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Geochemical and isotope analysis of produced water from the Utica/Point Pleasant Shale, Appalachian Basin†

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While development of the Utica/Point Pleasant Shale (UPP) is extensive in Ohio (U.S.) and increasing in Pennsylvania and West Virginia, few studies report the chemistry of produced waters from UPP wells. These data have important implications for developing best management practices for handling and waste disposal, or identifying the fluid in the event of accidental spill events. Here, we evaluated the elemental and isotope chemistry of UPP produced waters from 26 wells throughout Ohio, Pennsylvania, and West Virginia to determine any unique fluid chemistries that could be used for forensic studies. Compared to the Marcellus, UPP produced waters contain higher activities of total radium (^{226}Ra + ^{228}Ra) and higher $^{228}Ra/^{226}Ra$ ratios. As with the Marcellus Shale, elemental ratios (Sr/Ca) and isotope ratios ($^{87}Sr/^{86}Sr$) can distinguish UPP produced waters from many conventional oil and gas formations. Sr/Ca and $^{87}Sr/^{86}Sr$ ratios can fingerprint small fractions (~0.1%) of UPP produced water in freshwater. However, because Marcellus and UPP produced waters display similar major elemental chemistry (*i.e.*, Na, Ca, and Cl) and overlapping ratios of Sr/Ca and $^{87}Sr/^{86}Sr$, $^{228}Ra/^{226}Ra$ ratios may be the best tracer to distinguish these waters.

Environmental significance

It is important to understand the chemistry of Oil and Gas produced water to help (1) identify spatial variability in formation waters, (2) evaluate treatment strategies, and (3) identify accidental releases and track contamination through the environment. Multiple studies have discussed geochemical signatures of unconventional oil and gas wastewater, but many focused solely on water from the Marcellus Formation. Now, with the production of hydrocarbons from the Utica/Point Pleasant Formations (UPP) rapidly increasing along with the volume of produced water, it is vital to evaluate the chemistry of water produced from these formations. In this study, the chemistry of produced water from the UPP is documented along with elemental and isotopic tracers that could be used to identify freshwaters contaminated by UPP wastewaters.

Introduction

Oil and gas (O&G) production from low-permeability, unconventional shale formations continues to rise in the Appalachian Basin, U.S., generating over 45% of the domestic natural gas in 2018.[1] From 2007 to 2018 annual U.S. natural gas production from shale plays rose from 36 billion cubic meters (bcm) [1293 billion cubic feet (bcf)] to 617 bcm [22 054 (bcf)]. During that same timeframe the percentage produced from the Appalachian Basin in the states of West Virginia, Ohio, and Pennsylvania rose from less than 1% to over 45%, largely due to the continued development of two unconventional shale formations, the Marcellus and Utica/Point Pleasant (UPP).[1] O&G development was historically limited to permeable reservoirs known as conventional formations but has expanded into low permeability unconventional O&G formations over the last 20 years because of technical improvements in horizontal drilling and hydraulic fracturing. During hydraulic fracturing, large volumes of water (30 million liters per well for Marcellus and 38 million liters per well for UPP) mixed with other additives are pumped into the formation at high pressure causing the rock to fracture and stimulate hydrocarbon release.[2] After this process, millions of liters of a salty and radium-bearing fluid (*i.e.*, flow back and produced waters) returns to the surface where it is typically disposed in underground injection control (UIC) wells, reused to stimulate other wells, or treated for reuse at wastewater treatment plants.[3] Flowback waters are generally defined as fluids comprising mixtures of *in situ* formation waters and hydraulic fracturing fluids that flow from a well shortly after the stimulation pressure is released. Produced waters often refer to waters that return after the wells have been in production for some time and are thought to better represent the *in situ*

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formation waters or salts from the formation that could have been mobilized by hydraulic fracturing fluids rather than the chemistry of the hydraulic fracturing fluids that were injected.

The two largest unconventional shale reservoirs in the Appalachian Basin are the Marcellus and UPP Formations, which are estimated to contain over 2.4 trillion cubic meters (*i.e.*, 84.8 trillion cubic feet) and 1.1 trillion cubic meters (*i.e.*, 38.8 trillion cubic feet) of recoverable natural gas, respectively.[4,5] The Marcellus is the oldest organic rich shale in the Middle Devonian sequence and overlies the Onondoga Limestone. Currently, there are over 10 000 active Marcellus wells in Pennsylvania.[6] The UPP Shale is several hundred meters below the Marcellus Shale and has been called the "natural gas giant below the Marcellus".[7,8] The UPP Formation is present throughout Ohio, Pennsylvania, West Virginia, New York, Ontario, and Quebec ranging in depth from 2300 meters in northwest Pennsylvania to 4000 meters in West Virginia and southern Pennsylvania.[7] Throughout the Appalachian Basin, the Utica Shale directly overlies the Point Pleasant Shale with both formations having variable concentrations of carbonate (20–60%), clay (30–60%), and total organic content (~1–5%) that is likely related to their geographic location and varying depositional environments.[7] Collectively, the UPP is thickest (120 to 150 m) throughout southwest and northeast Pennsylvania and gets thinner in eastern Ohio (60–90 m).[7] Unconventional O&G development in the Appalachian Basin began in the Marcellus around 2007 but has expanded into the UPP since 2011.[6]

Most UPP development has occurred in Ohio but has recently increased in both Pennsylvania and West Virginia. As of January 2020, there were over 2700 UPP wells in Ohio and over 160 in Pennsylvania.[6,9] One of the largest environmental concerns with the increased unconventional O&G production throughout the Appalachian Basin is the possibility of ground water or surface water contamination by hydraulic fracturing fluids or produced waters. In areas dominated by Marcellus development, there are numerous incidents where spills (1181 spill events in Pennsylvania from 2005–2014),[10,11] surface water disposal,[12,13] improper management at wastewater disposal facilities,[14,15] and potentially faulty well casings[16] caused Marcellus produced waters to migrate to water resources. No similar incidents have been reported from the more recent growth in UPP O&G development; however, this could be because there is only one study that the authors are aware of that has tested freshwater for UPP produced water contamination.[17]

Despite the environmental concerns and wastewater management challenges associated with unconventional O&G development, UPP produced water chemistry has been published for only two wells.[18,19] Total dissolved solid (TDS) concentrations in produced waters are highly variable from unconventional shale formations because of variable amounts of dilution with injection waters.[20–22] Therefore, any comparisons of elemental concentrations among produced waters from different formations should be limited to water of similar TDS, preferably the most saline waters that represent original formation waters.[20–22] Comparisons among these high-salinity waters for different formations in the Appalachian Basin indicate that they can have significantly different concentrations of Ca, Sr, Ba, Ra, and B, among other elements. For instance, the Marcellus has unusually high concentrations of Ba, Sr, and ^{226}Ra relative to other formations in the Appalachian Basin. Formations throughout the Basin also have unique elemental or isotope ratios (*i.e.*, Sr/Ca, ^{228}Ra/^{226}Ra, ^{87}Sr/^{86}Sr, ^{11}B/^{10}B, and ^{7}Li/^{6}Li) that can identify small quantities (often <0.1%) of produced water mixed with groundwater, surface water, or stream sediments.[12,22–27] In almost every case study investigating potential O&G contamination events, unique isotope or elemental ratios were used as a forensic tool to determine the source of pollution (*i.e.*, unconventional brine *vs.* conventional brine *vs.* road salt *vs.* acid mine drainage). As development expands in the UPP, similar data could be important in fingerprinting UPP produced waters in the environment, understanding heterogeneities in the formation, and developing strategies for managing UPP produced water from various parts of the play. The existing data for UPP produced water chemistry is not adequate to conduct this fingerprinting because it is from only two wells and is limited to a few analytes (SO_4, Cl, Na, Ca, Mg, and K).[18,19]

The management of UPP produced waters in Pennsylvania, Ohio, and West Virginia fall under the same regulatory statutes and disposal practices as Marcellus fluids, which includes disposal through injection disposal wells, reuse without any treatment to fracture other wells, or treatment at zero liquid discharge treatment plants that remove some of the suspended solids and precipitate out barium-sulfate minerals before reuse for hydraulic fracturing.[28] Current and future concerns with handling the wastes from UPP development will likely be related to the proper disposal of radioactive sludge generated from facilities treating the fluids, faulty casings on gas-producing wells that may allow fluid migration, or potential spills at the surface. From 2010 to 2013, approximately 5% of the Marcellus Shale wells in Pennsylvania received violations for well cementing issues.[29] The greatest threat to water quality is likely from surface spill events which occur at approximately 10% of the unconventional wells each year.[30] Therefore, it is essential to develop forensic tools for identifying potential contamination from UPP development after the spill is diluted with freshwater.

The objectives of this work were to (1) document the chemistry of liquid wastes from UPP wells, and (2) determine unique isotope or elemental ratios for tracing UPP releases in the environment. To address these objectives, liquid wastes from the UPP were collected from producing wells and analyzed for inorganic chemistry (Cl, Br, SO_4, Na, Ca, Mg, Sr, K, Li, B, Ba, Fe, Pb, Cu, As, and U), radioactivity (^{226}Ra and ^{228}Ra), and isotope ratios (^{87}Sr/^{86}Sr). Unique signatures for tracing environmental contamination from UPP development were identified by comparing our results to analyses from other O&G formations in the Appalachian Basin.

Methods

Produced water collection

UPP produced waters were collected from 26 wells throughout Ohio, Pennsylvania, and West Virginia (Fig. 1). Based on well production reports and communication with collaborators from industry, all wells were in production for over 120 days, reducing chemical variabilities commonly observed in produced waters collected early after a well goes into production.[20,31] Produced water samples were collected from O&G water separators at well heads, stored in 10 liter high-density polyethylene (HDPE containers), and preserved to pH < 2 with nitric acid for cation analyses or unpreserved for anion analyses. Thereafter, 100 mL of each sample for cation analysis was digested with 6 mL of aqua regia for 4 hours at 70 °C. There were no suspended solids in any of the samples after digestion. Acid dissolution of suspended particulates could increase the possibility of excess dissolved Fe (and potentially other metals). However, because metal precipitation can occur rapidly after produced waters flow from a gas well,[21] all samples were digested prior to filtering to analyze total metals in solution. The true vertical depth of the sampled UPP wells varied from ~2300 m in northwest Pennsylvania, ~3500 m in northeast Pennsylvania, to ~3700 to 4000 m in West Virginia and southern Pennsylvania (Fig. 1).

Produced water characterizations

Major and minor trace element analyses were performed on a Thermo Scientific iCAP 6000 inductively coupled plasma optical emission spectrometer (ICP-OES; Na, Ca, Mg, Sr, K), Thermo X-Series 2 mass spectrometer (ICP-MS; Li, B, Ba, Fe, Pb, Cd, Cu, As, U) located at Penn State University's Energy and Environmental Sustainability Laboratories (EESL), and Dionex ICS-1100 ion chromatography (IC; Cl, Br, SO_4). Before elemental analyses, samples were filtered (0.45 µm cellulose acetate) and diluted in 2% nitric acid or ≥18 MΩ ultrapure water (Cl, Br, SO_4) to reach dilution factors of 2000 for Na, Ca, Mg, Sr, and K, 100 for Cl, Br, and SO_4, or 50 for all other metals. Mass interferences and matrix complications of analyzing high salinity samples by ICP-MS or ICP-OES were accounted for by using internal spikes (Sc, In, Re, Y) and high salinity, matrix-matched standards.[32] Calibration curves for all analyses were verified by confirming <5% differences between measured and known elemental concentrations in check standards (USGS M − 220, USGS T-227, and SRM1640a).

Isotope analyses were performed using a ThermoFisher Neptune Plus high resolution multicollector (MC-ICP-MS; $^{87}Sr/^{86}Sr$) located at Penn State University EESL and a small anode germanium detector gamma spectrometer from Canberra Instruments at the Tracing Salinity with Isotopes Lab (SALTs) also located at Penn State University ($^{228}Ra/^{226}Ra$). Radioactivity (^{226}Ra, ^{228}Ra) was measured in acid digested produced waters at geometries (20 mL and 3 L geometries) consistent with well characterized internal standards from an inter-laboratory comparison that reported most probable radium activities in three Appalachian Basin O&G produced waters.[32] After a 21 day equilibration, ^{226}Ra was calculated directly at 186.2 keV and then confirmed from the average activity of ^{214}Bi (609.3 keV) and ^{214}Pb (295.2 & 351.9 keV). Direct measurement of ^{228}Ra were performed using its ^{228}Ac daughter at 911.1 keV. Prior to $^{87}Sr/^{86}Sr$ analysis, strontium was separated from wastewaters with recoveries of 99% ± 3.7 using Sr Spec EICHROM resin and nitric acid (2 N) to yield 0.25 to 1 µg of strontium. Strontium isotope accuracy was determined by comparisons to NIST SRM 987. The average $^{87}Sr/^{86}Sr$ ratio of the

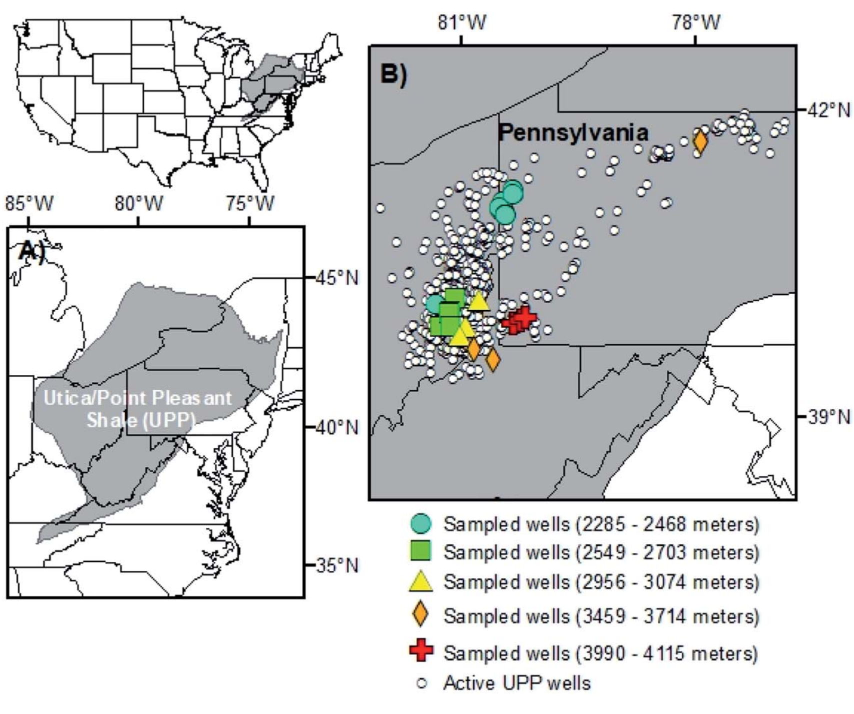

Fig. 1 Sampled oil and gas wells from the Utica/Point Pleasant (UPP) formation in the northern Appalachian Basin, U.S. (A) The UPP play is shaded gray. (B) Active O&G wells producing from the UPP formation are represented with white circles. Produced waters from 26 of the active wells were sampled throughout the Basin with well depths indicated by symbols.

SRM over 41 analyses was 0.710240 with a standard deviation of 0.000002 (actual value = 0.710240).

Additional data sources

Produced water chemistry from the UPP were compared to existing produced water chemistry from O&G formations in the Appalachian Basin. Produced water chemistry data from conventional and unconventional formations were compiled from the US Geological Survey (USGS) Produced Water Database version 2.3n.[33] Produced water chemistry from hydraulically fractured oil and gas wells is known to vary with time after a well goes into production. While all of the UPP wells sampled in this study were over 120 days of production and were believed to have a fluid chemistry reflective of the formation mineralogy or *in stu* formation fluids, an operational chloride threshold was used to reduce potential unknown sources of error in the UPP produced water chemistry and to allow for comparisons of produced water chemistry from different formations. The operational chloride threshold was defined as only including data from wells where chloride concentrations were ≥76 800 mg L^{-1} chloride (*i.e.*, the 5^{th} percentile chloride concentration from the 26 UPP samples collected for this study). This was a reasonable threshold in limiting potential sources of error (*e.g.*, mixing with hydraulic fracturing fluids) in the UPP produced water chemistry. One of the collected UPP samples (UPP 24 in Table S1†) that was excluded from statistical analyses by this threshold was later found to be compromised by a local hydraulic fracturing job. The sample (UPP 24) had lower TDS (*e.g.*, ~71 000 mg L^{-1}) than was expected for a well with over 120 days of production. After contacting the oil and gas company about this sample, the company stated that the produced water chemistry in sample UPP 24 was likely influenced by fracturing fluids that migrated along a fault line from the local hydraulic fracturing job.

In order to compare the UPP produced water chemistry to produced waters from other formations in the Appalachian Basin, all produced water data collected from the US Geological Survey (USGS) Produced Water Database was also filtered to only include samples with ≥76 800 mg L^{-1} chloride (*i.e.*, the 5^{th} percentile chloride concentration from the 26 UPP samples collected for this study). While the authors acknowledge that this data inclusion method could cause potential sources of bias, the method would likely bias results so formations would appear to have more similar fluid chemistries; therefore, any observed differences in fluid chemistries are likely real. The total conventional produced water data set from the US Geological Survey (USGS) Produced Water Database included 2434 analyses from 84 formations. Conventional wastewater results were reduced to 1122 entries by only including data from wells where chloride concentration was ≥76 800 mg L^{-1} chloride. Similarly, data for the Marcellus Shale were reduced from 448 entries to 128 by only including wells with ≥76 800 mg L^{-1} chloride.

Elemental and isotope ratios for the formations were also compared to ground and surface water resources in Appalachian Basin using the Water Quality Portal from the National Water Quality Monitoring Council.[34] Water quality data for streams, rivers, and ground water wells were collected from 2000–2005 ($n = 9006$). Of the 9006 entries, 5589 included Cl, 460 included Br, 24 included B, 3504 included Na, 5542 included Ca, 348 included Mg, 101 included Ba, 113 included Sr, 25 included ^{226}Ra, and 25 included ^{228}Ra. The $^{87}Sr/^{86}Sr$ ratios in freshwaters were also referenced from additional sources.[35]

Statistical analyses

All statistical analyses were performed in RStudio.[36] Shapiro Wilk tests for normality (Table S7†) confirmed that most of the data was not normal. Therefore, Kruskal–Wallis and Wilcoxon rank sum tests with Bonferroni corrections were used to determine if there were any statistical differences between the produced water chemistry from UPP, Marcellus, and conventional formations. Statistical differences between the compared formations were interpreted as being significant if p values were less than 0.05. Elements with concentrations below detection limits were not included in these analyses.

Results and discussion

Chemistry of produced waters from the Utica and Point Pleasant Shale

Consistent with produced waters from other O&G formations in the Appalachian Basin, UPP produced waters are dominated by

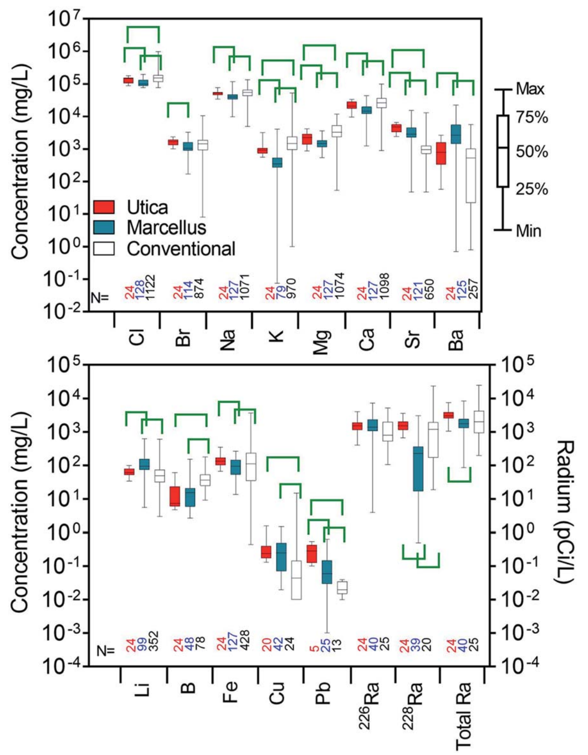

Fig. 2 Produced water chemistry from the UPP (red) analyzed in this study compared to other formations in the Appalachian Basin. Produced water analyses from the Marcellus (blue) and conventional O&G formations (white) were previously reported in the USGS Produced Water Database.[33] Numbers above the x-axis represent the number of analyses for each formation. Green brackets indicate comparisons between two formations that have significantly different produced water chemistry ($p < 0.05$).

sodium, calcium, and magnesium (accounting for >90% of the total cation charge equivalents) and are nearly 100% charge balanced by chloride (Fig. 2). Based on the data inclusion method used in this study (*i.e.*, wells with over 76 800 mg L^{-1} chloride), the UPP and conventional gas formations have produced waters with higher chloride, calcium, and sodium concentrations than produced waters from Marcellus wells. Median bromide concentrations in UPP produced waters were also 1.6 times higher than produced water from the Marcellus. These differences in bromide concentrations were greater than reported levels of analytical inaccuracy (*i.e.*, typically ± 20% accuracy for O&G wastewater[32]).

Like the Marcellus, UPP produced waters are characterized by high concentrations of barium (ranging from 57 to 2700 mg L^{-1}) and strontium (2000 mg L^{-1} to 6500 mg L^{-1}) (Table S1 and S3†). No sulfate was detected in any of the UPP produced waters (*i.e.*, all samples < 100 mg L^{-1} SO_4), indicating strong reducing conditions in the formation. Low sulfate concentrations allow high concentrations of dissolved alkaline earth metals that would otherwise precipitate in low solubility sulfate minerals (*e.g.*, K_{sp} of barite $\sim 10^{-10}$).[20] Both the Marcellus and UPP produced waters have median barium and strontium concentrations that are greater than the concentrations measured in produced waters from conventional gas wells (Fig. 2). High concentrations of these alkaline earth metals in produced waters are variously attributed to evaporated seawater brines reacting with local rock formations over geologic time[26,37] or reductive weathering of shales during hydraulic fracturing.[38,39]

UPP produced waters have high radioactivity. While the median ^{226}Ra activities in UPP produced water are similar to Marcellus produced waters (*e.g.*, 1522 pCi L^{-1} in UPP and 1417 pCi L^{-1} in Marcellus produced waters), the UPP has higher ^{228}Ra activities (*e.g.*, 1566 pCi L^{-1} in UPP and 228 pCi L^{-1} in Marcellus Shale produced waters). These differences in ^{226}Ra and ^{228}Ra radioactivity result in ^{228}Ra/^{226}Ra activity ratios in UPP produced waters (*i.e.*, 1.0 to 1.2 based on the 25th to 75th percentiles; Table S5†) that are greater than the values reported for Marcellus produced waters (*i.e.*, 0.01 to 0.4 based on the 25th to 75th percentiles). Differences in ^{228}Ra/^{226}Ra activity arise from different ratios of their respective radioactive parents (^{232}Th for ^{228}Ra and ^{238}U for ^{226}Ra) in the host reservoir rocks. Typically, the Th/U mass ratios for most silicate rocks fall in the range of 1.5 to 6.0 and generate ^{228}Ra/^{226}Ra activity ratios of 0.5 to 2.0 for both the rocks and for equilibrated formation waters.[40–42] To generate the median ^{228}Ra/^{226}Ra activity ratio in UPP waters (1.08, Table S5†), the UPP reservoir rocks would have to contain a ^{232}Th/^{238}U activity ratio of 1.0 and a Th/U mass ratio of 3.0 that is typical of clay-bearing silicate rocks.[40,41]

Elemental and isotopic ratios for identifying UPP produced water

Several elemental and isotopic ratios could be used to identify contamination from UPP (Fig. 3). Median Na/Cl, Cl/Br, (Ca + Mg)/Cl, (Ba + Sr)/Mg, and Sr/Ca molar ratios for all O&G produced waters from the Appalachian Basin are statistically different from freshwaters (Fig. 3 and Table S6†). However, the only ratios that are unique to the UPP produced waters are ratios that incorporate strontium or radium. For instance, (Ba + Sr)/Mg and Sr/Ca ratios for UPP and Marcellus produced waters are not statistically different from each other but are different from conventional O&G produced waters and freshwater (Fig. 3). ^{87}Sr/^{86}Sr ratios for UPP produced waters are also in a relatively narrow range (*e.g.*, ^{87}Sr/^{86}Sr = 0.71088 to 0.71143 based on the 25th to 75th percentiles; Table S5†) that could be

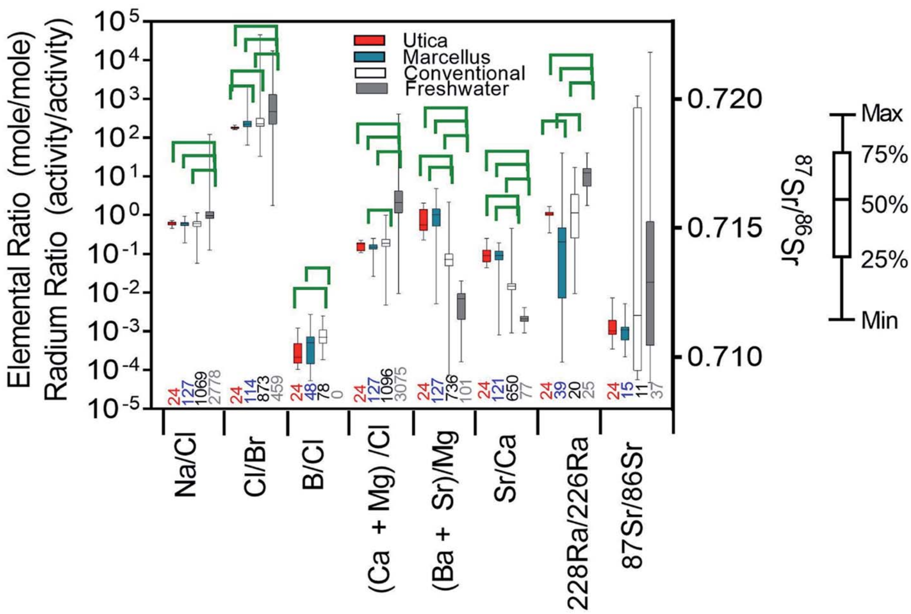

Fig. 3 Comparison between elemental and isotopic ratios in O&G produced waters and freshwaters throughout the Appalachian Basin. Green brackets indicate comparisons between two fluids that have significantly different ratios ($p < 0.05$).

useful in forensic applications. Additionally, the UPP has higher $^{228}Ra/^{226}Ra$ activity ratios than Marcellus produced waters but lower activity ratios than freshwaters. A framework is illustrated below that outlines how these different ratios could be used to identify freshwater contamination by the various O&G formations in the Appalachian Basin.

Conservative mixing models between freshwater and O&G produced waters were created in PHREEQC[43] to test the sensitivity of various elemental and isotopic ratios for identifying freshwater resources impacted by UPP produced water (Fig. 4). All produced water with ≥76 800 mg L^{-1} chloride (*i.e.*, the 5th percentile chloride concentration from the 26 UPP samples collected for this study) and all freshwater samples from the USGS Water Quality Portal (n = 9006 from 2000–2005) are included in Fig. 4 to show the potential endmembers that could be used in mixing models. For the purposes of identifying ratios that could be used to detect UPP produced waters in freshwaters, mixing models were performed with the 5th and 95th percentile concentrations for each of the endmembers.

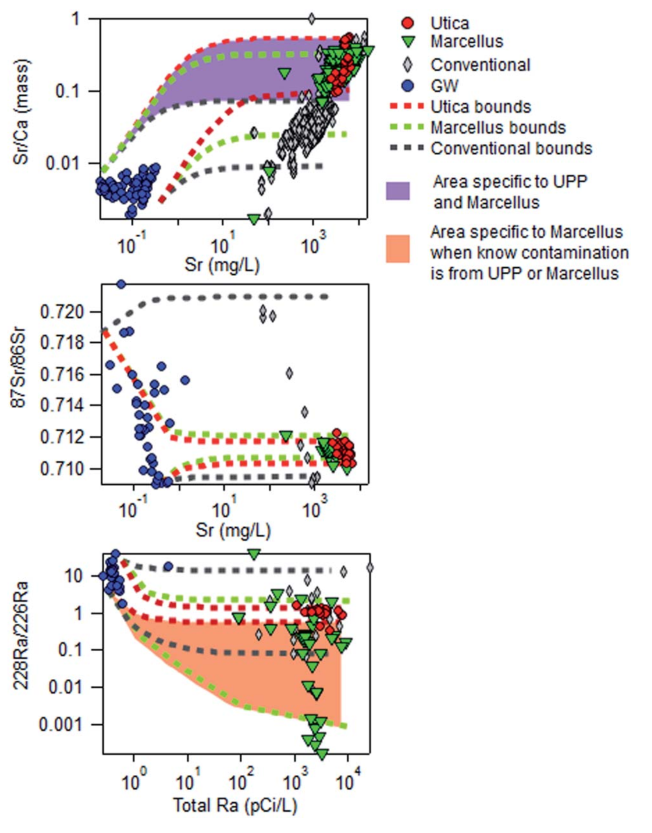

Fig. 4 Conservative mixing trends between freshwaters (blue) and produced waters from UPP (red), Marcellus (green), and conventional (gray) O&G formations. Dashed lines represent mixing trends between 5th and 95th percentile concentrations (or activities for radium) in O&G produced water and freshwater. (A) The purple shaded area shows Sr/Ca mass ratios and Sr concentrations that could definitively indicate contamination from with UPP or Marcellus produced water. (B) Panel B shows $^{87}Sr/^{86}Sr$ ratios and conservative mixing trends between freshwaters and produced waters from various formations. (C) If a sampled fluid has a Sr/Ca ratio and Sr concentration within the purple shaded area, the fluid could be analyzed for $^{228}Ra/^{226}Ra$ activity ratios to determine if the fluid is contaminated with UPP or Marcellus produced water. If the $^{228}Ra/^{226}Ra$ activity ratio and total radium activity is within the orange shaded area, the fluid is likely contaminated by Marcellus produced water instead of UPP produced water.

Freshwaters throughout the Appalachian Basin have highly variable Cl/Br mass ratios, ranging from 12 to 1700 (5th to 95th percentile, respectively). Cl/Br ratios in produced waters are also highly variable but are generally lower than freshwaters (*e.g.*, 5th to 95th percentile mass ratios of 52 to 250). Mixing trends between O&G produced water and freshwater show that the large variability in Cl and Br concentrations in freshwaters could make it difficult to utilize Cl/Br ratios in determining uncontaminated *versus* contaminated freshwater (Fig. S1†). However, this method could provide an initial indication of potential O&G contamination if the chloride concentrations measured in freshwater are greater than 100 mg L^{-1} and have Cl/Br mass ratios less than ~130 (*i.e.*, the 75th percentile Cl/Br mass ratio for Appalachian Basin O&G produced waters). While Cl/Br ratios could be used as an initial indicator of potential O&G contamination, they do not provide any specificity as to the source of contamination (*i.e.* produced waters from UPP, Marcellus Shale, or conventional O&G formations).

Many of the same elemental tracers that work for identifying Marcellus produced waters in the environment also work for identifying UPP produced waters. For example, UPP and Marcellus produced waters have higher Sr/Ca mass ratios (*e.g.*, 0.10 to 0.53 based on the 5th to 95th percentiles; Fig. 4A) than waters from conventional O&G formations, which have ratios of 0.01 to 0.07 (5th to 95th percentiles; Fig. 4A). Therefore, if sampled waters have Sr/Ca mass ratios greater than 0.07, this could indicate that the solution contains greater than 0.5% UPP or Marcellus water by volume. Smaller additions (*i.e.*, less than 0.5%) result in Sr/Ca ratios that overlap with conventional formations, making it difficult to distinguish if the contamination is from unconventional shale reservoirs or conventional O&G produced waters. The purple shaded area in Fig. 4A represents the Sr/Ca mass ratios and corresponding strontium concentrations that could definitively indicate contamination from UPP or Marcellus produced waters. The upper bounds for this shaded area are the 95th percentile mixing tends for UPP and the lower bounds are the 95th percentile mixing trends for conventional produced waters. Therefore, if sampled fluids have Sr/Ca and strontium concentrations that are within the purple shaded area, it is likely that fluids originate from or are contaminated by Marcellus Shale or UPP produced waters. The use of this tracer for detecting freshwater contamination by UPP produced waters is most applicable in eastern Ohio, where the current unconventional development is focused on the UPP. In areas where there is both UPP Shale and Marcellus development (*e.g.*, West Virginia and Pennsylvania), this tracer is also sensitive in identifying potential contamination events from these unconventional shale gas reservoirs; however, the overlap in Sr/Ca ratios between UPP and Marcellus produced waters reduces the effectiveness of this tracer in differentiating potential contamination from one of these two sources.

We further evaluated the sensitivity of isotope ratios ($^{87}Sr/^{86}Sr$ and $^{226}Ra/^{228}Ra$) as tracers for identifying UPP produced waters in the environment. These isotope ratios have advantages over the elemental ratios described previously as they are not subject to fractionation from ion exchange equilibria, mineral solubility, or changes in temperature and salinity.[12,44] Strontium isotope ratios ($^{87}Sr/^{86}Sr$) combined with Sr/Ca molar ratios are highly sensitive indicators for tracing Marcellus produced waters, detecting as low as 0.01% produced water additions to freshwater.[24,44] Similarly, this same isotope tracer works to identify contamination from UPP produced waters. Both the UPP and Marcellus have similar strontium isotope ratios (*e.g.*, $^{87}Sr/^{86}Sr = 0.71088$ to 0.71143 in UPP produced waters and $^{87}Sr/^{86}Sr = 0.71071$ to 0.71117 in Marcellus produced waters based on the 25th to 75th percentiles; Table S5†) that are traceable in freshwater and are distinguishable from some conventional produced waters that have $^{87}Sr/^{86}Sr$ ratios as high as 0.7200 (Fig. 4B). However, similar $^{87}Sr/^{86}Sr$ ratios in conventional, UPP, and Marcellus produced waters (p value = 1; see Table S3†) make them difficult to distinguish from each other if there is suspected contamination. Therefore, $^{87}Sr/^{86}Sr$ are not always an appropriate forensic tool for determining the source of produced water in the Appalachian Basin (Fig. 4B).

When it is essential to determine if the suspected contamination is from Marcellus Shale or UPP, radium isotopes are likely the best tracer (Fig. 4C). UPP produced waters have $^{228}Ra/^{226}Ra$ activity ratios (*i.e.*, 1.0 to 1.2 based on the 25th to 75th percentiles) that are greater than the values reported for Marcellus produced waters (*i.e.*, 0.01 to 0.4 based on the 25th to 75th percentiles). Therefore, to determine if a contamination event is from UPP or Marcellus Shale produced water, we recommend to analyze Sr/Ca ratios first to confirm if the fluid contains produced water from an unconventional shale formation (*i.e.*, UPP and Marcellus Shale produced water). Thereafter, if $^{228}Ra/^{226}Ra$ activities are less than 1.0 (*i.e.*, 25th percentile activity ratio for UPP produced waters) and total radium activities are greater than 4.4 pCi L^{-1} (*i.e.*, the highest radium activity for freshwater reported on the USGS water quality portal), then this could indicate that the water contains greater than 1% Marcellus produced water (Fig. 4C orange shaded area). In summary, if the Sr/Ca ratio and Sr concentration confirm that the fluid contains produced water from an unconventional shale formation and additional analyses show that the fluid has a $^{228}Ra/^{226}Ra$ activity ratio and total radium activity within the orange shaded region of Fig. 4C, it is likely that the fluid contains Marcellus produced water instead of UPP produced water.

Conclusions

Many of the same tracers that distinguish Marcellus produced waters from freshwater or other conventional O&G produced waters also work for UPP produced waters. In western Ohio where there is very little Marcellus development, Cl/Br, Sr/Ca, and $^{87}Sr/^{86}Sr$ ratios can identify potential UPP produced water contamination events. These isotope and elemental ratios in UPP produced waters are different than produced waters from conventional O&G development in Ohio, making them unique fingerprints that could identify potential contamination events from the UPP development. In regions of the Appalachian Basin with both UPP and Marcellus development, it may be more difficult to distinguish potential contamination between these two sources due to their overlapping Sr/Ca and $^{87}Sr/^{86}Sr$ ratios. However, these two formations have Sr/Ca ratios in their produced waters that are higher than conventional produced waters. Therefore, basic water quality analyses that utilize ICP or IC instrumentation to determine Cl, Br, Ca, and Sr concentrations can provide useful information in trying to determine if samples are contaminated with conventional or unconventional (*e.g.*, UPP or Marcellus) produced waters. These analyses can also be performed at a lower cost (~\$30 to \$60) than other isotopic methods (*e.g.*, gamma spectroscopy, MC-ICP-MS, *etc.*) which can cost over \$100 per sample. If it is necessary to identify if pollution is from Marcellus or UPP produced water, the $^{228}Ra/^{226}Ra$ ratio could distinguish UPP produced waters from Marcellus produced waters. The $^{228}Ra/^{226}Ra$ in UPP produced waters was the only tracer that was consistently different from the ratio observed in Marcellus produced waters.

There are also limitations with using elemental and isotopic tracers that need to be acknowledged before identifying potential contamination by unconventional or conventional produced waters. If freshwater is contaminated with UPP produced water, the resulting elemental ratios in the fluid mixture will be influenced by the volume of produced water that was mixed with the freshwater and the elemental concentrations of the two solutions. If no chemical or physical reactions occur after mixing, the resulting elemental concentrations could be calculated using a simple mass balance approach (*i.e.*, conservative mixing model). However, if the two solutions were incompatible or mixed together in a complex environment with multiple phases (*i.e.*, air, water, soil, *etc.*), the elemental concentrations in the combined fluid would not be explained by a conservative mixing model.[45] For instance, mixing strontium and barium-rich produced waters with sulfate or carbonate-rich fresh waters can result in mineral precipitation reactions that influence conservative mixing trends; similarly, cation-exchange reactions between contaminated freshwater and bedrock could result in the exchange of calcium (or other alkaline earth metals) ions in the contaminated water for sodium ions on clay minerals. While elemental and isotopic ratios are highlighted in this work as conservative tracers, the authors recommend that the type of mixing environment (*i.e.*, water, subsurface environment, soil, *etc.*) and the compatibility of the fluids being mixed together be considered in case-specific scenarios of suspected freshwater contamination.

Conflicts of interest

There are no conflicts to declare.

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