip 2 was also excluded because limited access prevented collection of a nonaerated sample. After excluding the rainwater and AMD samples, the remaining 86 samples in the study group had a median radon concentration of 213 pCi/L and a slightly higher mean of 315 pCi/L. There is no federally enforced guideline for radon in drinking water; however, 33 samples exceeded the recommended MCL of 300 pCi/L for radon in drinking water as specified by the 1996 Amendments to the Safe Drinking Water Act. No radon measurements exceeded the actionable level of 4,000 pCi/L. Note that the 300 pCi/L EPA recommendation is for municipal water supplies in states with no indoor air radon mitigation program.

RADIUM

A total of 96 samples were collected for radium analysis. A stream sample from trip 1 was not collected. After applying the same procedures noted above, and excluding stream, rainwater, and AMD samples, 90 samples were used in statistical and geospatial comparisons. No radium measurements exceeded the MCL of 5 pCi/L combined (226+228). Our range and mean values are similar to values reported in principal aquifers across the United States.³³

GROSS ALPHA

Ninety-three samples were analyzed for gross alpha. Gross alpha samples were not collected from a stream during trip 1 or from three wells during trip 7. All readings were below the minimal detectable activity (MDA) of 26 pCi/L. These data are consistent with the reported radium values < 5 pCi/L. We note that the MDA was greater than the MCL for gross alpha (15 pCi/L). Samples could therefore have gross alpha concentrations greater than the MCL but below the MDA, representing a limitation of the gross alpha method.

STATISTICAL COMPARISON OF GEOCHEMICAL DATA

Results of the one-sided test (applied to all sampled waters except surface waters, goodwill samples, the well water from one home that was only rainwater, and two well waters showing pH < 4.5 that were identified as affected by local AMD) using the pure-C control are presented in **Table 4** to highlight the significant differences or trends of the analyte concentrations between datasets.

As shown in Table 4, the comparisons of well and spring waters from hotspot, impoundment, and spill datasets with pure-C, nine species were higher than the pure-C (NO_3 , potassium [K], U, Rn, Cl, Ra, Pb, benzene, Cu), and two were lower (phosphorus [P], ethylbenzene). If we only focus on the set of treatment samples that showed statistically significant evidence of a higher concentration than the pure-C control sites (i.e., evidence of potential contamination related to the treatment), we conclude that for hotspot versus pure-C, NO_3 ,

Table 4. One-Sided Test Results of Wilcoxon-Mann-Whitney Rank Sum Test and Brunner-Munzel Tests for All Data (Springs and Wells, Except Goodwill Samples, the Rainwater Sample, and Two Acid Mine Drainage Samples)

Compared Dataset	Significant Difference	WMW	BM
Hotspots vs. pure-C	HS > pure-C	NO ₃ , K, U, Rn, Ra-226, Ra-228, Ra 226+228	Cl, NO ₃ , K, U, Rn, Ra-226, Ra-228, Ra 226+228
	HS < pure-C	P, ethylbenzene	P
Impoundments vs. pure-C	I > pure-C	Cl, Pb, Ra-226, Ra-228, Ra 226+228	Pb, benzene, Ra-226, Ra-228, Ra 226+228
	I < pure-C	P	P
Spills vs. pure-C	S > pure-C	K, Cu, Rn, Ra-228, Ra 226+228	K, Cu, Rn, Ra-226, Ra-228, Ra 226+228
	S < pure-C	—	—

WMW = Wil.

K, U, Ra-226, Ra-228, Ra 226+228, and Rn were higher using both WMW and BM tests and only Cl was also higher using the BM test. These results could mean that the hotspot areas are indeed sites where UOGD is causing contamination, as hypothesized by Shaheen and colleagues (2022).¹ However, K and NO₃ are not known to be common contaminants caused by UOGD; rather, they are often associated with agriculture, a land use common in the study area. Uranium-238, thorium-232, radium-226, and potassium-40 are all naturally occurring radioisotopes that are present in commercially available fertilizers.³⁸ Uranium, radium, and radon in our study could potentially be elevated because of fertilizer use. Given these associations, one hypothesis to explain the results is that the hotspot areas show evidence of agricultural contamination compared with the pure-C control sites.

We used the Benjamini-Hochberg procedure (also called the FDR procedure) to control the expected proportion of false discoveries.³⁹ We used FDR = 0.1, meaning that we accept up to 10% false positives. The procedure compares the ranked *P* values from our tests to those of an independent dataset. When we applied this procedure to the wells + springs dataset (without the goodwill sites, rainwater site, and AMD sites), significant results are shown in **Table 5**. Only NO₃, K, Ra-226, Ra-228, and Ra-226+228 remain significant for hotspots versus pure-C, and Ra-226, Ra-228, and Ra-226+228 for impoundments versus pure-C. The results remain significant for the BM test. No significant results remain for the WMW test.

For all the other analytes not discussed here for the total water dataset, we conclude that there is either no difference or a negative difference between the distributions for hotspot, impoundment, and spill versus the pure-C control. The complete statistical results for all waters are included in Appendix D, Table D-1.

Given the strong relationship between NO₃ (and the possibility of K, U, Ra, and Rn association) and agricultural contamination in waters, we inspected the dataset to look for evidence of agricultural effects. We noted that the subset of

waters in the dataset derived from springs had a statistically higher concentration of NO₃ than did well waters in the dataset. For that reason, we repeated the statistical tests as just described, but focusing only on the well waters. **Table 6** shows these results.

As shown in Table 6 for the well waters only, in comparisons of hotspot, impoundment, and spill with pure-C, seven species were higher than the pure-C (Cl, Mg, K, Rn, Pb, Cu, Ra), and two were lower (P, ethylbenzene). If we only focus on the set of treatment well water samples that showed statistically significant evidence of a higher concentration than the control sites (i.e., evidence of potential contamination related to the treatment), we conclude that for hotspot versus pure-C, K, Rn, Cl, Mg, Ra-226, Ra-228, and Ra-226+228 were higher using both the WMW and BM tests. These results could mean that the hotspots are indeed sites where UOGD is causing contamination, as hypothesized by Shaheen and colleagues (2022).¹ Other explanations include random occurrence or other unconstrained factors such as differences in geology.

For impoundment sites, Cl (WMW only) and Ra-226, Ra-228, Ra-226+228, Pb (both WMW and BM) were slightly higher in well waters in the treatment set compared with the pure-C set. For spill sites, concentrations of K, Ra-226+228, Ra-228, and Cu were slightly elevated compared with the pure-C sites. These findings could indicate that the impoundment sites and/or the spill sites might have contaminated the groundwater nearby.

For all other analytes in the well water dataset not discussed here, we conclude that the distributions for hotspot, impoundment, and spill showed either no difference or a negative shift relative to the pure-C control.

*Water samples were collected from 89 residential properties. One residential property was unable to take the survey due to time constraints. Efforts to follow up with residents of the property to complete the survey were unsuccessful.

Table 5. One-Sided Test Results of Wilcoxon-Mann-Whitney Rank Sum Test and Brunner-Munzel Tests for All Data (Springs and Wells, Except Goodwill Samples, the Rainwater Sample, and Two Acid Mine Drainage Samples) with a False Discovery Rate of 0.1

Compared Dataset	Significant Difference	WMW	BM
Hotspots vs. pure-C	HS > pure-C	–	NO ₃ , K, Ra-226, Ra-228, Ra 226+228
	HS < pure-C	–	–
Impoundments vs. pure-C	I > pure-C	–	Ra-226, Ra-228, Ra 226+228
	I < pure-C	–	–
Spills vs. pure-C	S > pure-C	–	–
	S < pure-C	–	–

BM = Brunner-Munzel; HS = hotspot; I = impoundment; S = spill; WMW = Wilcoxon-Mann-Whitney.

Table 6. One-Sided Test Results of Wilcoxon-Mann-Whitney Rank Sum Test and Brunner-Munzel Tests for Well Data Only (Excluding Goodwill Samples, the Rainwater Sample, the Two Acid Mine Drainage Samples, and All Spring Samples) in Comparison with Pure-C Control

Compared Dataset	Significant Difference	WMW	BM
Hotspots vs. pure-C	HS > pure_C	Cl, K, Mg, Rn, Ra-226, Ra-228, Ra 226+228	Cl, K, Mg, Rn, Ra-226, Ra-228, Ra 226+228
	HS < pure_C	P, ethylbenzene	P, ethylbenzene
Impoundments vs. pure-C	I > pure_C	Cl, Pb, Ra-226, Ra-228, Ra 226+228	Pb, Ra-226, Ra-228, Ra 226+228
	I < pure_C	P	P
Spills vs. pure-C	S > pure_C	K, Cu, Ra-228, Ra 226+228	K, Cu, Ra-228, Ra 226+228
	S < pure_C	–	–

BM = Brunner-Munzel; HS = hotspot; I = impoundment; S = spill; WMW = Wilcoxon-Mann-Whitney.

We also applied the Benjamini-Hochberg procedure with an FDR = 0.1 to the wells-only dataset (without the goodwill sites, the rainwater site, and AMD sites). Using the FDR procedure, we observed that Ra-226, Ra-228, and Ra-226+228 concentrations in the hotspot and impoundment treatment sites were greater than in the pure-C control with the BM test. Ra-228 and Ra-226+228 were statistically greater in impoundments compared with pure-C for the WMW test (**Table 7**).

GEOSPATIAL ANALYSIS

Tables 8–10 summarize the correlations between 12 analytes (SC, Cl, Na, SO₄, Ba, Sr, Br, Fe, CH₄, Ra-226, Ra-228, and Rn) and proximity to UOG wells within the hotspot, impoundment, and spill sites (including brownfields), respectively. For these calculations, all well and spring water samples were used except for the AMD and rainwater sites (hotspot, impoundment, spill, control, pure-C, and goodwill samples). Similar tests completed on the wells-only dataset yielded similar results, as discussed below (see Appendix C, Tables C-1, C-2, and C-3).

As shown in Table 8, two analytes in the wells + springs dataset showed a statistically significant correlation with UOG wells (Na, methane). Both showed positive correlations, indicating that no analytes tend to increase in concentration as the distance to UOG wells decreases for this dataset. This conclusion does not change if we look at the wells-only dataset.

As shown in Table 9, three analytes (Na, Sr, Br) in the wells + springs dataset showed a statistically significant correlation with distance to impoundments. Of these, only Sr showed a negative correlation (for two of the four statistical tests), indicating that only Sr tends to increase in concentration as the distance to impoundments decreases. This conclusion does not change if we do the same analyses for the wells-only dataset.

As shown in Table 10, four analytes (Na, Ba, SO₄, CH₄) showed a statistically significant correlation with respect to distance to spill sites. Of these, only Na, Ba, and CH₄ showed a negative correlation, indicating that those three analytes tend to increase in concentration as distance to spill sites

Table 7. One-Sided Test Results of Wilcoxon-Mann-Whitney Rank Sum Test and Brunner-Munzel Tests for Well Data Only (Excluding Goodwill Samples, the Rainwater Sample, the Two Acid Mine Drainage Samples, and All Spring Samples) in Comparison with Pure-C Control with a Benjamini-Hochberg Procedure to Reduce False Discoveries with an FDR = 0.1

Compared Dataset	Significant Difference	WMW	BM
Hotspots vs. pure-C	HS > pure-C	–	Ra-226, Ra-228, Ra 226+228
	HS < pure-C	–	–
Impoundments vs. pure-C	I > pure-C	Ra-228, Ra 226+228	Ra-226, Ra-228, Ra 226+228
	I < pure-C	–	–
Spills vs. pure-C	S > pure-C	–	–
	S < pure-C	–	–

BM = Brunner-Munzel; FDR = false discovery rate; HS = hotspot; I = impoundment; Ra-228 = radium-228; Ra 226+228 = combined radium-226 and radium-228; S = spill; WMW = Wilcoxon-Mann-Whitney.

Table 8. Regression and Correlation Coefficients Calculated Between Brine-Related Species' Concentrations and the Distance (km) to Hotspots for the Set of All Well and Spring Waters, Including Goodwill Samples but Not Including the Rainwater and Acid Mine Drainage Samples

	SC	Na	Cl	Ba	SO ₄	Sr	Br	Fe	CH ₄	Ra-226	Ra-228	Rn
OLS_slope	2.93	3.055 ^a	0.119	0.003	–0.588	–0.005	0.012	0.002	0.206 ^a	0.001	0.002	–5.476
Spearman	–0.099	0.026	–0.051	–0.041	–0.206	–0.109	0.086	0.139	0.310 ^a	0.044	0.006	–0.113
Kendall's tau	–0.071	0.022	–0.038	–0.029	–0.133	–0.069	0.058	0.104	0.214 ^a	0.030	0.007	–0.082
ATS slope	–3.793	0.121	–0.192	0	–0.686	–0.006	2.26×10 ^{–4}	0	9.55×10 ^{–5a}	0.001	2.39×10 ^{–4}	–6.490

Ba = barium; Br = bromine; CH₄ = methane; Cl = chlorine; Fe = iron; Na = sodium; Rn = radon; SC = specific conductance; SO₄ = sulfate; Sr = strontium.

^aStatistically significant features at the significance level of 95%.

Table 9. Regression and Correlation Coefficients Calculated Between Brine-Related Species' Concentrations and the Distance (km) to Impoundments for the Set of All Well and Spring Waters, Including Goodwill Samples but Not Including the Rainwater and AMD Samples

	SC	Na	Cl	Ba	SO ₄	Sr	Br	Fe	CH ₄	Ra-226	Ra-228	Rn
OLS_slope	11.504	4.617 ^a	1.86	0.007	0.077	–0.005	0.029 ^a	–0.002	0.097	–4.56×10 ^{–4}	–6.36×10 ^{–5}	–8.447
Spearman	–0.063	0.05	–0.085	–0.129	0.028	–0.225^a	–0.051	–0.156	0.144	–0.162	–0.192	0.01
Kendall's tau	–0.034	0.033	–0.05	–0.086	0.03	–0.151^a	–0.037	–0.117	0.095	–0.124	–0.133	0.01
ATS slope	–2.310	0.170	–0.236	–0.001	0.160	–0.014 ^a	–1.61×10 ^{–4}	0	2.49×10 ^{–5}	–0.003	–0.004	0.447

Ba = barium; Br = bromine; CH₄ = methane; Cl = chlorine; Fe = iron; Na = sodium; Rn = radon; SC = specific conductance; SO₄ = sulfate; Sr = strontium.

^aStatistically significant features. Bold font highlights statistically significant negative correlations indicating a contaminant increases near the feature.

Table 10. Regression and Correlation Coefficients Calculated Between Brine-Related Species' Concentrations in All Water Samples and the Distance (km) to Spill Sites for the Set of All Well and Spring Waters, Including Goodwill Samples but Not Including the Rainwater and AMD Samples

	SC	Na	Cl	Ba	SO ₄	Sr	Br	Fe	CH ₄	Ra-226	Ra-228	Rn
OLS_slope	-15.816	-5.954^a	-4.165	-0.014^a	1.072	-0.011	-0.026	-0.005	-0.286	-0.004	-0.004	3.651
Spearman	1.98×10 ⁻⁴	-0.307^a	-0.119	-0.084	0.208 ^a	-0.048	-0.101	0.034	-0.259^a	-0.085	-0.110	-0.025
Kendall's tau	-0.002	-0.209^a	-0.084	-0.054	0.145 ^a	-0.037	-0.069	0.024	-0.172^a	-0.058	-0.075	-0.019
ATS slope	-0.143	-1.199^a	-0.521	-0.001	1.106 ^a	-0.005	-4.00×10 ⁻⁴	0	-9.41×10^{-5a}	-0.002	-0.003	-1.286

Ba = barium; Br = bromine; CH₄ = methane; Cl = chlorine; Fe = iron; Na = sodium; Rn = radon; SC = specific conductance; SO₄ = sulfate; Sr = strontium.

^aStatistically significant features. Bold font highlights statistically significant negative correlations indicating a contaminant increases near the feature.

decreases. Those conclusions remain the same if the calculations were made for the wells-only dataset.

SEEKING SIGNATURES OF SALT AND GAS ORIGIN

Isotopic data and major element ratios can sometimes be used to interpret the provenance of dissolved salts and gases. Such interpretations are never 100% certain because most dissolved constituents have many sources. Here, we discuss isotopic ratios of Sr (the ratio of ⁸⁷Sr to ⁸⁶Sr) and C (the ratio of ¹³C to ¹²C) along with chloride and bromide concentrations.

For all the groundwater samples where Sr isotopes were measured for dissolved Sr, **Figure 2** shows ⁸⁷Sr/⁸⁶Sr versus strontium-to-chloride concentration ratios ([Sr]/[Cl]). In the figure, the size of the symbol for the groundwater sample indicates the [Cl] of the sample, and the color indicates the type of sample (control, impoundment, spill, hotspot). Samples of UOG produced waters are also shown and labeled as UOG. The maximum and minimum ⁸⁷Sr/⁸⁶Sr ratios for the produced waters are shown as faint dashed lines. ⁸⁷Sr/⁸⁶Sr ratio values in the groundwater are similar to ratios measured in produced waters from UOG (i.e., Marcellus Shale), whereas most impoundment samples had ratios exceeding the maximum UOG produced water ratio. The figure emphasizes that some of the more saline groundwater samples (larger symbols) have lower [Sr]/[Cl] than most produced waters.

The waters from different site types plot in almost all parts of the diagram in Figure 2, documenting that the different site types do not vary consistently with respect to ⁸⁷Sr/⁸⁶Sr. Consistent with this inference shown in Figure 2, **Figure 3** shows that the ⁸⁷Sr/⁸⁶Sr values for the different site types are indistinguishable and similar to those of UOG produced waters in Pennsylvania. Figure 3 also shows that the groundwaters sampled in this project are dissimilar in ⁸⁷Sr/⁸⁶Sr from conventional oil and gas produced waters (i.e., from formation waters derived from reservoirs shallower than the Marcellus).

*One sample had a dissolved methane level of 9.4. The research team called this home to discuss these results, even though the value did not exceed the DOI warning level of 10 mg/L.

We can use a similar approach to interrogate the provenance of the gases identified in the groundwaters (**Figure 4**). Here, C₁, C₂, and C₃ refer to the concentrations of methane, ethane, and propane, respectively. The y-axis of the figure, C₁/(C₂+C₃), is often used to distinguish gases of thermogenic versus biogenic origin. Thermogenic gases, formed at elevated temperatures in the subsurface, contain higher-chain alkanes, such as C₂ and C₃, and this means that thermogenic gases plot at lower C₁/(C₂+C₃). Biogenic gases, generally formed at lower temperatures near or at the Earth's surface, plot at high C₁/(C₂+C₃) because ethane and propane are seldom produced by bacteria.⁴¹ In the figure, boxes for thermogenic (pink) and biogenic (blue) gases show where we have also incorporated the observation that δ¹³C measured in methane (δ¹³C-CH₄) is seldom larger than -50‰ (parts per thousand) for biogenic gases.⁴²

Figure 4 shows the groundwater samples as circular symbols, the size of which increases with the measured methane concentration. Consistent with the summarized literature values, the natural gases from UOG wells in Pennsylvania (green squares) plot almost entirely in the thermogenic box. None of the groundwater samples, in contrast, plot in the thermogenic box, whereas two plot in the biogenic box. These data are most consistent with primarily biogenic gas in some samples, with possible mixing that includes a thermogenic component in a smaller subset; however, the figure alone does not quantify the mixing fraction or rule out other explanations.

The chloride-to-bromide concentration ratios (Cl/Br) can sometimes be used to distinguish the source of elevated chloride in water samples in hydrocarbon basins such as the Appalachian Basin.⁴³ Chloride sources such as road salt and organic wastes (septic systems or animal waste) contain little bromide and therefore have relatively high Cl/Br ratios.⁴⁴ Cl/Br ratios of ~52 samples are higher than those measured in Pennsylvania formation waters (Appalachian Basin brines or ABB) that emit naturally into surface and groundwater throughout the state and also return to the land surface with natural gas during UOGD, while about 32 samples show Cl/Br ratios within the range of ABB values. The brines are characterized by higher Br concentrations and much lower Cl/Br

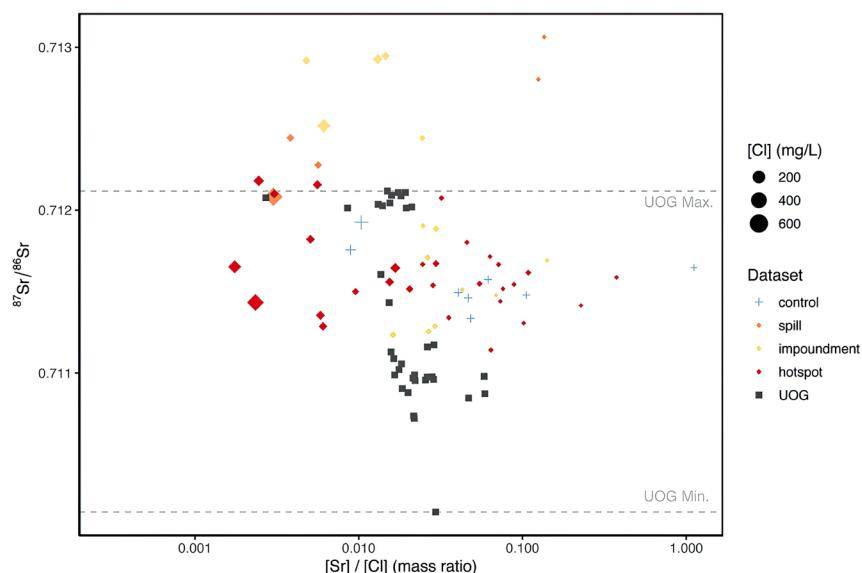


Figure 2. Sr isotopic ratios (^{87}Sr versus ^{86}Sr) for groundwater samples plotted against the strontium-to-chloride concentration ratios (expressed in mg/L). Larger symbol sizes indicate higher chloride concentrations for the same samples, as shown in the legend. Symbol color denotes sample type (spill, hotspot, etc.). Dashed lines indicate the upper and lower limits of the chemistries for produced waters published from the relevant UOG wells in Pennsylvania.⁴⁰

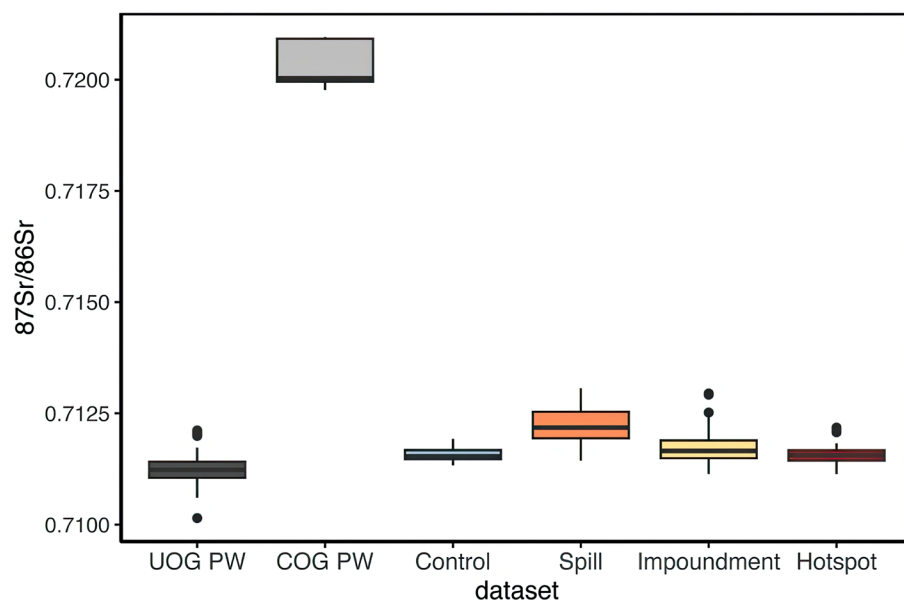


Figure 3. Box and whisker plots for each type of water as indicated. UOG PW refers to produced water from unconventional oil and gas wells; COG PW refers to produced water from conventional oil and gas wells. UOG and COG waters plotted in this figure represent published water chemistries from produced waters from the relevant well types in Pennsylvania.⁴⁰

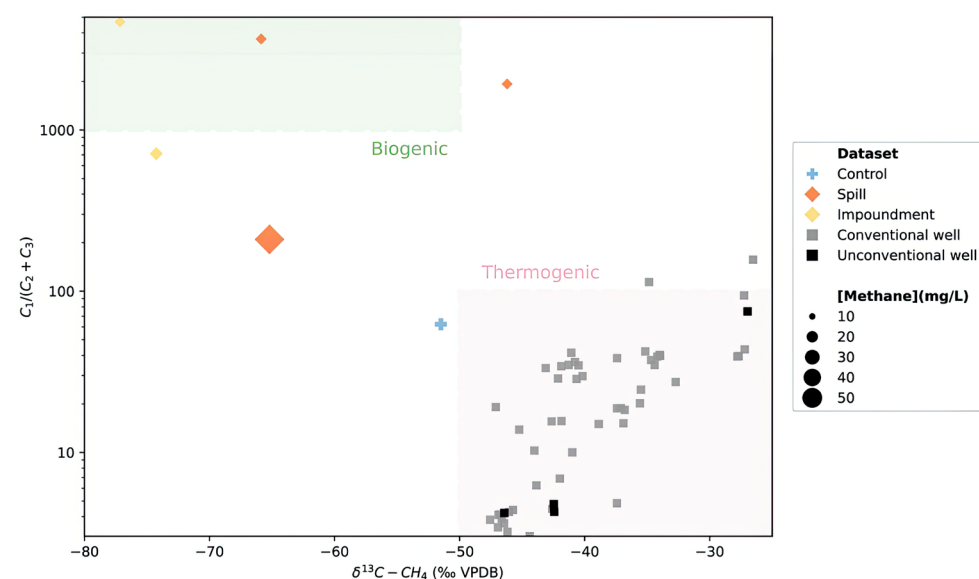


Figure 4. Concentrations of methane (C_1) versus ethane (C_2) + propane (C_3) plotted versus $\delta^{13}\text{C}-\text{CH}_4$ measured in groundwater and produced water samples.

The symbols are sized according to methane concentration, [methane], as shown in the legend and colored according to sample type (control, spill, etc.). Squares, plotted for comparison, represent production gas samples of conventional and unconventional oil and gas wells in Pennsylvania, compiled in the Global Inventory of Gas Geochemistry Data.⁶⁵ The boundaries for the biogenic and thermogenic boxes are referred to from the Bernard plot.^{66,67}

ratios.⁴⁵ Calculated Cl/Br ratios for this dataset are shown in **Figure 5**. The majority of samples with higher concentrations (>100 mg/L) of Cl plot with relatively higher Cl/Br ratios, whereas one sample plots closer to the Appalachian Basin brine zone, and its high [Br] (5.81 mg/L) is consistent with a non-negligible brine contribution, either from natural ABB or produced water.

Cl/Br ratios presented in box and whisker plots (**Figure 6**) show that most samples collected in this study, regardless of treatment type, contained Cl/Br ratios much higher than those typical of UOG wastewaters.

SURVEY AND LITERATURE REVIEW

Surveys were administered at 88 residential properties.* As detailed in **Table 11**, the average household size was 2.5 people (median 2). The average number of years living in the sampled homes was 22.8 years (median 20 years). The average age of occupants was 44.2 years (median 48 years); the average education level was some college, and the average household income was self-reported as \$75,000–\$99,999 (median \$100,000–\$149,000). All households sampled were White. These demographics largely accord with recent census data for Washington County, Pennsylvania, which reports a median household income of \$77,450, a median resident age of 44 years old, and a largely White population (89.2%).⁴⁷ Our sample has a higher educational attainment than the Washington County average, as only 32.7% of the county's residents have attained a bachelor's degree or above.⁴⁷

Home characteristics are reported in **Table 12**. The average year the home was built was 1956 (median 1974). Several homes had more than one water source, although we only used one response for each home. We ran the analyses for each well/spring on the property but only conducted the survey analysis once for each home ($n = 88$). Although several houses had multiple wells/springs, we selected the primary water source for this analysis. The average well depth was 110 ft (median 100 ft) with a minimum of 10 ft and a maximum of 250 ft. The depth of 10 ft was a spring, however, and the next shallowest depth of 22 ft was defined as a well by the homeowner. We recorded well depths from well caps, if available, or they were self-reported by homeowners.

For each of the 88 homes included in this analysis, 85 self-reported a distance to a well pad, with the average distance being 0.85 miles (0.5 miles median), with a minimum distance of 0.05 miles and a maximum distance of 10 miles. The distance to an impoundment hydraulic fracturing pond was slightly farther from the reported homes ($n = 31$) with

an average distance of 2.14 miles (median 1.3 miles), a minimum of 0.1 miles, and a maximum of 10 miles. However, this distance is still closer than our comparative confounding variable of the nearest gas station, which was reported by 87 of the homes with a mean of 3.8 miles (median 3 miles), a minimum of 0.125 miles, and a maximum of 10 miles, corresponding with the rural location of the homes.

As detailed in **Table 13**, most homes use their primary well for drinking water ($n = 47$). Of those that do not use a well, 26 reported drinking bottled water only, nine reported using spring water, two were on municipal water, and three reported another source. Of those that reported choosing not to drink their well water ($n = 40$), the most common responses as to why were a lack of trust ($n = 11$), drinking water from a spring ($n = 10$), concerns over hydraulic fracturing or drilling ($n = 3$), bad taste ($n = 4$), or poor quality ($n = 7$).

In terms of compounding contamination pathways (**Table 14**), a majority of the homeowners tested in this region grew their own fruits and vegetables ($n = 59$); of those that grew their own fruits and vegetables, 34 used well water to water them. Additionally, 22 of the original 88 homeowners raised food animals (chickens, beef, etc.), of which 11 used well water to provide them with drinking water. An additional 10 used crops from their own property to feed their food animals.

Literature Review

The three analytes of statistical significance from geochemistry analysis are Ba, Sr, and Na. Of these, the MCL for Ba is 2 mg/L, and the health reference limit for Sr is 4 mg/L. Na does not currently have a water standard. EPA findings suggest that Ba has potential short-term health effects from exposure to Ba, including gastrointestinal disturbances and muscular weakness. Potential long-term health effects from exposure to Ba include elevated blood pressure and adverse effects on the kidneys.⁴⁸ According to EPA guidance, exposure to high levels of Sr through drinking water has been associated with impaired bone growth in children, anemia, and cancer.⁴⁹

Results Dissemination

All water quality analysis results were returned by mail and email to study participants between November 2024 and January 2025. Each results packet contained a cover letter, a table visualizing the participant's results, and a table with the participants' raw results (Additional Materials 4). All results were compared with water standards (MCLs, SMCLs), if they exist, and with results in Beaver, Washington, and Greene counties. If the results were not above standards or detection limits, the packets included cover letter A (Additional Materials 4). If results were above standards or detection limits, we prepared a cover letter to describe the specific findings and to provide the participant with additional mitigation resources. For the homes with dissolved methane limits near or above the DOI action level of 10 mg/L ($n = 3$)[†] and barium above the MCL of 2 mg/L ($n = 1$), participants were also called to

*Water samples were collected from 89 residential properties. One residential property was unable to take the survey due to time constraints. Efforts to follow up with residents of the property to complete the survey were unsuccessful.

†One sample had a dissolved methane level of 9.4. The research team called this home to discuss these results, even though the value did not exceed the DOI warning level of 10 mg/L.

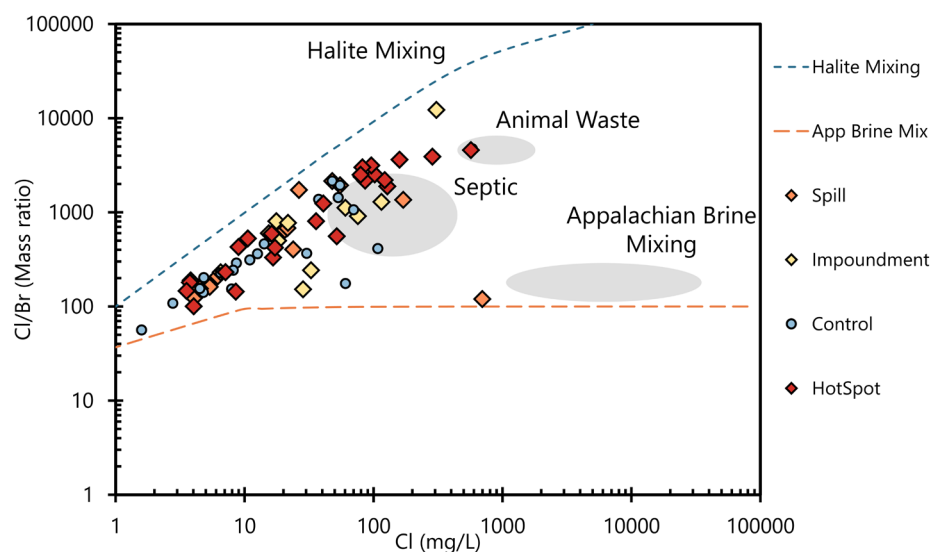


Figure 5. Cl/Br mass ratios for spill, impoundment, pure-C control, and hotspot samples; sample type denoted by shape and color (similar to Figure 1). Halite and Appalachian brine mixing curves are shown as dashed lines. Gray areas for septic and animal waste are based on Katz and colleagues (2011).⁴⁴ The gray area for Appalachian Basin brines reported for Pennsylvania is based on Blondes and colleagues (2023).⁴⁶ Basin brines, natural brines that are emitted into groundwater and surface water throughout Pennsylvania, are also brought to the surface with natural gas as produced waters during UOGD.

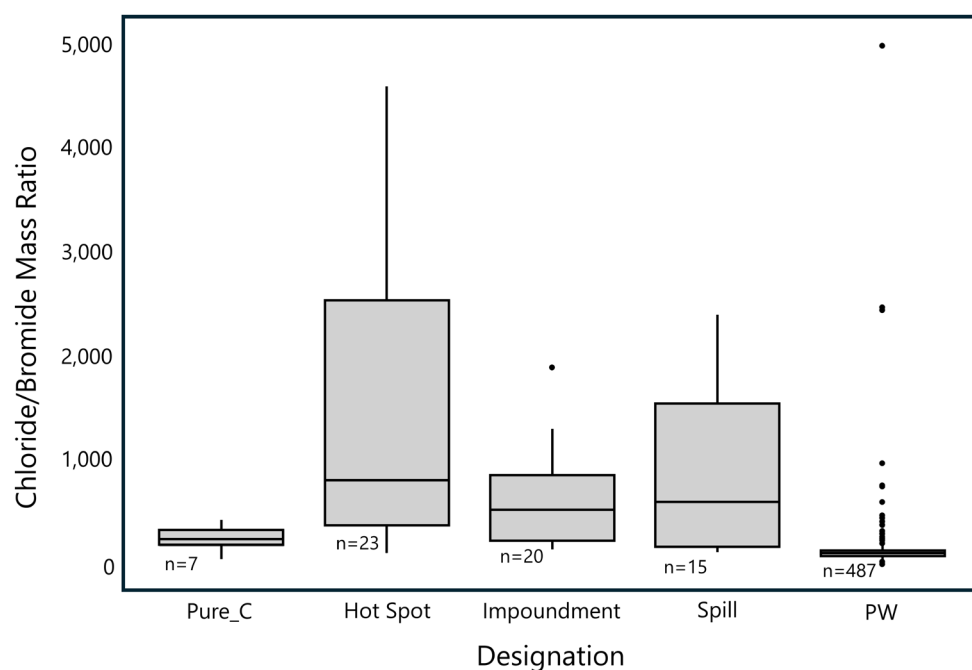


Figure 6. Cl/Br mass ratio box and whisker plots for pure-C, hotspot, impoundment, and spill samples, as well as for the produced waters dataset for Pennsylvania from Blondes and colleagues (2023).⁴⁶ Data Cl/Br range from 0 to 5,000 shown.

inform them about the results and to encourage them to take additional measures to have their water retested or install mitigation measures.

A community meeting to discuss the overall study results was held in Washington, Pennsylvania, on May 14, 2025. We followed the approach described in our Community Engagement Plan (Appendix B) in disseminating results to study participants.

DISCUSSION AND CONCLUSIONS

PUBLIC HEALTH OBSERVATIONS

We compared all well, spring, and stream samples ($n = 97$) with the public health limits. No samples exceeded EPA limits for beryllium, nickel, copper, arsenic, cadmium, thallium, lead, or uranium. This finding is noteworthy because

Table 11. Household Demographics of Sampled Homes

	n (Missing)	Mean	Median [Min, Max]
Household size	88 (0)	2.45	2 [1, 7]
Years lived in home	88 (0)	22.8	20 [0, 72]
Age	211 (24)	44.2	48 [1, 92]
Education level	211 (20)	Some college	Some college [middle school or lower, postgraduate training] ^a
Household income	88 (20)	\$75,000–\$99,999	\$100,000–\$149,999 [< \$25,000, >\$200,000] ^b

^aThe following categorical variable was used to calculate this statistic: middle school or lower (1); some high school (2); high school (3); some college (4); associate's or other 2-year degree (4); trade school program (4); bachelor's or other 4-year degree (5); MD or other graduate degree not listed (6); master's degree (6); PhD (6).

^bThe following categorical variable was used to calculate this statistic: <\$25,000 (1); \$25,000–\$49,999 (2); \$50,000–\$74,999 (3); \$75,000–\$99,999 (4); \$100,000–\$149,999 (5); \$150,000–\$199,999 (6); >\$200,000 (7).

Table 12. Home Age, Well Depth, and Distance from Potential Contaminant Sources

	n (Missing)	Mean	Median [Min, Max]
When home was built (year)	82 (6)	1958	1975 [1780, 2022]
Well depth (feet)	61 (27)	110.9	100 [10, 250]
Distance from oil or gas well pad (miles)	84 (4)	0.86	0.50 [0.05, 10.00]
Distance from impoundment pond (miles)	31 (57)	2.14	1.30 [0.10, 10.00]
Distance from gas station (miles)	86 (2)	3.83	3.00 [0.13, 10.00]

Table 13. Descriptive Statistics of Categorical Variables Related to Water Usage

Categorical Variables	Frequency (%)
Primary source of drinking water: (n = 87)	
Well	47 (54.0%)
Bottle	26 (29.9%)
Spring	9 (10.3%)
Municipal source	2 (2.3%)
Other	3 (3.5%)
Reason for not drinking well water: (n = 40)	
Lack of trust	11 (27.5%)
Water from the spring is preferred	10 (25.0%)
Concerns from hydraulic fracturing/drilling	3 (7.5%)
Bad taste	4 (10.0%)
Poor quality	7 (17.5%)
Other	5 (12.5%)

Table 14. Compounding Contaminants

Compounding Contaminants	Frequency (%)
Grow fruits/vegetables: (n = 87)	
Yes	59 (68%)
No	28 (32%)
Water fruits/vegetables with well water: (n = 59)	
Yes	34 (58%)
No	25 (42%)
Raise food animals: (n = 86)	
Yes	22 (26%)
No	64 (74%)
Food animals drink well water: (n = 22)	
Yes	11 (50%)
No	11 (50%)
Food animals fed with homegrown crops: (n = 22)	
Yes	10 (45%)
No	12 (55%)

Shaheen and colleagues (2022)¹ calculated that groundwater used for drinking water by some households within the hotspots (Figure 1) could be characterized by concentrations of thallium (and possibly arsenic, beryllium, and cadmium or other metals found at relatively high concentrations in UOG produced waters) at levels of potential public health concern. We saw no evidence of such contamination.

Most of the 19 samples that had total dissolved solids above the suggested EPA guideline for drinking water (500 mg/L) showed evidence of hard water chemistry related to carbonate-containing aquifers. These were not deemed to be of public health concern. However, five samples equaled or exceeded the EPA-suggested SMCL for chloride, including one sample with [Cl] = 697 mg/L. One sample equaled the MCL for barium within error ([Ba] = 2.05 mg/L). These “salty” samples are discussed further in the next section.

The 20 samples exceeding the EPA SMCLs for aluminum (0.2 mg/L), iron (0.3 mg/L), or manganese (0.05 mg/L), or all three, are primarily of aesthetic concern. Such samples are common in Pennsylvania because these three are among the most common elements in local bedrock. These elements are typically found in drinking water as particulates small enough to pass through filtration. One or two samples have elevated dissolved aluminum and iron concentrations as well as relatively high dissolved methane, which could be evidence of particulates mobilized in the presence of natural gas bubbles.²⁰

In our study area, none of the BTEX compounds were observed at concentrations above public health limits. The most concerning finding from a public health perspective was that three of the 97 samples (3.1%) were characterized by dissolved methane above the DOI level, requiring further investigation (10 mg/L),³⁷ and one of these by dissolved methane above the Department of Interior action level (28 mg/L) because of explosion concern.⁵⁰ The provenance of gas in these samples is discussed in the next section.

GEOCHEMISTRY

Statistical and Geostatistical Tests Shaheen and colleagues (2022)¹ determined hotspots using Cl concentrations in a large dataset and hypothesized that these areas had elevated Cl because of UOG development. In our smaller set of ground-water samples from wells, we also observed higher Cl concentrations in hotspot areas than in pure-C controls. However, when applying the Benjamini-Hochberg procedure (accepting an FDR of 10%),* only the treatment sets (hotspots and impoundments) showed higher concentrations of the radium isotopes analyzed compared with the pure-C control.

We observed no statistically significant negative correlations between concentrations of 12 target analytes (SC, Na, Cl, Ba, SO₄, Sr, Br, Fe, CH₄, Rn, Ra-226, and Ra-228) and distance to UOG wells within hotspots. However, at the 95% confidence level, we observed that Sr concentrations increase with proximity to impoundments (in three of four statistical tests) and that Na (in all statistical tests), Ba (one of four), and methane concentrations (three of four) increase with proximity to spill sites. These results could indicate that Sr, Na, Ba, and methane contamination are related to UOGD but not to leakage from UOG wells within hotspots. A potential explanation for these observations is that Sr, Na, and Ba from wastewater brines have entered aquifers near the impoundment sites and spill sites along with natural gas, and these are still eluting from the subsurface. For example, we observed that 69.8% (67 of 96) of the samples had detectable [CH₄], a proportion that is higher than observations for groundwater across the state reported in an early study.⁵⁰

*We applied the Benjamini-Hochberg procedure with an FDR of 0.1 to account for multiple comparisons across 41 analytes. The choice of 0.1 reflects a balance between minimizing false positives while also maintaining statistical power in an exploratory dataset with limited sample sizes, consistent with common practice in environmental geochemistry and epidemiology. Importantly, our results are not sensitive to the specific FDR threshold: When we applied a stricter cutoff of 0.05, all apparent one-sided test discoveries were also eliminated. Thus, regardless of whether the FDR is set at 0.1 or 0.05, our key conclusion remains unchanged — there is no statistically significant evidence of elevated analyte concentrations in treatment versus control sites after correction for multiple testing.

Provenance of Strontium and Hydrocarbon Gases One way to investigate the source of dissolved salts or gases in groundwater is to look at isotopic signatures. For example, Sr isotopic measurements indicate that Sr in the groundwaters could originate from the Marcellus Shale or from other local geological or anthropogenic sources. However, although the most salt-rich samples show $^{87}\text{Sr}/^{86}\text{Sr}$ values consistent with Marcellus Shale, the $[\text{Sr}]/[\text{Cl}]$ ratios are dissimilar (Figure 2). Similarly, for samples with enough CH_4 to measure C isotopes, along with measurable concentrations of ethane and propane, Figure 4 shows that the isotopes and gas chemistries did not indicate 100% thermogenic gas in any sample. Rather, all the samples were consistent either with biogenic gas or a mixture of thermogenic and biogenic gas. Even the most methane-rich sample contains a significant fraction of biogenic gas.

Provenance of Chloride Cl/Br ratios for most of the samples with elevated chloride could reflect mixing of shallow groundwater with septic or animal waste rather than UOG wastewaters. These samples include most that had elevated Cl collected from hotspot treatment zones. One notable exception is the sample with the highest Cl, Ba, Br, and F concentrations collected in the spill treatment area. This sample had a Cl/Br ratio consistent with mixing of shallow groundwater with a brine typically found at depth in Pennsylvania and sometimes observed in shallow groundwater.⁴⁵ Importantly, the Cl/Br ratio alone cannot determine whether the brine reflects natural migration and mixing or contamination from UOG wastewater spilled at the surface.

RADIONUCLIDES

Radon in groundwater varies widely across Pennsylvania, mainly controlled by the geology of the aquifers. Radon levels in water collected in this study are consistent with the limited number of values published for the local counties and, importantly, are lower than the areas in Pennsylvania with known radon issues. Regardless, values above 300 pCi/L in water could indicate risk from exposure to indoor air for homeowners. We therefore recommended an indoor air test for the 33 homes with radon in water >300 pCi/L. Variations in mineralogy or permeability in the hotspot regions compared with controls could explain the relatively elevated radon observed in hotspot regions in this study.

A comparison of radon across different treatment areas revealed there were no statistical differences between impoundment areas and control areas. However, the average radon sampled from within hotspot and spill treatment areas was significantly ($P < 0.05$) higher than the average radon of control areas.

Statistically significant differences in radium activity were observed between treatment areas (hotspots and impoundments) and pure-C controls after the procedure used to control false discoveries. The differences are in radium 226, radium 228, combined radium (226+228) for hotspots (BM only), and impoundments (WMW [excluding Ra-226] and BM).

The radium concentrations we observed fall within the typical range reported for principal aquifers across the United States. Some spatial variations were noted, but these patterns may reflect a variety of factors and cannot be attributed to any single source. Because we did not analyze land use practices or geological controls — both of which strongly influence radium occurrence — it is difficult to determine the underlying drivers. UOGD remains one possible explanation, but the observed differences between treatment groups can also be readily explained by land use differences (e.g., agriculture) or natural aquifer characteristics such as mineralogy and permeability.

LIMITATIONS

We note three possible limitations to our study. First, it was challenging to identify and gather appropriate control samples because of the extensive UOGD-related development within Washington and Greene counties. Although we identified a possible region for control samples in Allegheny County that was within the same lithology as the UOGD sites in Washington and Greene counties, we were unable to recruit participants in this area despite the recruitment efforts we described previously. Second, the well depths used in the study were a mix of self-reported depths and depths listed on well caps. Third, both funding and time limited how many sites we could sample. If contamination by UOGD in this area is relatively rare, the small sample size might have precluded our ability to find the small number of potentially problematic sites.

IMPLICATIONS OF FINDINGS

Overall, very few instances of contamination above established or proposed drinking water standards were observed during these analyses. For analytes above public health standards, no statistically significant differences between treatment and control sites were identified. Some analytes were found to increase slightly in concentration near impoundments (Sr) and spills (Ba, CH_4 , Na). Sr and Ba have been associated with health risks in the literature, including gastrointestinal disturbances, muscular weakness, elevated blood pressure, and adverse effects on the kidneys for Ba and impaired bone growth in children, anemia, and cancer for Sr. Isotopic analysis of Sr and CH_4 , however, is not wholly consistent with UOGD contamination as the source of these analytes in groundwater. The geological, geographical, and land use variation across the study area could also explain or contribute to the correlations, especially considering the small number of sites sampled.⁵⁰

The best way to determine whether correlations observed for Sr, Na, Ba, and methane are indicative of contamination related to UOGD is intensive field study and sampling using a multiple-lines-of-evidence approach. Similarly, discerning the potential health effects of contamination can include

evaluating hair or blood samples for suspected contaminants, as well as considering potential compounding effects, such as health effects associated with eating or drinking foods produced using contaminated water. Both avenues of research are beyond the scope of the present study, but they would be valuable areas for future research.

DATA AVAILABILITY STATEMENT

The survey questions are in Additional Materials 2. Complete water analysis results data are in Appendix E. The statistical code files for both geochemistry and survey data are in Additional Materials 5 and 5a.

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HEI QUALITY ASSURANCE STATEMENT

Eastern Research Group, Inc. (ERG) provided an independent quality assurance (QA) audit for this study. ERG staff members Dr. Mary Ellen Tuccillo, Dr. William Morgan, and Elaine Whetstine conducted a remote audit of the final report and associated appendices. An on-site audit was not conducted for this study. The ERG auditors are experienced in QA oversight and the subject matter relevant to this study, including geochemistry, hydraulic fracturing, geospatial analysis, and statistical methods. Dr. Tuccillo, an environmental scientist, served as the lead auditor and interacted with principal investigators, reviewed the water quality descriptive statistics, the survey recruitment, and survey results. Dr. Morgan reviewed the statistical and geospatial analyses, including all code. Ms. Whetstine evaluated consistency among tables, figures, text, and public health limits.

The remote audit of the final report was conducted from December 2025 through March 2026. The objectives of this audit were to ensure that study methods were well documented, the final report was understandable, reported results were accurate, and key study findings and limitations were highlighted. The audit also evaluated whether the documented study protocols were adhered to. To meet these objectives, the ERG auditors reviewed the final report text, tables, and figures to verify their accuracy and clarity. Study and QA protocols were also reviewed for consistency with reported methods. Raw water quality data, Python and R codes and associated output files, and survey results were provided to ERG. These were compared to the methods and findings described in the final report.

ERG auditors focused their review on the final report text, tables, and appendices, evaluating whether they were consistent with the raw data and how they adhered to study protocols and documented analyses. Auditors identified parts of the final report text that could be improved for clarity and accuracy; the research team has addressed these. Minor discrepancies identified during the audit have been addressed. The audit findings did not affect the overall conclusions of this research study.

Audit findings were documented in an ERG audit report, and the resulting responses by the research team have been documented. The overall approach has been adequately described, and key results were adequately presented in tables and figures. The ERG audit team is satisfied that the final study report is representative of the research conducted and that the study followed a valid set of procedures documented in study protocols.



Mary Ellen Tuccillo, PhD, Environmental Scientist, Quality Assurance Auditor



William Morgan, PhD, Environmental Modeler, Quality Assurance Auditor



Elaine Whetstine, Geoscientist, Quality Assurance Auditor

SUPPLEMENTARY APPENDICES AND ADDITIONAL MATERIALS

Appendices A through E and Additional Materials 1 through 5 contain additional material not included in the main report. They are available on the [HEI website](#).

Appendix A. Field Methods and Chemical Analyses

Appendix B. Community Engagement Plan

Appendix C. Wells-Only Statistical Results Tables

Appendix D. Statistical Summary of Entire Groundwater and Spring Dataset

Appendix E. Complete Water Analysis Results

Additional Materials 1. Recruitment Postcard

Additional Materials 2. Penn State Groundwater Sampling Household Survey

Additional Materials 3. Consent for Exempt Research

Additional Materials 4. Analysis of Sampled Water

Additional Materials 4a. Cover Letter Template

Additional Materials 4b. Additional Cover Letter Language for Analytes Above MCL/SMCLs/Detection Limits

Additional Materials 5. Geochemical Statistics Code

Additional Materials 5a. Survey Statistics Code

ABOUT THE AUTHORS

Jennifer Baka, co-principal investigator, is an associate professor of geography and an associate at the Earth and Environmental Systems Institute at The Pennsylvania State University. She is an energy geographer with expertise in studying UOGD regulatory processes in the United States and Canada. She focuses specifically on how stakeholders engage regulatory processes and with what effects. In recent years, she has been researching the emerging petrochemical corridor in Northern Appalachia and has developed extensive ties with community, government, and industry stakeholders. She has a PhD in environmental studies from the Yale School of the Environment and an MPP from the University of California, Berkeley.

Susan L. Brantley, co-principal investigator, is the Atherton Professor and Evan Pugh University Professor Emerita of Geosciences at The Pennsylvania State University. Her research focuses on natural and human-induced reactions among water, rock, gas, biota, and soil, with particular interest in the effects on fresh water of unconventional oil and gas development. She has long been interested in the rates and mechanisms of water-rock reactions in the field and in the laboratory, including how we measure them, reproduce them in the laboratory, and model them. She has a PhD and an MA in geological and geophysical sciences from Princeton University.

Tao Wen is an associate professor of earth and environmental sciences at Syracuse University. He is a geochemist and environmental data scientist driven by research interests at the interface of humankind and the coupled elemental and water cycles. He uses field-based and geochemical laboratory-based approaches (e.g., noble gases, stable isotopes, and water chemistry) to shed light on the environmental implications of human activities on water resources. He also develops and applies data mining and machine learning algorithms to explore the spatiotemporal patterns of water quantity and quality in the coupled natural and human system. He has a PhD and an MS in geology from the University of Michigan.

Nathaniel Warner is an associate professor of civil and environmental engineering at The Pennsylvania State University. He is an environmental engineer interested in water quality, hydraulic fracturing, salinization, and isotope geochemistry. He formerly worked as a professional geologist and environmental consultant and aims to incorporate those real-world experiences into his teaching. He holds a PhD in earth and ocean sciences from Duke University and an MS in geology from Miami University.

Casey Pinto is an associate professor of public health sciences at The Pennsylvania State University. She works in the division of epidemiology. Her research focuses on rural/urban health disparities, specifically related to sexually transmitted infections and cancer. She focuses on how social determinants geographically vary and affect these specific health outcomes. She has worked as a nurse practitioner in infectious disease since 2009 and has worked for the Commonwealth of Pennsylvania sexually transmitted infection clinics since 2015. She is also associate medical director for the York City Bureau of Health, where she collaborates with health bureau staff to respond to and prevent outbreaks, treat patients, and improve overall health for York City residents. She has a PhD and an MS in nursing as well as an MPH from The Pennsylvania State University.

Zachary Bitzer is an assistant professor of public health sciences at The Pennsylvania State University. His primary research interest is in environmental toxicology, including how toxins are produced, how they interact with the human body, and novel biomarkers that could be developed to determine exposure levels. His current research focuses on toxins and oxidants (e.g., free radicals, aldehydes) produced from tobacco products and electronic cigarettes. He also has a strong

interest in the role dietary phytochemicals play in reducing oxidative stress and inflammation in the body. He has a PhD in food science from The Pennsylvania State University.

Brandon Forsythe is an assistant research professor with the Earth and Environmental Systems Institute at The Pennsylvania State University. He has broad experience in the environmental sciences, primarily focused on water resources and surface water. He began with the US Geological Survey, preparing water quality equipment for field and laboratory use and gaining experience with several types of water quality sondes and sampling methods. He works to manage, design, and implement a wide range of instrumentation systems to include soil moisture, stream flow, water quality, and meteorology sensors in the Shale Hills Critical Zone Observatory.

Allison Fenske was an environmental engineering PhD candidate at The Pennsylvania State University, advised by Nathaniel Warner. As of fall 2026, she will be an assistant professor at Juniata College in Huntingdon, Pennsylvania. Her research investigates current and potential water quality impacts from energy development in Pennsylvania, including coal mining and natural gas production. This research involves measuring radioactive species in groundwater and expanding on her previous work regarding alternative materials in coal mine drainage treatment. She earned an MS in environmental engineering from The Pennsylvania State University. Her master's project considered the chemical, economic, and environmental feasibility of utilizing recycled concrete as a replacement for limestone in passive acid mine drainage treatment. She earned an Honors BS in construction management and an Honors BA in interdisciplinary studies with a focus on sustainable engineering from the University of Texas at Arlington.

Lara Williams is pursuing an MS degree in the department of geosciences at The Pennsylvania State University, researching weather and sediment transport in the mountains of Taiwan. She graduated from Tufts University with a BS in geological sciences and German language and literature and has completed the Postbaccalaureate Certificate in GIS at The Pennsylvania State University.

Evelyn Mahugu is pursuing a PhD in epidemiology at The Pennsylvania State University. She possesses extensive experience as an infectious disease epidemiologist and microbiologist. Her research interests center on a one-health approach to addressing antibiotic resistance by integrating human, animal, and environmental health strategies. Her current research focuses on sexually transmitted infections and antimicrobial resistance, with a strong interest in improving health outcomes for underserved populations.

Jianfeng Su is a PhD student in earth and environmental sciences at Syracuse University. His research primarily focuses on groundwater contamination and greenhouse gas emissions associated with oil and gas wells. With a strong background in environmental engineering, he aims to employ data-driven methodologies to assess and address these persistent environmental challenges, promoting innovation in sustainable practices.

OTHER PUBLICATIONS RESULTING FROM THIS RESEARCH

Fenske A, Su J, Baka J, Forsythe B, Williams L, Shaheen SW, et al. 2026. Matrix-derived radium mobilization in shallow aquifers near unconventional oil and gas operations. *Environ Sci Technol* 60:24342–24351, <https://doi.org/10.1021/acs.est.6c05003>.

Su J, Williams L, Fenske A, Shaheen SW, Brantley SL, Forsythe B, et al. 2026. Targeted sampling reveals localized brine signals without evidence of regional water quality impacts from unconventional oil and gas development. *Environ Sci Process Impacts* 28:1927–1940, <https://doi.org/10.1039/d6em00142d>.

Research Report 233, *Hydrocarbon Extraction and Risk to Groundwater in Pennsylvania: Part 2: An Analysis of Water Quality in the Oldest Hydrocarbon Basin in the United States*, by J. Baka and S.L. Brantley* et al.

INTRODUCTION

The advent of high-volume and multistage hydraulic fracturing combined with horizontal drilling in the early 2000s has led to a substantial increase in onshore oil and natural gas development in the United States. This increase in the rate and scale of energy development now includes longer periods of development, with more materials being brought to and from larger well pads, and more solid and liquid waste being generated on-site. This rapid expansion has increased opportunities for human exposure to chemical and nonchemical stressors and has generated concerns about their effects on human health.

This form of oil and gas production — often referred to as unconventional oil and gas development (UOGD)[†] — allows operators to access oil and gas in sandstone or shale formations. While UOGD has expanded into new areas, it is often co-located in areas with a history of extractive energy practices, such as conventional oil and gas development or coal mining. A challenge to understanding exposure to UOGD in areas with legacy energy development is that many potential contaminants of concern are the same.

In 2020, HEI Energy issued Request for Applications [RFA E20-2: Community Exposures Associated with Unconventional Oil and Natural Gas Development](#) to fund research to assess community exposures to chemicals in surface or groundwater originating from UOGD. Specifically, HEI was interested in research that (1) would help determine the UOGD processes that have led or may lead to releases to water, (2) quantify the magnitude, frequency, and duration of potential exposures to chemicals released to water from specific UOGD processes, and (3) identify and define the influence of various factors (e.g., varying geology) on exposures. The proposed research would engage local communities and should maximize the generalizability of the research, inform

Jennifer Baka's and Susan L. Brantley's 1-year study, "An Analysis of Water Quality in the Oldest Hydrocarbon Basin in the United States," began in May 2024. Total expenditures were \$350,771. The draft Investigators' Report from Baka, Brantley, and colleagues was received for review in March 2025. A revised report, received in September 2025, was accepted by the HEI Energy Review Committee in October 2025.

During the review process, the HEI Energy Review Committee and the investigators had the opportunity to exchange comments and clarify issues in both the Investigators' Report and the Review Committee's Commentary. This Commentary has not been reviewed by public or private party institutions, including those that support HEI Energy, and may not reflect the views of these parties; thus, no endorsements by them should be inferred.

*Co-principal investigators.

†A list of abbreviations and other terms appears at the end of this volume.

decision-making, and, to the extent practicable, distinguish potential UOGD exposures from those associated with other conventional oil and gas development and any other background sources.

In response to the RFA, Drs. Jennifer Baka and Susan L. Brantley (The Pennsylvania State University) submitted a successfully funded application.¹ Baka, Brantley, and colleagues used statistical analyses and machine learning to identify links between various UOGD sources and potential water contamination and used focus groups to understand community concerns regarding UOGD. During their initial investigation, the investigators found evidence of potential groundwater contamination in localized areas, and they reported that residents in Southwestern Pennsylvania were principally concerned about potential health effects of UOGD related to water quality, waste disposal, and radioactive contaminants. Drs. Baka and Brantley, therefore, additionally proposed conducting water quality surveys in areas where evidence suggested that groundwater may have been contaminated by UOGD. HEI's Energy Research Committee recommended funding this additional study because it added value to the ongoing research by measuring water quality in areas where their research suggested groundwater might be contaminated by UOGD and by addressing concerns of people living in these locations.

This Commentary provides the HEI Energy Review Committee's independent evaluation of Part 2 of the study, entitled "An Analysis of Water Quality in the Oldest Hydrocarbon Basin in the USA." It is intended to aid the sponsors of HEI Energy and the public by highlighting both the strengths and limitations of the study and by placing the results presented in the Investigators' Report in a broader scientific and regulatory context.

SCIENTIFIC AND REGULATORY BACKGROUND

UOGD OVERVIEW

UOGD refers to the development and production of oil and natural gas through multistage hydraulic fracturing in horizontal wells.² UOGD processes occur on and off the well pad and include

- **Field development:** exploration, pad preparation, vertical and horizontal drilling, well completion (casing and cementing, perforating, acidizing, hydraulic fracturing, millout, flowback, and well testing) in preparation for production, and management of wastes

- **Production operations:** extraction, gathering, processing, and field compression of gas extraction and processing of oil and natural gas condensates; management of produced water and wastes; and construction and operation of field production facilities
- **Post-production:** well closure and land reclamation

High-volume, multistage hydraulic fracturing along lengthy horizontal wells — often extending more than a mile — injects millions of gallons of water and chemicals, sometimes in proprietary mixtures, into tight formations under high pressures to release oil or natural gas. This mixture of water and anthropogenic chemicals, along with naturally occurring compounds (such as arsenic or petroleum hydrocarbons), is returned to the surface during flowback. Oil and gas wastewater, known as produced water, is generated at the onset of the production phase and continues to be generated over the life of the well.

Although some UOGD operations are regulated at the federal level under the Clean Air Act, the Clean Water Act, and the Safe Drinking Water Act, state-level regulations play a larger role in governing UOGD more generally. Such regulations vary among states, with some states defining minimum setback distances between UOGD and specific land uses, such as residential homes and schools, to protect local populations.

UOGD AND WATER QUALITY

The rapid expansion of UOGD has given rise to concerns about effects on human health from potential exposure to contamination of water sources. This concern is particularly acute in rural areas where many residents rely on private groundwater wells. An early review by the US Environmental Protection Agency (US EPA) did not identify extensive contamination of water related to UOGD but cited instances in which contamination has occurred.³ To date, relatively few studies have examined the likelihood or frequency of exposure to drinking water sources potentially contaminated by UOGD.^{4,5}

UOGD-related chemical releases to surface or groundwater can result from authorized or accidental discharges to the environment. Examples of authorized releases include permitted discharge of produced water to surface water or for applications outside the oil and gas production site (e.g., road treatments for dust or ice). Although protections have been put in place to prevent unintentional chemical releases to groundwater and surface water, releases can occur as a result of wellbore failures, malfunctioning equipment, or other accidental conditions.⁶

Research on changes in surface water or groundwater quality from accidental UOGD releases is challenging given the practical limits on knowing when and where such releases might occur. When accidental releases do occur, determining the extent and severity of impacts and the subsurface conditions that influence the mobility of contaminants often requires substantial effort and resources.

One of the major challenges to understanding or quantifying potential human exposures to UOGD-contaminated water is distinguishing UOGD-related exposures from other geogenic or anthropogenic sources of the same chemicals. Many UOGD basins overlap with ongoing or historical conventional oil and gas development or coal extraction. Furthermore, many of the contaminants associated with leaks of oil and natural gas occur naturally or have other possible sources. Because produced water is highly saline, contamination from produced water can be inferred through increased salt species. For example, barium and strontium have been used previously as tracers for produced water released to the environment.⁷ While a subset of water quality studies has used isotopic tracers and other markers associated with UOGD to isolate its effects from other sources, this type of fingerprinting is not typically conducted outside of specialized labs or for research purposes.⁵

The amount of data on levels of UOGD-related chemicals in the environment continues to increase along with efforts to use the data to quantify human exposure. In *Part 1* of the study, Baka, Brantley, Xue, and colleagues used previously collected, publicly available data to predict areas of potential contamination.^{1,8} Part 2 of the study is designed to evaluate these predictions and address community concerns about contamination in privately owned drinking water wells by collecting and analyzing new water samples.

STUDY OBJECTIVES AND APPROACH

The overarching objective of this study was to confirm or refute the investigators' previous findings in *Part 1* and evaluate potential exposures to contaminants from UOGD through drinking water. The original study, based on publicly available water quality data primarily collected before 2014, suggested slight increases in groundwater salinity potentially linked to UOGD activities, such as produced water spills or surface leaks. In Part 2, discussed here, Baka, Brantley, and colleagues collected water samples near hotspots, impoundments, and spills for evidence of ongoing contamination from UOGD-related analytes in Southwestern Pennsylvania. The investigators analyzed water quality to address two questions. The first was whether drinking water sources contain contaminants associated with UOGD that are of concern for human health. The second was whether water sources identified in *Part 1* of the study as being at elevated risk of contamination from UOGD exhibited evidence of actual impact attributable to those activities.

To achieve their objectives, the investigators conducted multiple field campaigns in 2024 to collect and analyze water samples from private groundwater wells, springs, and streams in areas potentially affected by UOGD to compare with samples taken outside those areas. They also identified "goodwill" sample sites to increase goodwill and interest in the study. They then surveyed residents using these water sources to assess any potential exposures if evidence of contamination was found.

The investigators focused on the following analytes: measures of salinity that may indicate potential impacts from UOGD wastewater; analytes found in produced water at higher concentrations than other types of wastewaters; and analytes that are indicators of contamination given their sensitivity to dissolved oxygen and other ambient chemical conditions. Overall, the investigators focused primarily on produced water-related chemicals that are of concern to human health to better understand the effects of exposure to oil and gas development through drinking water. Therefore, the investigators compared the results to US EPA Drinking Water Standards or, lacking those, other health-based benchmarks.

Finally, they conducted a literature review to determine possible health risks resulting from exposure to any metals and metalloids identified in the water sampling analysis.

SUMMARY OF METHODS

SITE IDENTIFICATION

The investigators defined three types of sites for sampling (hotspots, impoundments, and spill sites), collectively referred to as “treatment” areas. “Hotspot” areas occurred in locations where groundwater chemistry showed evidence that chloride concentrations were increased near one or more unconventional oil and gas wells,⁹ and sample sites were defined to be within a 2-km radius of unconventional oil and gas wells.

“Impoundment” sites were defined as those located within 2 km of produced water impoundments that were ultimately directed by the Pennsylvania Department of Environmental Protection to either close or store only fresh water. Well pad locations for these impoundments were used as the centroid of the area targeted for water sampling.

“Spill” sites were defined to be within a 3-km radius of three spills that had occurred in Greene County in 2022 and 2023, and a produced water spill that occurred during the ongoing water sampling campaign in September 2024. The sampling area was expanded from 2–3 km because of low population density within the original buffer zone. Additionally, the investigators included 12 UOGD-related brownfield sites in Washington County in the spill site sample sets.

Finally, “control” sites were defined by the investigators to be located within 5 and 7 km from the centroids of impoundments and hotspots and more than 5 km from the recent spill or brownfield sites.

RECRUITMENT AND SAMPLING

The investigators used information from tax records to identify homes within the three types of treatment areas and control areas. Overall, the investigators were able to recruit 68 volunteers who would allow their private water sources to

be sampled within the treatment and control areas. They also collected water samples from 13 “goodwill” sites that did not meet the outlined criteria but were included to generate interest and goodwill in the study. They sampled 14 homes that were thought to represent control sites but were ultimately determined to be less than 5 km from a spill. Those were included in the goodwill sample set.

During seven field campaigns conducted between May 2024 and November 2024, the investigators used a standardized sampling plan to collect 97 water samples from 79 groundwater wells, 14 springs, and four streams at 94 sites, comprised of 91 residential properties and three public sites. Sixty-two samples were collected from treatment areas, roughly evenly distributed among the three treatment types (hotspots, impoundments, and spill sites), with some samples drawn from overlapping treatments (**Commentary Figure 1**). An additional eight samples came from control areas, and 27 in total were classified as goodwill samples.

FIELD WORK

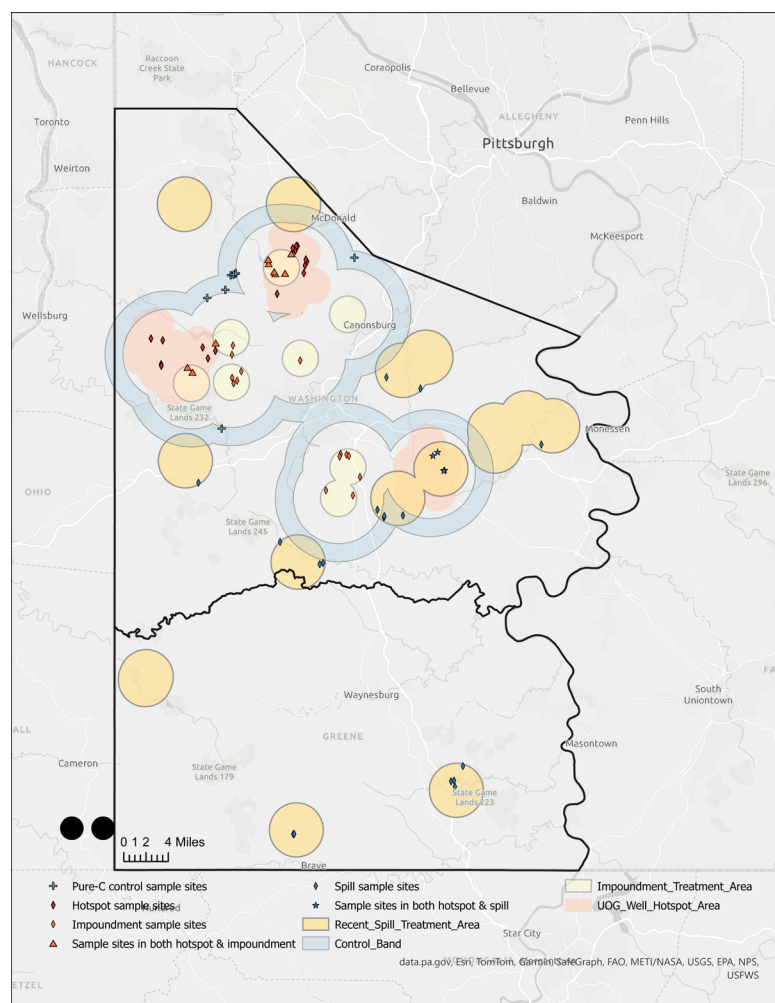
Water Sampling and Chemical Analysis

Baka, Brantley, and colleagues analyzed samples from each site for six field parameters and a range of chemical analytes. Details of these analyses are summarized in **Commentary Table 1** and in the IR Appendix A.

The investigators selected these analytes for two reasons. First, *Part 1* of this study had shown these analytes were the chemical species most likely to be elevated if UOGD contamination had occurred. Specific conductivity, chloride, and sodium are measures of groundwater salinity that may indicate potential impacts from UOGD wastewater. Other analytes were chosen because (1) they are found in produced water at higher concentrations than other types of wastewaters, or (2) are indicators of contamination given their sensitivity to dissolved oxygen and other ambient chemical conditions. However, the investigators focused primarily on produced water-related chemicals that are of concern to human health to better understand the effects of exposure to oil and gas development through drinking water.

Survey Design

The investigators developed and administered a household survey to better characterize household demographics, drinking water sources, and land use practices of sampled homes. The survey sought to solicit information on possible exposure pathways to any contaminants — should they be found — in residential water sources through questions on household water systems and use, water well characteristics (including well construction, screening levels, and well-depth estimations), and resident demographics.



Commentary Figure 1. Map of the study treatment and control areas and sample locations in Washington and Greene Counties, Pennsylvania.
Source: Investigators' Report Figure 1.

DATA ANALYSIS

To determine whether the water samples had chemicals at concentrations of concern for human health, the investigators compared the results to US EPA Primary and Secondary Drinking Water Standards^{10,11} and, when these standards were not available, other health-based benchmarks established by federal agencies.

Statistical and Geospatial Analyses

The investigators employed several different statistical analyses to elucidate any potential effects specifically on groundwater from UOGD. See **Commentary Table 2** for a summary of the datasets and comparative and geostatistical methods used in the study. For this assessment, they excluded stream samples because surface water chemistry is influenced by different hydrologic processes. To assess whether groundwater in the treatment areas exhibited higher analyte concentrations than groundwater did in the control areas, the investigators used two nonparametric statistical tests, which can be applied under various assumptions of the underlying dataset. The investigators applied the Benjamini-Hochberg

procedure to account for potential false discoveries, which are significant results that appear real but are actually due to chance. Additionally, the investigators conducted geospatial analyses using a combination of regression and correlation methods to evaluate relationships between analyte concentrations and distance from UOGD wells.

Origin of Salt and Gas Analytes

To develop additional lines of evidence for evaluating potential UOGD impacts on groundwater in the treatment areas, the researchers used isotopic data and element ratios to interpret the origin of light hydrocarbon gases and major elements in the water samples.

First, they plotted strontium isotopic signatures (⁸⁷Sr/⁸⁶Sr) against strontium-to-chloride ratios ([Sr]/[Cl]) for the groundwater samples and compared these values with regional ranges for UOGD produced water. The investigators also compared strontium isotopic signatures alone across treatment and control areas to those from conventional and UOGD produced water.

Commentary Table 1. Summary of Analytical Methods of Field Parameters and Water Sample Analytes

Analytes	Method
Field Parameters and General Water Quality Characteristics	
pH, temperature, dissolved oxygen, specific conductance	YSI ProDSS multiparameter digital water quality meter with pH/ORP (oxidation reduction potential), dissolved oxygen, conductivity and temperature sensors
Methane concentration (in air)	Bascom-Turner Gas Rover
Radon	Durridge RAD7 radon detector with H2O attachment
Alkalinity	Sulfuric acid titration
Anions	
Chloride, fluoride, bromide, sulfate, nitrate	Ion chromatography (IC)
Major Elements	
Aluminum, barium, calcium, iron, potassium, magnesium, manganese, sodium, phosphorus, silicon, strontium	Inductively coupled plasma atomic emission spectroscopy (ICP-AES)
Trace Elements	
Lithium, beryllium, nickel, copper, arsenic, cadmium, thallium, lead, uranium	Inductively coupled plasma mass spectrometer (ICP-MS)
Dissolved Carbon Compounds	
Dissolved inorganic carbon	TOC-L analyzer
Hydrocarbon gases (methane, ethane, propane)	Gas chromatography at commercial lab (IsoTech Laboratories)
Isotopes	
Strontium (87/86 Sr)	Thermal ionization mass spectrometry (TIMS)
Methane ($\delta^{13}\text{C}$, δD), ethane ($\delta^{13}\text{C}$)	Chromatographic separation followed by combustion and dual-inlet isotope ratio mass spectrometry
Radionuclides	
Radium	Gamma Ray Spectrometer
Gross alpha	Alpha disintegrations were measured using a PerkinElmer Tri-Carb Liquid Scintillation Analyzer
Volatile Organic Compounds	
Benzene, toluene, ethylbenzene, and xylene (BTEX)	Headspace gas chromatography coupled with mass spectrometry (GC MS/MS)

To assess gas origins, the investigators plotted methane concentrations (expressed as the fraction of methane relative to the sum of ethane and propane) against the carbon-13 isotopic signature of the methane measured in groundwater.

Finally, the investigators examined chloride-to-bromide ratios to evaluate potential chloride sources such as organic waste, road salt, or deep formation water.

Literature Review

The investigators searched the scientific literature for studies assessing the potential human health effects associated with exposure to water contaminated with metals or

metalloids. They used findings from the literature search to contextualize findings in outreach materials

RESULTS DISSEMINATION

As described in Appendix B of the Investigators' Report, the investigators developed a Community Engagement Plan with their approach to disseminating the results of the water sampling campaign. The investigators provided all participants with letters written at a 5th-grade reading level. Additionally, the investigators held a community outreach session to share results in person and be available to answer any questions.

Commentary Table 2. Summary of Statistical Methods

Analysis Type	Treatment Areas ^a	Method	Rationale
Comparison with standards or other guidelines (IR Appendix E)	All samples: $n = 97$ (79 groundwater wells, 14 springs, 4 streams)	Compare all values with standards ^b or other guidelines (where available)	Determine whether residents are potentially exposed to contaminants of concern through drinking water
Descriptive statistics (IR Appendix D)	Total sample set: $n = 90$ samples ^c (76 groundwater wells; 14 springs), for each chemical analyte	Minimum and maximum concentration; mean and median concentrations; concentrations at 5th, 25th, 75th, and 95th percentiles	Describe main characteristics of the dataset
Statistical comparison of sample treatment groups (IR Tables 6–7)	$n = 63$ samples ^d for each chemical analyte Samples within hotspots ($n = 30$), impoundment ($n = 24$), and/or recent spill areas ($n = 17$) versus the control areas ($n = 8$)	Nonparametric tests: Wilcoxon–Mann–Whitney rank sum (WMW) test, assumes homoscedastic conditions (similarly shaped distributions), and the Brunner–Munzel (BM) test, assumes heteroscedastic conditions (nonsimilar distributions)	Determine whether the treatment groups are significantly different from the control areas
Geospatial analysis (IR Tables 8–10; IR Appendix C)	$n = 63$ samples ^d for concentrations of the following chemical analytes: Specific conductivity, chloride, sodium, sulfate, barium, strontium, bromide, iron, methane, radon, radium-226, radium-228 Samples within hotspots ($n = 30$), impoundment ($n = 24$), and/or recent spill areas ($n = 17$) versus the control areas ($n = 8$)	Ordinary Least Squares (OLS) linear regression Spearman rank correlation Kendall's tau Theil-Sen (ATS) slope estimator	Examine the correlations between concentration of brine- or hydrocarbon-related chemical species relative to the closest wells within hotspots, impoundments or recent spills, and quantify the strength, direction and magnitude of observed trends

^aSome water sources fell within multiple areas of treatment. These sources included 10 samples within impoundment and hotspot areas, and four samples within both spill and hotspot areas.

^bEighty-six samples were analyzed for radon, 96 samples were analyzed for radium, and 93 samples were analyzed for gross alpha.

^cDoes not include the four samples taken from streams. Furthermore, after analyzing the groundwater samples, the investigators found that two samples had low pH and elevated aluminum and sulfate, indicating the water was likely influenced by acid mine drainage sites found to be located nearby. They also found a third sample that appeared to be mainly rainwater, as suggested by its geochemistry and corroborated by information provided by the homeowner. These additional three samples were removed from the dataset.

^dIn addition to excluding the stream samples and the rain and acid mine drainage impacted samples, this dataset also excluded the 27 goodwill samples.

SUMMARY OF KEY RESULTS

FIELD MEASUREMENTS AND LABORATORY ANALYSIS

In *Part 1* of the study, the investigators' findings suggested that certain metals and metalloids could be present at concerning levels.¹ However, the findings from Part 2 of the study indicate concentrations of most of the metals and metalloids selected for this study did not exceed regulatory standards or other guidance values (**Commentary Table 3**). Concentrations

of BTEX compounds did not exceed drinking water standards in any sample. None of the 96 water samples collected and analyzed for radium exceeded the maximum contaminant levels established for drinking water. Furthermore, the investigators note that the radium concentrations were within the typical range reported for principal aquifers across the United States.

Some samples exceeded secondary drinking water standards for aluminum, iron, or manganese. Secondary standards are nonenforceable guidelines intended to support aesthetic quality of drinking water (taste, color, odor, or staining); con-

Commentary Table 3. Summary of Measured Analytes That Exceeded Either Drinking Water Standards or Other Guidance Values

Analyte	Exceedances	
	US EPA Primary Drinking Water Standards	Secondary Drinking Water Standards or Other
pH	0	12
Fluoride	0	1
Chloride	0	5
Sulfate	0	2
Bromide	0	1
Aluminum	0	2
Barium	1	0
Iron	0	7
Manganese	0	19
Lithium	0	46
Radon	0	33
Methane	0	3
Calc. Total Dissolved Solids	0	19

^aOne sample equaled the Primary Drinking Water Standard for barium.

taminants present at these concentrations are not considered health hazards. The investigators note that aluminum, iron, and manganese are the most common elements in Pennsylvania bedrock. Nineteen samples were above the secondary standard for total dissolved solids, and five samples equaled or exceeded the secondary standard for chloride. One sample equaled the primary drinking water standard for barium.

Currently, no drinking water standard exists for radon. The primary human health risk from radon in water comes from inhalation, as radon is released into indoor air during household water use, such as showering or washing dishes. The investigators, therefore, compared the radon concentrations in water samples to the US EPA proposed standard of 300 pCi/L, which has not been promulgated. Concentrations above this proposed level could lead to risk from radon in indoor air as it escapes from the water into the air during its use. Of the 86 samples tested for radon, 33 samples exceeded the proposed standard of 300 pCi/L. In these instances, the investigators recommended indoor air radon tests.

Similarly, no drinking water standard has been established for lithium, but EPA has set a health-based screening level of 10 µg/L. This screening level was exceeded in 46 of the samples.

The investigators measured detectable levels of methane in ambient air at 15% of the total sites, with a maximum reading of 132 ppm. They found dissolved methane in the groundwater of 70% of samples, including two with concentrations above the Department of Interior (DOI) action level for further investigation (10 mg/L) and a third with concentrations above the DOI action level for explosion concern (28 mg/L).

UOGD INFLUENCE ON GROUNDWATER DRINKING WELLS

Statistical Comparison of Analyte Concentrations

Baka, Brantley, and colleagues conducted statistical comparisons only on samples taken from treatment and control areas (Commentary Table 2), excluding goodwill samples, stream samples, and three samples that were later found to be likely influenced by either rainwater or acid mine drainage (polluted runoff from mining sites). When comparing the treatment and control samples, the investigators found that concentrations of nine of the analytes were statistically higher in the treatment areas and two were lower in the treatment areas, although the chemicals identified as significantly higher or lower varied by statistical test.

The investigators found that the 10 spring water samples (including one sample from a control area) showed statistically higher concentrations of nitrate, which they hypothesized came from agricultural contamination. They therefore removed this subset of samples from the dataset and repeated the statistical comparison. Here, the investigators found that only seven species were higher in the treatment areas. However, when accounting for potential false discovery rates for each of the comparisons, they found that only radium concentrations were significantly higher in hotspots and impoundments as compared to control sites.

Geospatial Analysis

To understand whether concentrations of 12 UOGD-related analytes were associated with distance to UOGD wells within treatment areas (hotspot, impoundment, and spill sites), the investigators used regression and correlation analysis on the same set of samples as described above (i.e., excluding goodwill samples, stream samples, and the rainwater- and acid mine drainage-impacted samples). Similarly, they repeated these analyses on the sample set with and without spring water samples and obtained similar results.

In hotspot treatment areas, the investigators found no analyte concentrations increased closer to wells; instead, sodium and methane concentrations increased farther away. Near impoundment areas, they found that strontium concentrations increased closer to impoundments, while sodium and barium increased farther away. Near spill areas, sodium, barium, and methane concentrations all increased closer to spill sites, whereas sulfate concentrations increased farther away. The researchers did not find any correlation (positive or negative) for radium concentrations with respect to distance to wells.

The investigators concluded that the presence of some analytes (strontium, sodium, barium, and methane) in groundwater wells and springs may be associated with produced water leaks from impoundment sites or spills at well pads rather than with the UOGD wells themselves.

Origin of Salt and Gas Analytes

The assessment of isotopic data and element ratios, which can help identify the geological source of dissolved constituents in groundwater, provided additional lines of evidence for the investigators to evaluate the potential influence of UOGD. The assessments of isotopic strontium versus strontium-to-chloride ratios showed no consistent patterns between groundwater from treatment and control areas, indicating that these combined signatures do not distinguish between the two areas. Furthermore, a comparison of strontium isotopic signatures alone in groundwater was similar across all samples (control and treatment) but was aligned more closely with UOGD produced water than with conventional sources.

When the investigators plotted methane concentrations against the carbon-13 isotopic signature of the methane measured in groundwater, the results indicated mixtures of biogenic and thermogenic gases, with thermogenic components typically linked to oil and gas development. Even the most methane-rich sample, however, contained a significant fraction of biogenic gas. This mixed signature makes it difficult to attribute the presence of thermogenic gas conclusively to UOGD.

Finally, chloride-to-bromide ratios, which can help distinguish organic waste or road salt, from deep formation water, suggested chloride primarily originated from organic wastes in all but one sample; however, this single outlier could not be used to confirm whether its signature reflected natural upwelling or produced water.

Combined Results

The results of this 2024 sampling campaign showed no conclusive evidence of UOGD-related contamination in private drinking water. Collectively, the statistical comparison of analyte concentrations, geospatial comparisons, and examination of salt and gas analyte origins could not identify UOGD as the source of these analytes in groundwater. Observed variations in analytes between treatment and control areas, including radium, strontium, sodium, barium, and methane, may instead reflect differences in local geology or land use.

HEI ENERGY REVIEW COMMITTEE’S EVALUATION

In its independent evaluation, the HEI Energy Review Committee found that this follow-on study provided valuable evidence to assess predictions of potential groundwater

contamination and addressed community concerns, with results indicating no conclusive evidence of UOGD impact on the sampled groundwater wells. By implementing a robust and transparent sampling campaign, the researchers found that few analytes exceeded drinking water standards, and exceedances were primarily limited to secondary standards, which are based on aesthetic qualities rather than health effects. This study contributes valuable data that can inform future monitoring and risk assessment efforts. The following sections describe the strengths and limitations of the research.

STUDY DESIGN, DATASETS, AND ANALYTICAL APPROACHES

The Committee recognized that a key strength of this study lies in its rigorous analytical approach, which focused on a well-considered subset of water quality analytes relevant to both potential UOGD-related contamination and health effects if present at concerning levels. Additionally, the investigators included analyses to examine the provenance of methane and major elements to generate additional lines of evidence for source apportionment. The sampling plan included protocols that incorporated multiple quality assurance and quality control steps, a thorough sampling and collection design, and included best practices, such as using field duplicates and blanks to ensure accurate sampling and analyses.

The Committee acknowledged the quality of the study design, which incorporated multiple types of treatment areas to assess different sources of potential UOGD contamination through groundwater, along with limited control sites, where available. Implementing this study design is a considerable achievement given the challenges posed by the regional history of legacy hydrocarbon development and other extractive activities.

The Committee also appreciated the statistical analyses, which employed multiple approaches and accounted for false discoveries using the Benjamini–Hochberg procedure. This approach helps to ensure that findings are not artifacts and that they are more likely to be reliable. The investigators provided transparent reporting of both significant and nonsignificant findings.

Finally, the Committee recognized the value of the community-centered approach, which responded directly to concerns about water quality identified through the first study and accommodated community requests for increased and transparent water sampling. The investigators not only provided each participant with a letter explaining the findings and their relevance to homeowners but also held a community meeting and offered follow-up calls to discuss the findings. While the study was not directly aimed at indoor air quality, the researchers paid special attention to potential radon or methane hazards and included recommendations to the homeowners informed by their findings.

The Committee recognizes that, given a study of this size and scope, many analyses cannot be conducted and types

of data are difficult or impossible to obtain. By design, the investigators relied on existing groundwater wells, which is beneficial in two ways. First, this study was able to directly measure potential exposure to contaminants of concern by sampling drinking water sources. Second, it reduced costs because drilling new groundwater sampling wells is time-intensive, costly, and beyond the scope of this project.

However, the authors did not discuss how limitations of relying on existing wells may have affected the conclusions of the study. The study approach does not account for the complexity of subsurface groundwater flow paths and directionality of the hydraulic gradient. While the Committee recognizes that in-depth hydrogeologic modeling was outside the scope of this work, some approaches could have been considered to explore likely flow paths and clarify the relevance or limitations of a proximity-based correlation study, such as conservative solute modeling or desktop hydraulic gradient estimation. Even though modeling was not included in the scope of the study, a discussion of this limitation would have strengthened the report. Furthermore, the investigators were unable to find control groundwater wells that were more evenly distributed over the study area (Commentary Figure 1). This uneven spatial distribution of control samples may have affected the ability of the investigators to establish representative background conditions. These limitations might introduce uncertainty into the conclusion that there is no significant statistical difference between the treatment and control areas, which were not discussed by the investigators in the report.

Additionally, there was insufficient data on groundwater well construction, including no information on screening levels, reliance on self-reported well-depth estimates, and missing data for approximately 30% of the wells. These limitations can lead to a potential mismatch between contamination sources and the sampled wells. The Committee acknowledges that these data are difficult, if not impossible, to obtain. It also recognizes that these limitations do not affect whether the measured analyte concentrations in these samples reflect the level of exposure of residents who use these water sources. However, it is important to note that these missing data are an additional limitation to collecting water samples that can be used to delineate potential groundwater contamination impacts from UOGD in the region, which were not discussed by the investigators.

The Committee also found that, as presented, the study population and demographic data were underutilized. While the water quality findings may not have warranted additional analyses given the low likelihood of exposure, this was not discussed, nor was how the demographic data might have been used. There was no clear indication that these data were collected with a follow-up assessment in mind, for example, to examine whether exposure differed among subpopulations or to evaluate the generalizability of the findings to the broader population.

FINDINGS AND INTERPRETATION

Irrespective of the findings of the water quality analysis, the investigators shared each result via mail and email with each study participant. The investigators found a few instances of analytes at concentrations above standards or guidelines. In those cases, they provided a cover letter describing the specific findings and information on potential mitigation resources and followed up with phone calls with the homeowners. The Committee appreciated the strong, consistent communication with the community.

This report gives a balanced presentation of the analytical results and statistical analyses of the data, including reporting of significant and null results before and after false discovery rate correction. However, there are several examples of findings that were reported without further explanation or discussion. While the Committee acknowledges that some results may lack clear explanations, researchers could have drawn on existing science and professional judgment to explore plausible interpretations. For example, further discussion could have addressed the patterns of strontium isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) observed across different treatment areas, and why both treatment and control samples appear more similar to produced water from unconventional wells than to that from conventional wells. Another example is the absence of discussion on the implications of the positive correlation between sulfate and other analyte concentrations and distance from treatment areas.

Other findings are presented without context to understand the significance of such results. In the discussion of public health observations, the report does not address the implications of the 46 samples that exceeded the EPA's health-based screening level for lithium, nor does it indicate whether or how this information was communicated to participants. Some analytes, such as manganese, may only have secondary maximum contaminant levels established for aesthetic concerns; however, they may also have other nonregulatory, health-based guidance values, which were not explored further here. The report also says the levels of radium found in drinking water were concentrations that are "within the typical range reported for principal aquifers across the United States." The Committee questioned why these data were not reported relative to regional radium concentrations, which would be more relevant to interpreting the findings, or, if unavailable, why this was not noted as a data gap.

The Committee also questioned why the investigators suggest in future work that analyses of blood and hair of residents could be used to discern the potential effects of contamination. Given the findings of this study, such an intervention seems unwarranted and unsupported.

CONCLUSIONS

In [Part 1](#) of the study, Baka, Brantley, Xue, and colleagues found statistically significant increases in certain inorganic constituents near UOGD wells, produced water spills, and

impoundments. They also found through community focus groups that residents in Southwestern Pennsylvania were concerned about potential drinking water contamination, particularly radioactive elements, from wastewater management practices. Importantly, Part 2 of the study directly addressed these community concerns by investigating whether private drinking groundwater wells were contaminated, and whether UOGD activities were affecting their water quality. Exceedances of drinking water standards were rare and limited to secondary drinking water standards, which are based on aesthetics. Although the investigators found that radium concentrations in hotspot and impoundment areas were higher than those in the control sites, isotopic analyses of geochemical tracers and methane did not indicate produced water influence on groundwater, and measured concentrations were below drinking water standards.

This study tested whether private drinking groundwater wells presumed to be at higher risk of UOGD contamination showed evidence of UOGD-related impacts and found no conclusive evidence that they did. Overall, these results contribute to the broader understanding of groundwater quality in areas proximate to UOGD and add valuable data that may help distinguish localized UOGD impacts from broader regional effects of legacy extraction and geological factors.

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ABBREVIATIONS AND OTHER TERMS

[x]	concentration of x component	MDL	method detection limit
‰	per mille, parts per thousand	μS/cm	microSiemens per centimeter
AEI	advanced electron impact	Mg	magnesium
Al	aluminum	Mn	manganese
AMD	acid mine drainage	MnO	manganese oxide
As	arsenic	N	normality
ATS	Theil-Sen slope(s)	n	number of observations
Ba	barium	Na	sodium
Be	beryllium	ng	nanogram(s)
BM	Brunner-Munzel (test)	Ni	nickel
Br	bromide	NO ₃	nitrate
BTEX	benzene, toluene, ethylbenzene, xylenes	NO ₃ -N	nitrate as nitrogen
¹² C	carbon-12	NO ₃ - NO ₃	nitrate as nitrate
¹³ C	carbon-13	OLS	ordinary least squares
C ₁	methane concentration	ORP	oxidation-reduction potential
C ₂	ethane concentration	P	phosphorus
C ₃	propane concentration	PADEP	Pennsylvania Department of Environmental Protection
Ca	calcium	PAGWIS	Pennsylvania Groundwater Information System
CaCO ₃	calcium carbonate	Pb	lead
Cd	cadmium	pCi	picocuries
Cl	chloride	PI	principal investigator
CH ₄	methane	PSU AAL	Penn State University Agricultural Analytical Laboratory
COG	conventional oil and gas	PSU EESL	Penn State University Earth and the Environment Sustainability Laboratory
Cr	chromium	PSU LIME	Penn State University Laboratory for Isotopes and Metals in the Environment
CRD	carbonate removal device	PSU SALTS	Penn State University Laboratory SAL inity with IsoTopeS
Cu	copper	PTFE	polytetrafluoroethylene (nonstick material)
δ ¹³ C	“delta 13 carbon,” ratio of carbon isotopes (¹³ C/ ¹² C)	PW	produced water
δD	“delta deuterium,” ratio of hydrogen isotopes (² H/ ¹ H)	Ra	radium
DI	deionized	²²⁶ Ra	radium-226
DIC	dissolved inorganic carbon	²²⁸ Ra	radium-228
DL	detection limit	Rn	radon
DO	dissolved oxygen	S	spill
F	fluoride	SC	specific conductance
Fe	iron	Si	silicon
FDR	false discovery rate	SMCL	secondary contaminant level
GC-MS/MS	gas chromatography-mass spectrometry/mass spectrometry	SO ₄	sulfate
HCl	hydrochloric acid	Sr	strontium
HPIC	high-pressure ion chromatography	⁸⁶ Sr	strontium-86
HS	hotspot	⁸⁷ Sr	strontium-87
I	impoundment	SWPA	Southwestern Pennsylvania
IC	ion chromatography	TDS	total dissolved solids
ICP-AES	inductively coupled plasma atomic emission spectroscopy	²³² Th	thorium-232
ICP-MS	inductively coupled plasma mass spectrometry	TIMS	thermal ionization mass spectrometry
IRB	Institutional Review Board	Tl	thallium
IQR	interquartile range	U	uranium
K	potassium	²³⁸ U	uranium-238
⁴⁰ K	potassium-40	UOG	unconventional oil and gas
keV	kilo electron volts	UOGD	unconventional oil and gas development
LDPE	low-density polyethylene	US DOI	US Department of the Interior
Li	lithium	US EPA	US Environmental Protection Agency
Lu	lutetium	USGS	US Geological Survey
MCL	maximum contaminant level	VOC	volatile organic compound
MCLG	maximum contaminant level goal	WGS	World Geodetic System
MDA	minimal detectable activity	WMW	Wilcoxon-Mann-Whitney

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Judy S. LaKind* Adjunct Associate Professor, Department of Epidemiology and Public Health, University of Maryland School of Medicine

Christopher Paciorek Adjunct Professor and Research Computing Consultant, Department of Statistics, University of California, Berkeley

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Health Effects Institute

One Beacon Street Suite 21300
Boston, Massachusetts 02108
USA
+1-617-488-2300

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