

New Tracers Identify Hydraulic Fracturing Fluids and Accidental Releases from Oil and Gas Operations

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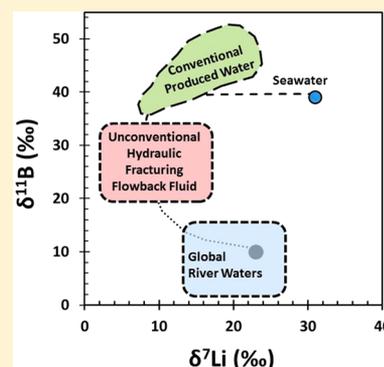
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Supporting Information

ABSTRACT: Identifying the geochemical fingerprints of fluids that return to the surface after high volume hydraulic fracturing of unconventional oil and gas reservoirs has important applications for assessing hydrocarbon resource recovery, environmental impacts, and wastewater treatment and disposal. Here, we report for the first time, novel diagnostic elemental and isotopic signatures (B/Cl, Li/Cl, $\delta^{11}\text{B}$, and $\delta^7\text{Li}$) useful for characterizing hydraulic fracturing flowback fluids (HFFF) and distinguishing sources of HFFF in the environment. Data from 39 HFFFs and produced water samples show that B/Cl (>0.001), Li/Cl (>0.002), $\delta^{11}\text{B}$ (25–31‰) and $\delta^7\text{Li}$ (6–10‰) compositions of HFFF from the Marcellus and Fayetteville black shale formations were distinct in most cases from produced waters sampled from conventional oil and gas wells. We posit that boron isotope geochemistry can be used to quantify small fractions ($\sim 0.1\%$) of HFFF in contaminated fresh water and likely be applied universally to trace HFFF in other basins. The novel environmental application of this diagnostic isotopic tool is validated by examining the composition of effluent discharge from an oil and gas brine treatment facility in Pennsylvania and an accidental spill site in West Virginia. We hypothesize that the boron and lithium are mobilized from exchangeable sites on clay minerals in the shale formations during the hydraulic fracturing process, resulting in the relative enrichment of boron and lithium in HFFF.



INTRODUCTION

Extraction of oil and gas from low-permeability organic-rich shale formations through horizontal drilling and high volume hydraulic fracturing (HVHF) has dramatically increased energy production in the U.S.¹ The development of several unconventional formations (e.g., Marcellus, Barnett, and Fayetteville) (Figure 1) has increased the percent of electricity generated using natural gas from $\sim 20\%$ in 2000 to $\sim 30\%$ in 2012, with projections for $\sim 50\%$ by 2040.² The expansion of HVHF has also been associated with increasing volumes of hydraulic fracturing flowback fluids (HFFF) that are typically highly saline and contain naturally occurring and man-made chemicals at toxic concentrations.^{3,4} During HVHF typically 15–20 million liters of water per unconventional well⁵ is injected under high pressure to stimulate hydrocarbon release from the shale formations composed of nanopores, nonconnected pore space, and the natural and stimulated fracture networks.¹ Following HVHF, the water that returns to the surface (i.e., HFFF) is a mixture of the injected water and hypersaline brine (formation water) that is released from within or adjacent to the shale formations.⁶

The potentially hazardous materials associated with HFFF have led to controversy regarding their overall impact on surface water,^{7,8} stream sediments,⁹ groundwater,^{10–13} and human health.¹⁴ In one of the largest unconventional plays, the Marcellus Formation in the Appalachian Basin, U.S., previous studies have suggested that higher density of unconventional drilling (and HVHF) is associated with a greater frequency of accidental releases of contaminants.⁴ However, in many cases the exploration of unconventional shale gas takes place in areas with historical conventional oil and gas production, and the chemical distinction between conventional oil and gas wastewater and HFFF is not always clear. In the Marcellus region, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in HFFF and produced water (PW) are distinct from some conventional Appalachian PW and many surface waters and their applications as environmental tracers are promising,^{15,16} although some isotopic overlap has been identified,^{9,17} which limits the use of this tracer. Resolving a

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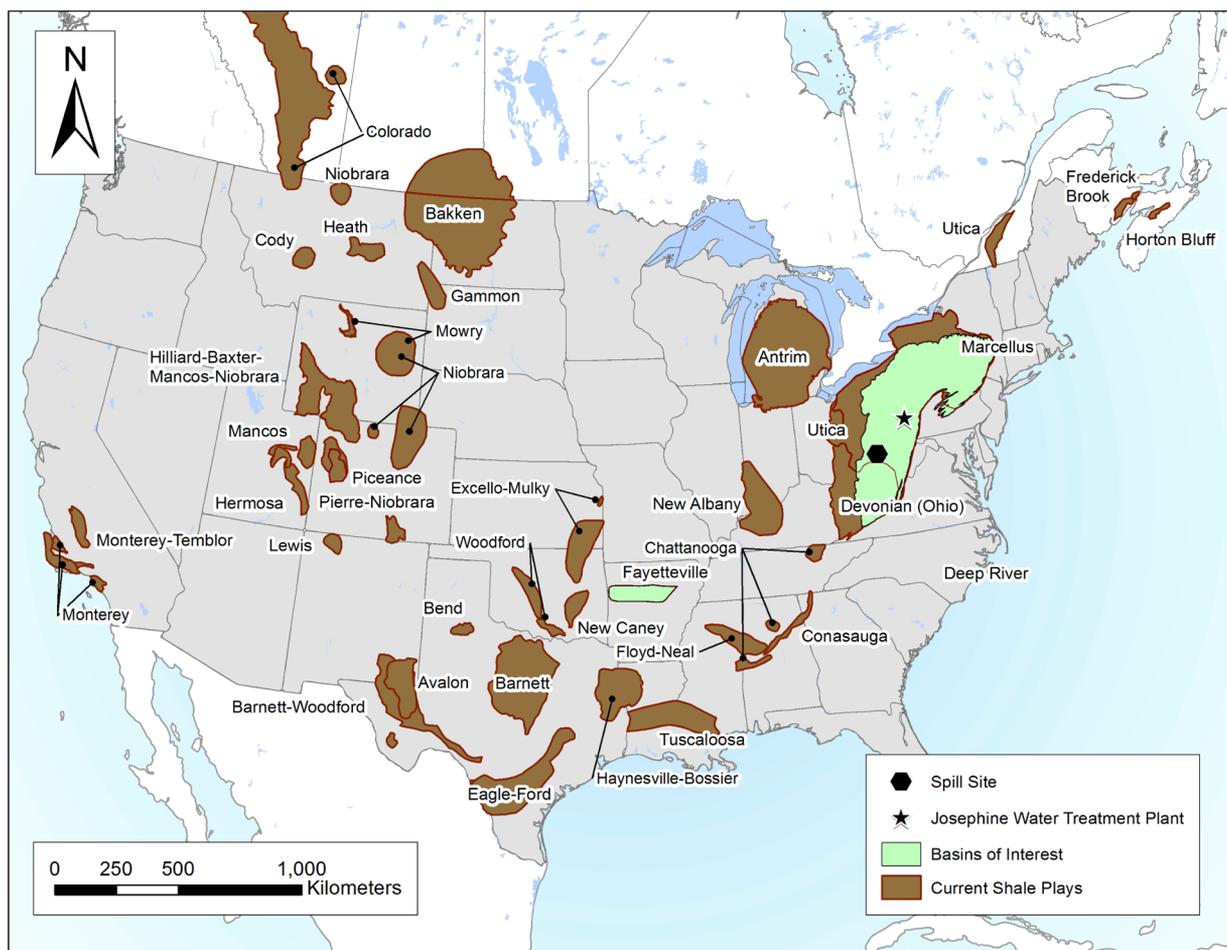


Figure 1. Shale plays in United States and Canada. Marcellus and Fayetteville shale plays, which are investigated in this study, are highlighted in green. The locations of the spill site and one wastewater treatment plant (Josephine Brine Treatment Facility) that discharges treated wastewater effluent to surface water are marked on the map. The distribution of the shale plays was taken from Review of Emerging Resources: U.S. Shale Gas and Shale Oil Plays, U.S. Energy Information Administration, July 2011 (http://www.eia.gov/pub/oil_gas/natural_gas/analysis_publications/maps/maps.htm). Background on the map was from Carnegie Museum of Natural History Pennsylvania Unconventional Natural Gas Wells Geodatabase. In Pittsburgh, PA: Carnegie Museum of Natural History: 2000–2013.

distinct signature for HFFF has important implications for forensic evaluations of releases because of the limited use of artificial tracers that could definitively identify fluids from HVHF. Additionally, the continued use of proprietary chemicals has led to public concerns with the HVHF process. These concerns could be partially mitigated if novel techniques existed to definitively distinguish HFFF in the environment.

Therefore, in this study we focus on the variations of inorganic chemicals in HFFF that can be affected by the hydraulic fracturing process. We hypothesize that the injection of fresh water into shale formations would cause the release of elements such as boron and lithium from exchange sites on the surface of clay minerals. The enrichment of boron and lithium in fluids could be used to differentiate HFFF from conventional produced water. In order to test this hypothesis, our study has three objectives: (1) characterize the chemical and isotopic (boron, lithium) compositions of solutes in produced water and HFFF, (2) identify the unique geochemical fingerprints of HFFF that could be used as environmental tracers, and (3) apply the geochemical tracers at field sites to validate the utility of this new method. While Marcellus HFFF is characterized by major element chemistry that is very similar to Appalachian Basin PW from conventional oil and gas wells, this study shows

that HFFFs have distinct Li and B elemental and isotopic signatures. Our new geochemical tracers, including elemental boron- and lithium- to chloride ratios and isotope ratios ($\delta^{11}\text{B}$ and $\delta^7\text{Li}$), are used to identify for the first time accidental releases of HFFF associated with HVHF. These signatures are consistent in HFFF across several shale plays in the U.S. and, combined with mixing models, may be applied universally to distinguish HFFF from conventional produced water in the Appalachian Basin as well as other areas of shale gas development.

■ MATERIALS AND METHODS

Six types of water samples from 14 oil and gas formations were used in this analysis: (1) 39 produced waters from conventional or unconventional formations (See Supporting Information (SI) Table 1); (2) a single sample of hydraulic fracturing fluid prior to injection (PAGB 4–0); this sample was composed, in part, by recycled flowback fluid; (3) 15 samples of hydraulic fracturing flowback fluids, collected from two separate Marcellus wells in the days (1–25) following HVHF and six separate Fayetteville wells;¹⁸ (4) shallow groundwater collected from a salt spring overlying the Marcellus Formation; (5) effluent of treated oil and gas wastewater that was discharged

into surface water between 2010 and 2012 at the Josephine Brine Treatment facility in western Pennsylvania; and (6) a surface water sample collected at an accidental spill site in West Virginia where, on January 2, 2014 on a well pad located in Tyler County West Virginia, a tank holding an unknown fluid burst and released its contents. The fluid migrated beyond the well pad containment and onto the ground surface. A sample of this accidental spill was collected January 3, 2014 from a pool of water adjacent to the well pad, presumed to be from the tank.

Major element chemistry for many of the samples was reported previously.^{9,18–20} Brine samples were analyzed for major and minor elements coupled with $\delta^{11}\text{B}$, and $\delta^7\text{Li}$ ratios (SI Table 1). Major cations, anions, trace metals, and boron isotopes were analyzed at Duke University. Major anions were determined by ion chromatography, major cations by direct current plasma optical emission spectrometry (DCP-OES), and trace-metals by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometer (ICP-MS). Boron isotopes were analyzed by thermal ionization mass spectrometer (TIMS) on a ThermoFisher Triton at the TIMS lab in Duke University. $^{11}\text{B}/^{10}\text{B}$ ratios were collected in negative mode with a signal between 50 and 900 mV at an ionization temperature between 870 and 920 °C. The average $^{11}\text{B}/^{10}\text{B}$ of NIST SRM-951 during this study was 4.0055 ± 0.0015 . The long-term standard deviation of $\delta^{11}\text{B}$ in the standard through replicate measurements was $<0.5\%$. Standard deviations for $\delta^{11}\text{B}$ in replicate analysis of brine produced water and HFFF samples were $<1\%$.

Lithium isotopes were measured using the Neptune MC-ICP-MS in the Laboratory Division of BRGM (Bureau de Recherches Géologiques et Minières). $^7\text{Li}/^6\text{Li}$ ratios were normalized to the L-SVEC standard solution (NIST SRM 8545) following the standard-sample bracketing method. Typical in-run precision on the determination of $\delta^7\text{Li}$ is about 0.1–0.2‰ ($2\sigma_m$). Chemical separation of lithium from the matrix was achieved before the mass analysis following a procedure using cationic resin (BioRad AG 50W-X12, 200–400 mesh), and HCl acid media (0.2N) for 30 ng of lithium.

RESULTS AND DISCUSSION

Origin of Formation Waters in the Appalachian Basin.

In the Appalachian Basin, coproduced brines from conventional oil and gas wells are likely the remnants of Silurian-age seawater that evaporated beyond the level of halite precipitation and then underwent significant secondary water-rock interactions that further modified the major element chemistry.⁶ Distinctive high Br/Cl ratios ($>5 \times 10^{-3}$ [low Cl/Br mass ratio ~ 90]) (SI Table S1) suggest a ~ 25 -fold evaporation of the Silurian-age seawater, beyond the halite saturation stage; this halite saturation stage is likely associated with thick beds of evaporites (Upper Silurian-age Salina Formation) reported throughout the northwestern portion of the Appalachian Basin. Additional evidence for evaporation is provided by the relatively high $\delta^{18}\text{O}$ and $\delta^2\text{H}$.^{19,21}

The evaporated seawater was further modified, likely through dolomitization and clay mineral weathering that resulted in elevated Ca/Cl ratios (enrichment factor of 35–55) and low Mg/Cl (depletion factor of 18–25) relative to 25-fold evaporated seawater (Figure 2). The Ca-chloride and elevated Br/Cl composition of the hypersaline formation water is consistent across formations from different geological units, including the Middle Devonian Marcellus Shale (SI Table S1). The relative depletion of boron and potassium compared to the projected evaporated seawater implies additional modification,

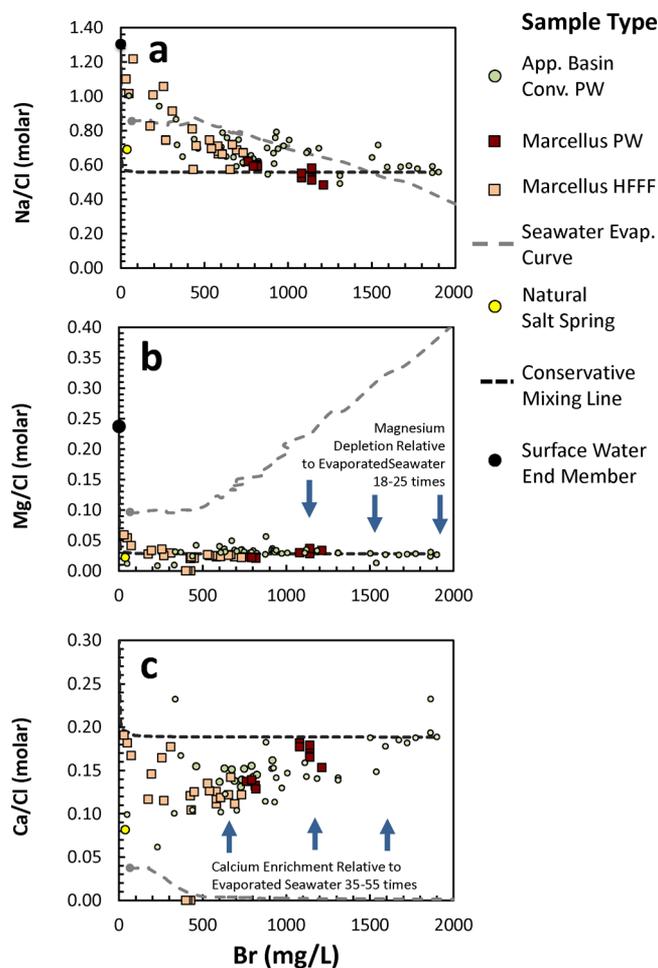


Figure 2. Major element ratios (a) Na/Cl, (b) Mg/Cl, and (c) Ca/Cl ratios for conventional Appalachian Basin produced water (PW) brines, HFFF and PW (here >90 days after commencement of flowback) from unconventional Marcellus shale wells, and a natural saline spring from Pennsylvania plotted versus their respective Br concentrations. Also plotted are the seawater evaporation curve and a conservative mixing line between the high-Br end member and median background surface water (black circles) (SI Table S2). Note the overlap in geochemical values for Marcellus PW and conventional Appalachian basin PW, indicating a common origin for the fluids (i.e., a highly evaporated seawater). HFFF values indicate dilution of the PW (brine) with fresh water that results in lower Br concentrations, but higher ratios to Na/Cl, Ca/Cl, and Mg/Cl relative to a natural salt spring, which represents a natural dilution of Appalachian Basin brine with groundwater.

probably through clay diagenesis (i.e., illitization).²⁰ The overall variations in salinity (SI Table S1) and stable isotopes^{19,21} in the brines within the Appalachian Basin suggest variable dilution with fresh water across diverse formations and locations. While the mechanism of dilution is not completely understood, the $\delta^2\text{H}$ of the brines ($\delta^2\text{H} \sim -40$) is consistent with seawater evaporated under slightly humid conditions, followed by dilution with local fresh and shallow groundwater.²¹

The B/Cl ratio (1.1×10^{-5} to 1.7×10^{-4}) and $\delta^{11}\text{B}$ (36–51‰) of formation water from conventional oil and gas wells in the Appalachian Basin (Figure 3a) are different from what one would expect from 25-fold evaporated seawater (2.7×10^{-3} , 42–43‰, respectively;²² based on a Br/Cl molar ratio of 4×10^{-3} (Cl/Br mass ratio 90)). This difference suggests

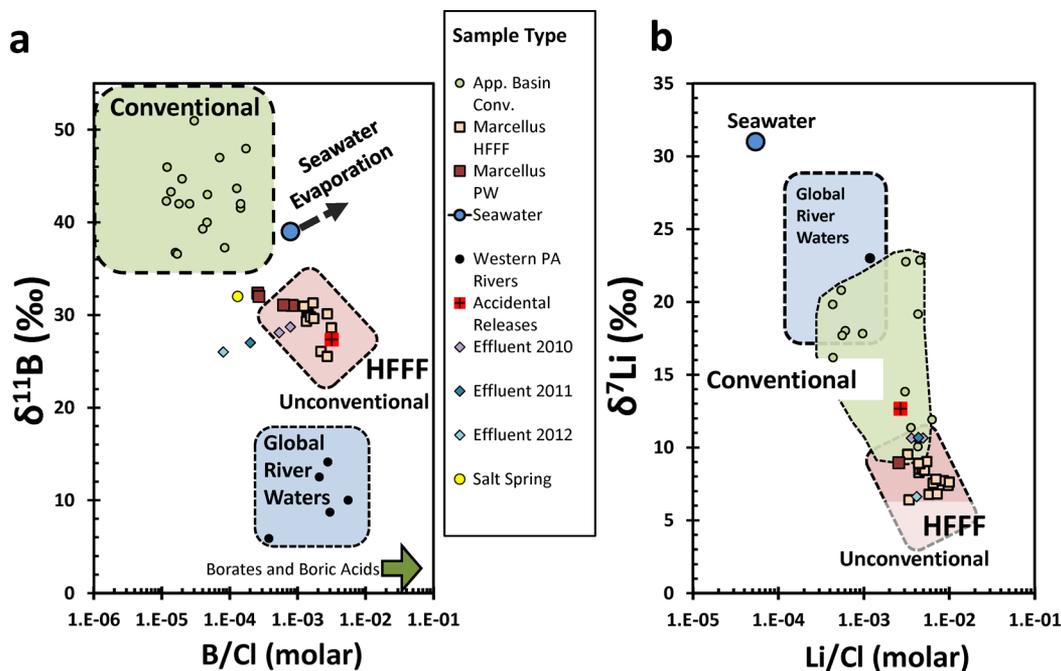


Figure 3. (a) $\delta^{11}\text{B}$ versus molar B/Cl ratios; and (b) $\delta^7\text{Li}$ versus molar Li/Cl ratios in conventional and unconventional produced waters, HFFF, fluids from an accidental release in WV, effluent from the Josephine Brine treatment facility in western PA (2010–2012), evaporated seawater, western PA surface water, and global river water.^{38,39} Conventional produced waters from the Appalachian Basin formations display higher $\delta^{11}\text{B}$ and $\delta^7\text{Li}$ with lower B/Cl and Li/Cl compared to both produced water and HFFF from the Marcellus unconventional shale formation. Importantly, HFFF values of $\delta^{11}\text{B}$ (24–31‰) do not overlap with known anthropogenic sources of boron such as borate salts with lower $\delta^{11}\text{B}$ (0–5‰) that might have been added during hydraulic fracturing. Instead, the HFFF composition appears to reflect mobilization of desorbable boron and lithium sourced from exchange sites on clays within the shale, which helps to distinguish HFFF from conventional PW and surface water.

additional modification of the original brine through preferential adsorption of ^{10}B onto clays.^{23,24} Higher Li/Cl ratios (4.3×10^{-4} to 6.2×10^{-3}) observed in the Appalachian brines could be consistent with evaporated seawater, but the lower $\delta^7\text{Li}$ (10–23‰) in brines relative to evaporated seawater could indicate preferential mobilization of ^6Li from clay minerals, which resulted in lower $\delta^7\text{Li}$ and higher Li/Cl ratios relative to evaporated seawater.²⁵

Distinguishing HFFF from Conventional Oil and Gas Produced Waters. The similarity in major element composition between brine produced from the Marcellus Formation (>90 days following HVHF) and brines produced from conventional oil and gas wells throughout the Northern Appalachian Basin (See Figures 2a–c and SI Table S1), suggests a common origin.⁶ In contrast, the salinity of Marcellus HFFF (Days 0–90 following HVHF) is typically lower than the conventional Northern Appalachian Basin PW. For example, a Wilcoxon–Mann–Whitney (Wilcoxon rank sum) test of element concentrations (Cl, Br, Ca, Mg, Na, Li, and B) showed a significant difference ($p < 0.0001$) between Marcellus HFFF and conventional PW from the Appalachian Basin. Note that Ba and Sr concentrations were not statistically different between conventional PW in the Northern Appalachian Basin and Marcellus HFFF.

Lower solute concentrations in HFFF reflect the dilution of the hypersaline formation water with the injected fresh water during HVHF. While the dilution does not affect the major element chemistry (e.g., Br/Cl ratio), we observed differences in B/Cl and Li/Cl ratios and B and Li isotopic ratios in HFFF relative to the compositions of the Appalachian PW. The HFFF is characterized by higher B/Cl ($p < 0.001$), and Li/Cl ($p < 0.001$) and low $\delta^{11}\text{B}$ and $\delta^7\text{Li}$ relative to the conventional

Appalachian PW and projected evaporated seawater curves (Figures 3a, b). Importantly, conservative mixing between injected surface water and Marcellus PW can account for the majority of observed inorganic chemistry in HFFF (i.e., concentrations of Br, Cl, Ca, Mg), but cannot account for the observed temporal B/Cl, Li/Cl, $\delta^{11}\text{B}$, and $\delta^7\text{Li}$ variations in HFFF (Figure 4a–d). These data indicate injected fluid mixes with formation brines (e.g., Cl in Figure 4e) but also desorbs boron and lithium from clays during interactions between injected freshwater and the shale mineral matrix. The desorption of Li and B contribute to the unique geochemistry of the HFFF relative to PW from conventional oil and gas wells (Figures 3a, 3b, and 5).²¹

In addition to distinguishing HFFF from conventional brines, boron and $\delta^{11}\text{B}$ can help elucidate the origin of the formation water trapped in the shale formations, thermal maturity of the formations, and water–rock interactions. Here we evaluate boron in the Appalachian Basin: assuming that the presumably Silurian-age seawater had a modern seawater $\delta^{11}\text{B}$ (39‰)²⁶ and that during 25-fold seawater evaporation (based on the Br/Cl ratio of 4×10^{-3} [Cl/Br mass ratio ~ 90]), B/Cl, and $\delta^{11}\text{B}$ would increase from seawater values to 2.7×10^{-3} , and 42–43‰, respectively.²² Instead, PW from conventional oil and gas wells in the Appalachian Basin are characterized by B/Cl (1.1×10^{-5} to 1.7×10^{-4}) and $\delta^{11}\text{B}$ (36–51‰) (Figure 3a) that reflect additional modification through preferential adsorption of ^{10}B onto clays.^{23,24}

In contrast to conventional Appalachian PW, the unconventional Marcellus PW contains elevated B/Cl ratios ($2\text{--}3 \times 10^{-3}$) that are more similar to evaporated seawater but $\delta^{11}\text{B}$ (31–33‰) is lower than the projected evaporated seawater (>39‰; Figure 3a). An alternative mechanism to boron

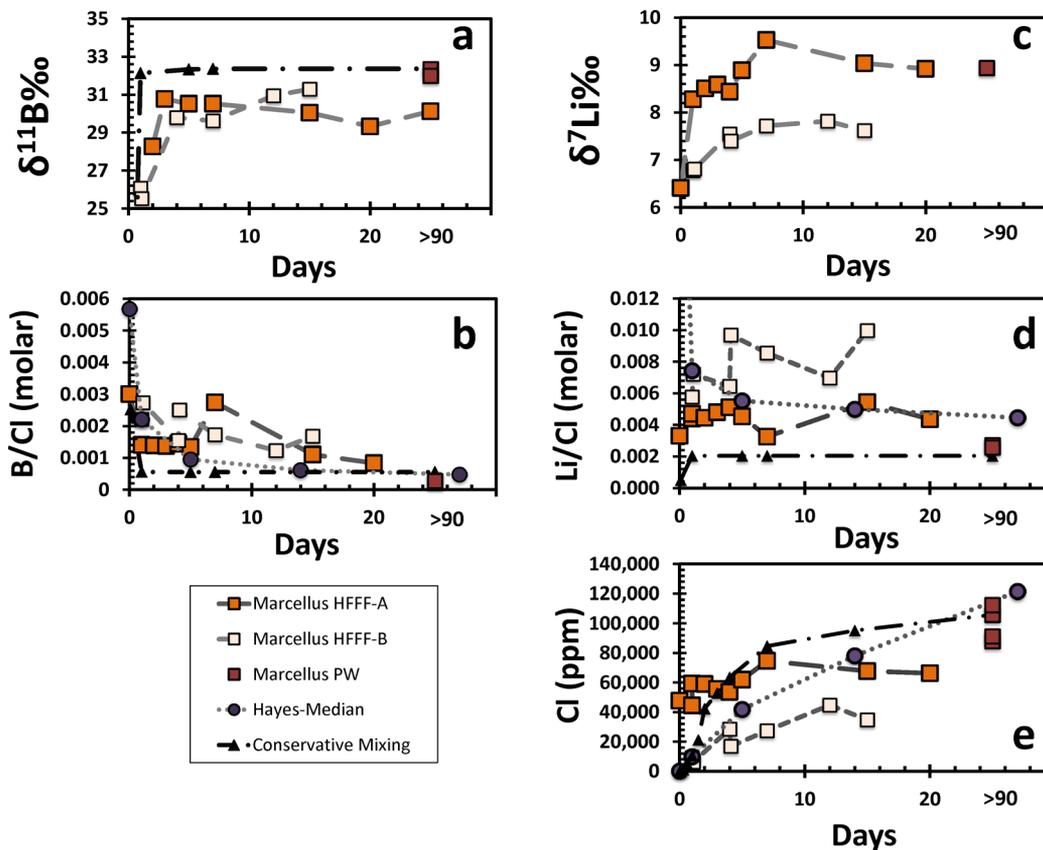


Figure 4. Variations of $\delta^{11}\text{B}$ (a), B/Cl (b), $\delta^7\text{Li}$ (c), Li/Cl (d), and Cl (e) in HFFF with time following hydraulic fracturing. The time series reflect HVHF end-members using recycled HFFF (Marcellus HFFF A), freshwater (Marcellus HFFF B), the median values for HFFF from 19 wells reported previously (Hayes-Median)³⁰ and Marcellus produced water (PW). A modeled conservative mixing line between a median Pennsylvania surface water (SI Table S2) and Marcellus PW are shown for comparison. B/Cl ratios in Marcellus HFFF decreased with time while both $\delta^{11}\text{B}$ and $\delta^7\text{Li}$ increase with time. Combined these data indicate injected fluid mixes with formation brines but also desorbed boron and lithium from clays, which contribute to the observed chemistry in HFFF and distinguish HFFF from conventional PW.

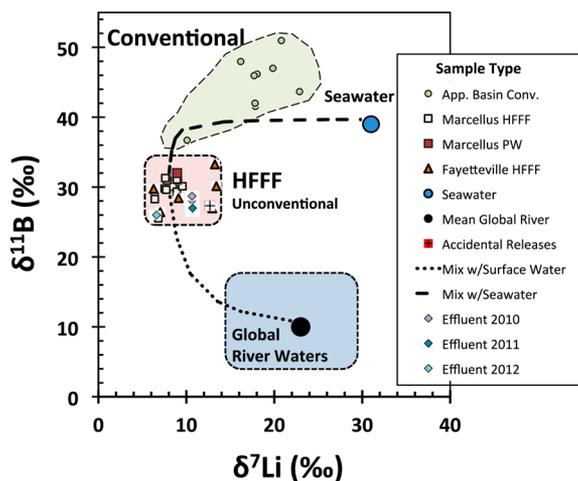


Figure 5. $\delta^{11}\text{B}$ versus $\delta^7\text{Li}$ in conventional produced waters, unconventional HFFF, seawater, discharged treated effluent, an accidental spill, and global river water. Conservative mixing-model calculations predict the isotopic variations upon release of HFFF and mixing with seawater and global river water.^{38,39} The use of the combined isotopic tracers provides a sensitive methodology to delineate and quantify contamination of freshwater with HFFF at low HFFF fractions of 0.1%. Importantly, these tracers are able to distinguish HFFF from conventional PW in the Appalachian Basin.

adsorption is necessary because adsorption is associated with selective ^{10}B removal²³ that would result in lower B/Cl and higher $\delta^{11}\text{B}$. Instead, the combination of relatively low B/Cl and $\delta^{11}\text{B}$ within the Marcellus could reflect boron incorporation into the crystal lattice during the transformation of smectite to Illite,²⁷ which decreases both the residual boron concentrations (and thus B/Cl) and $\delta^{11}\text{B}$ by 20–30%²⁸ relative to evaporated seawater. Compared to Marcellus PW, HFFF has relatively higher B/Cl (5×10^{-4} to 3×10^{-3}) and generally lower $\delta^{11}\text{B}$ (Figures 2a and 5). The lowest values of $\delta^{11}\text{B}$ ($\sim 27 \pm 1\%$) were observed in the earliest HFFF stage (Days 1–2) relative to 30–32‰ in the Marcellus PW (Days 4–365) (Figure 4b). These $\delta^{11}\text{B}$ values are typical for exchangeable boron on marine clay minerals.²³

By assuming the ratios of the inorganic constituents to chloride are preserved upon mixing of Marcellus brine with fresh water, we conducted a mass-balance calculation to evaluate the expected concentrations of all dissolved constituents, $\delta^{11}\text{B}$, and $\delta^7\text{Li}$. The Spearman correlations for Mg, Ca, Sr, and Br with chloride were highly significant ($p < 0.001$), suggesting a strong relationship and conservative mixing between the injected water and the saline formation water. In contrast, B/Cl and Li/Cl in HFFF were enriched relative to the expected conservative brine-freshwater mixing relationships, indicating mobilization of these ions following the injection of fluid during HVHF processes, regardless of the use of recycled HFFF waters (See HFFF-A, Figure 4) or freshwater (HFFF-B,

Figure 4). The $\delta^{11}\text{B}$ and $\delta^7\text{Li}$ in HFFF were slightly (2–4 ‰) lower than the expected conservative mixing values, further supporting the influence of B and Li desorption from solids within target formations. With time, HFFF show a gradual increase in salinity (Figure 4e) as well as changes in B/Cl, $\delta^{11}\text{B}$, Li/Cl, and $\delta^7\text{Li}$ toward the compositions of the Marcellus PW (Figures 4a–d).

Origin of Boron and Lithium in HFFFs. Boron and lithium in the Marcellus HFFFs could be derived from the following possible sources: (1) brine that was entrapped/associated with the Marcellus Formation; (2) exchangeable boron and lithium on clay surfaces; (3) boron associated with organic matter;²⁹ and (4) anthropogenic chemical additives to the fracturing fluid.¹ While borates are added during HVHF, lithium is not, and thus the co-occurrence of boron and lithium in HFFF limits the likelihood of the anthropogenic source. Additionally, unlike boron, lithium is not thought to be associated with organic material, but instead the result of weathering reactions in formation waters.²⁵

We further evaluate the chemical variations of HFFF resulting from fresh water/formational brine mixing coupled with water-rock interactions through mass-balance calculations on a time series of HFFF samples collected following HVHF of Marcellus wells. The time series reflect HVHF end-members using recycled HFFF (i.e., HFFF from a different Marcellus well; HFFF A), freshwater used for HVHF (Marcellus; HFFF B), and the median values for HFFF from 19 wells reported previously.³⁰ To calculate the relative proportions of formation water and the injected fresh water in the HFFF, we used the Cl^- content (105 800 mg/L in the Marcellus PW end-member, SI Table S1) and median background surface water, ($\text{Cl} = 26$ mg/L, $\text{B} = 20$ $\mu\text{g/L}$ and $\delta^{11}\text{B} = 9\text{‰}$ SI Table S2). The fraction of the original brine in the HFFF increases from 5 to 8% in the first day of return flow to 50% after 12 days (SI Table S1), which reflects the rapid mixing of the injected water (<21 days) with formational brine. It is important to note that variations in boron content vary across formations (SI Figure S1), implying that boron and lithium enrichment in HFFF is relative to conventional PW from the same basin and does not represent an exclusive range.

Lithium behaves similarly to boron with higher Li/Cl ratios (>0.001) and lower $\delta^7\text{Li}$ (5–10‰) in HFFF relative to both evaporated seawater ($\delta^7\text{Li} \sim 31\text{‰}$) and Appalachian PW from conventional oil and gas wells ($\delta^7\text{Li} = 10\text{--}25\text{‰}$) (Figures 3b and 5). Additionally, $\delta^7\text{Li}$ follows a similar trend to $\delta^{11}\text{B}$ with time following HVHF; with early stage (Days 0–1) HFFF having lower $\delta^7\text{Li}$ ($\sim 7\text{‰}$) relative to higher $\delta^7\text{Li}$ (9‰) in the later stage and Marcellus PW (Figure 4c). This trend likely indicates release of ^6Li from exchangeable sites on clays in the shale formation.³¹ Elevated lithium concentrations with depleted ^7Li in formation water from the Appalachian Basin are thought to reflect higher burial temperatures and release of lithium associated with clays.²⁵ Note that the Appalachian Basin PW samples reported here, which contain the highest Li/Cl ratios with the lowest $\delta^7\text{Li}$ (9–13‰) that overlap with the Marcellus HFFF range, were collected specifically from Lower Silurian formations that apparently experienced the greatest burial temperatures of any samples in this study. Consequently, the overlap of Li/Cl and $\delta^7\text{Li}$ in PW from Lower Silurian conventional oil and gas wells and Marcellus HFFF is similar to that observed in other studies from the Appalachian Basin²⁵ and infers limitation of the use of Li as a tracer. Nonetheless, Upper Devonian PW has lower Li/Cl ($2.5\text{--}6.8 \times 10^{-4}$) and

higher $\delta^7\text{Li}$ (17–20‰) that are distinctive from the HFFF composition.

We evaluated the potential of the new proposed geochemical tracers to universally identify HFFF in the environment using previously published B/Cl data from the Marcellus and other unconventional basins.^{18,29,30,32–34} The data show that B/Cl ratios in HFFF are higher throughout the Marcellus Basin³⁰ compared to the ratios in PW from conventional oil and gas reservoirs in the Appalachian Basin (Figure 6). In other

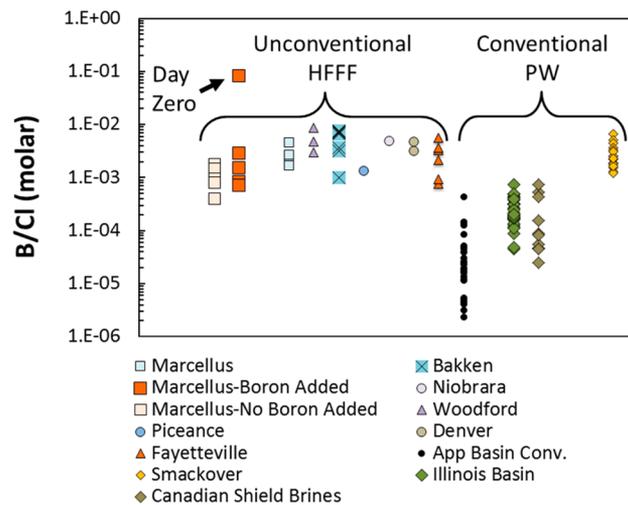


Figure 6. Compiled data of boron to chloride ratios reported for unconventional HFFF and conventional oil and gas produced waters from different basins in the U.S. Unconventional HFFF are characterized by higher B/Cl ratios relative to conventional produced water, with the notable exception of data from the Smackover Formation, which contains intervals of organic-rich, fine grained carbonate. Together the compiled data from several sources^{18,29,30,32–34} and the new data, reinforce the validity of the application of B/Cl ratios to trace HFFF in other shale plays and distinguish HFFF from conventional PW.

unconventional plays (e.g., Bakken, Woodford) (Figure 1) reported B/Cl ratios were also higher (Figure 6).^{32,35} Importantly, our data from HFFF from the Fayetteville Shale show similar B/Cl and Li/Cl ratios and corresponding $\delta^{11}\text{B}$ (26–33‰)¹⁸ and $\delta^7\text{Li}$ (5–10‰) ranges (Figure 5) overlap those observed in Marcellus HFFF. Source-rock formations targeted for HVHF typically contain marine shales that have been buried and heated to elevated pressures and temperatures (>100 °C) associated with the formation of hydrocarbons. The common burial history of the formations leads to consistent ranges of B/Cl, Li/Cl, $\delta^{11}\text{B}$, and $\delta^7\text{Li}$ in HFFF across multiple shale formations and can likely serve as a proxy for specifically identifying HFFF in the environment. The injection of fresh water into pore space and fractures saturated with saline formation water during HVHF is similar to the “freshening” process observed in several coastal saline aquifers. In this scenario, seaward flow of fresh water causes changes in the adsorption–desorption equilibrium of several ions in exchangeable sites on marine clay minerals, which releases Na, Li with low $\delta^7\text{Li}$ (0–5‰), and B with $\delta^{11}\text{B} \sim 15\text{‰}$.²³

Applications As Environmental Tracers. We tested the validity of the new tracers in two environmental settings; treated oil and gas wastewater effluent collected from the discharge outfall of a brine treatment facility in western Pennsylvania (Josephine Brine Treatment facility) and effluents

from a shale gas well spill site in Tyler County, West Virginia. The Josephine Brine Treatment facility has treated oil and gas wastewater for decades and recently (2007–2011) also treated HFFF.³⁶ Previous work has shown that in 2010 the majority of effluents discharged to a local stream (Blacklick, Indiana County) from the Josephine site were HFFF. The $^{87}\text{Sr}/^{86}\text{Sr}$ ^{17,37} and $^{228}\text{Ra}/^{226}\text{Ra}$ ratios in the effluents overlapped with the ratios of the Marcellus produced water and HFFF. Then, in 2011 and 2012, $^{228}\text{Ra}/^{226}\text{Ra}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in effluent increased, which suggested a reduction of the relative quantity of Marcellus HFFF.⁹ Similarly, the B/Cl and $\delta^{11}\text{B}$ tracers presented in this study reflect a change in the relative proportion of HFFF in the effluent discharged from the wastewater treatment facility over time (Figure 3a), while the interpretation of the Li/Cl and $\delta^7\text{Li}$ values is less clear (Figure 3b). These findings are consistent with state authority records of efforts to reduce the impact of HFFF disposal on waterways (SI Table S2).

Likewise, fluid collected from the spill site in West Virginia (Figure 1 and SI Table S3) had elevated salinity (Cl > 18 000 mg/L) and geochemical (Br/Cl, B/Cl, Li/Cl) and isotopic ($\delta^{11}\text{B}$, and $\delta^7\text{Li}$) composition that overlap the compositions of the HFFF (Figures 3a, b). Importantly, the geochemical (Br/Cl and B/Cl ratios) and isotopic ($\delta^{11}\text{B} \sim 26\text{‰}$) fingerprints of the spilled fluid were distinct from those in a local naturally occurring shallow saline groundwater spring (e.g., a salt spring at Salt Springs State Park), and conventional produced water in the Appalachian Basin¹⁷ (Figure 3a). While the B/Cl and $\delta^{11}\text{B}$ proxies suggest that the spill originated from an accidental release of HFFF, Li/Cl and $\delta^7\text{Li}$ data are not as conclusive, and could be interpreted as contamination from either conventional oil or gas PW or HFFFs (Figure 3b). Yet, the integration of these tracers provides a clearer and more powerful distinction for evaluating contamination sources associated with both conventional and unconventional oil and gas wastewater and the environmental risks of extensive shale gas development.

As hydraulic fracturing expands globally, surface water is expected to be a principal source for HVHF operations. Major river systems (e.g., Amazon, Mississippi, Seine, Colorado) have low Cl (6–40 ppm), B (6–200 ppb), Li, (1–50 ppb), $\delta^{11}\text{B}$ (3–14‰), and typically $\delta^7\text{Li}$ of $\sim 23\text{‰}$.^{38,39} We used these values to test the sensitivity of B/Cl and $\delta^{11}\text{B}$ as tracers using a mixing model of HFFF and average global river water³⁹ as well as seawater (Figure 5). Assuming Cl and B behave conservatively, a blend of 0.1% HFFF ($\delta^{11}\text{B} = 26\text{‰}$ and Cl = 105 800), mixed with 99.9% surface water (assuming $\delta^{11}\text{B} = 9\text{‰}$ and Cl = 26 ppm) would result in a 5‰ increase in $\delta^{11}\text{B}$ of the contaminated surface water. Importantly, the sensitivity of $\delta^{11}\text{B}$ is apparently not compromised by the reuse of HFFF (Figure 4 and SI Table S1), which currently is a common practice that aims to reduce the volume of HFFF that requires disposal/treatment. Given the low concentration of boron in fresh water relative to formation water, a typical mixture of 10% recycled HFFF and 90% fresh water would be geochemically similar to the HFFF that originated from using 100% fresh water as the injection fluid.

Limitations of the Proposed Method. One factor complicating this analysis is the possible addition of boric acid as a cross-linker that increases viscosity during the latter stages of HVHF.⁴ Elevated B/Cl ratios in some Marcellus fracturing fluid samples collected prior to injection³⁰ (Day 0; Figure 6) display anomalously high B/Cl ratios relative to other HFFF and produced water. Hypothetically, our observed boron

enrichment in HFFF could be derived from an anthropogenic addition of boric acid to fracturing fluid, but our data do not support this option for three reasons. First, the co-occurrence of B and Li suggests that the enrichment of these elements is derived from similar water-rock interactions instead of selective boron addition. Second, $\delta^{11}\text{B}$ values observed in HFFF (26–32‰) are significantly higher relative to commercial sources of boric acid (0–5‰)⁴⁰ and do not follow conservative mixing models. Third, despite the apparent addition of boric acid to fracturing fluids prior to injection in some wells (Day 0; Figure 6) but not others, the B/Cl ratios and the $\delta^{11}\text{B}$ values in HFFF (Days 1–90⁺) that resulted from HVHF were similar (Figure 4). Instead, the injection of fresh water into the formation likely releases exchangeable B and Li from adsorption sites on clay mineral surfaces. The $\delta^{11}\text{B}$ values observed in HFFF (26–32‰) reflect the original evaporated seawater with $\delta^{11}\text{B}$ (>39‰) and $\delta^7\text{Li}$ ($\sim 31\text{‰}$) modified by subsequent isotopic fractionation associated with boron (boric acid-borate fractionation; $\Delta\delta \sim 27\text{‰}$) and lithium ($\Delta\delta = 10\text{--}20\text{‰}$) adsorption on clays.

A second complicating factor to consider is the possible release of boron associated with organic matter²⁹ that is present within the formation. Both dissolved inorganic carbon (DIC)/Cl and dissolved organic carbon (DOC)/Cl ratios decrease with time following HVHF,⁴¹ the same trend as observed for B/Cl, Li/Cl, and Na/Cl ratios. Although Li follows the same trends as B, Li is not expected to be associated with organic matter; instead, the combined results most likely reflect desorption from exchange sites on clay minerals. However, the association of boron with organic matter and hydrocarbons in some formations²⁹ is still an area that requires additional analysis during HVHF.

In the Marcellus region, the application of B/Cl and $\delta^{11}\text{B}$ to trace contamination of shallow groundwater resources by HFFF might have limited applications because of the wide range of $\delta^{11}\text{B}$ observed in shallow groundwater (11.7–27.0‰), which overlaps with values for HFFF reported here.^{10,42} Likewise, the range of $\delta^{11}\text{B}$ observed in shallow groundwater in Arkansas (4.0–33.0‰) overlaps with values of HFFF from the underlying Fayetteville Shale ($\delta^{11}\text{B} = 26.4\text{--}33.2\text{‰}$).¹⁸ Nonetheless, the increase of salinity and boron content in contaminated groundwater, combined with changes in the water chemistry toward a Ca-chloride composition (e.g., high Br/Cl) would still reflect contamination by Marcellus HFFF despite minimal changes in $\delta^{11}\text{B}$.

We conclude that the unique geochemical and boron and lithium isotopic fingerprints of HFFF result from water-rock interactions within the shale formations during the HVHF process. The proposed tracers can be used to delineate the release of HFFF to the environment and to provide a clear distinction from legacy contamination associated with conventional oil and gas operations and/or naturally occurring salinization that are common in some areas of shale gas development. This combined assembly of elevated salinity, Ca-chloride composition with high Br/Cl ratios, high B/Cl, and Li/Cl ratios, and distinct $\delta^{11}\text{B}$ signature was identified in the accidental spill site in West Virginia and provides direct evidence for HFFF contamination of the environment.

■ ASSOCIATED CONTENT

📄 Supporting Information

The SI includes one figure and three tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Vidic, R. D.; Brantley, S. L.; Vandenbossche, J. M.; Yoxtheimer, D.; Abad, J. D., Impact of shale gas development on regional water quality. *Science* **2013**, *340*, (6134).
- (2) USEIA. *Review of Emerging Resources: U.S. Shale Gas and Shale Oil Plays*; U.S. Department of Energy, 2011.
- (3) Abualfaraj Noura, G. P. L.; Olson Mira, S. Characterization of Marcellus Shale flowback water. *Environ. Eng. Sci.* **2014**, *31* (9), 514–524.
- (4) Vengosh, A.; Jackson, R.; Warner, N. R.; Darrah, T.; Kondash, A. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* **2014**, *48* (15), 8334–8348.
- (5) Lutz, B. D.; Lewis, A. N.; Doyle, M. W. Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resour. Res.* **2013**, *49* (2), 647–656.
- (6) Haluszczak, L. O.; Rose, A. W.; Kump, L. R. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Appl. Geochem.* **2013**, *28*, 55–61.
- (7) Hladik, M. L.; Focazio, M. J.; Engle, M. Discharges of produced waters from oil and gas extraction via wastewater treatment plants are sources of disinfection by-products to receiving streams. *Sci. Total Environ.* **2014**, *466*, 1085–1093.
- (8) Wilson, J.; Vanbriesen, J. Source water changes and energy extraction activities in the Monongahela River, 2009–2012. *Environ. Sci. Technol.* **2013**, *47* (21), 12575–12582.
- (9) Warner, N. R.; Christie, C. A.; Jackson, R. B.; Vengosh, A. Impacts of shale gas wastewater disposal on water quality in western Pennsylvania. *Environ. Sci. Technol.* **2013**, *47* (20), 11849–11857.
- (10) Osborn, S. G.; Vengosh, A.; Warner, N. R.; Jackson, R. B. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 8172–8176.
- (11) Molofsky, L. J.; Connor, J. A.; Wylie, A. S.; Wagner, T.; Farhat, S. K. Evaluation of methane sources in groundwater in northeastern Pennsylvania. *Groundwater* **2013**, *51* (3), 333–349.
- (12) Jackson, R. B.; Vengosh, A.; Darrah, T. H.; Warner, N. R.; Down, A.; Poreda, R. J.; Osborn, S. G.; Zhao, K.; Karr, J. D. Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (28), 11250–11255.
- (13) Darrah, T. H.; Vengosh, A.; Jackson, R. B.; Warner, N. R.; Poreda, R. J. Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 14076–14081.
- (14) Kassotis, C. D.; Tillitt, D. E.; Davis, J. W.; Hormann, A. M.; Nagel, S. C. Estrogen and androgen receptor activities of hydraulic fracturing chemicals and surface and ground water in a drilling-dense region. *Endocrinology* **2013**, *155* (3), 897–907.
- (15) Kolesar Kohl, C. A.; Capo, R. C.; Stewart, B. W.; Wall, A. J.; Schroeder, K. T.; Hammack, R. W.; Guthrie, G. D. Strontium isotopes

test long-term zonal isolation of injected and Marcellus formation water after hydraulic fracturing. *Environ. Sci. Technol.* **2014**, *48* (16), 9867–9873.

(16) Johnson, J. D.; Graney, J. R.; Capo, R. C.; Stewart, B. W., Identification and quantification of regional brine and road salt sources in watersheds along the New York/Pennsylvania border, U.S.A. *Appl. Geochem.*

(17) Warner, N. R.; Jackson, R. B.; Darrah, T. H.; Osborn, S. G.; Down, A.; Zhao, K.; White, A.; Vengosh, A. Geochemical evidence for possible natural migration of Marcellus formation brine to shallow aquifers in Pennsylvania. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (30), 11961–11966.

(18) Warner, N. R.; Kresse, T. M.; Hays, P. D.; Down, A.; Karr, J. D.; Jackson, R. B.; Vengosh, A. Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville Shale development, north-central Arkansas. *Appl. Geochem.* **2013**, *35*, 207–220.

(19) Osborn, S. G.; McIntosh, J. C. Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl. Geochem.* **2010**, *25* (3), 456–471.

(20) Osborn, S. G.; McIntosh, J. C.; Hanor, J. S.; Biddulph, D. Iodine-129, 87Sr/86Sr, and trace elemental geochemistry of northern Appalachian Basin brines: Evidence for basinal-scale fluid migration and clay mineral diagenesis. *Am. J. Sci.* **2012**, *312* (3), 263–287.

(21) Dresel, P.; Rose, A. *Chemistry and Origin of Oil and Gas Well Brines in Western Pennsylvania: Pennsylvania Geological Survey*; Pennsylvania Department of Conservation and Natural Resources, 2010.

(22) Vengosh, A.; Starinsky, A.; Kolodny, Y.; Chivas, A. R.; Raab, M. Boron isotope variations during fractional evaporation of sea-water—New constraints on the marine vs nonmarine debate. *Geology* **1992**, *20* (9), 799–802.

(23) Spivack, A. J.; Palmer, M. R.; Edmond, J. M. The sedimentary cycle of the boron isotopes. *Geochim. Cosmochim. Acta* **1987**, *51* (7), 1939–1949.

(24) Vengosh, A.; Starinsky, A.; Kolodny, Y.; Chivas, A. R. Boron isotope geochemistry as a tracer for the evolution of brines and associated hot-springs from the Dead-Sea, Israel. *Geochim. Cosmochim. Acta* **1991**, *55* (6), 1689–1695.

(25) Macpherson, G. L.; Capo, R. C.; Stewart, B. W.; Phan, T. T.; Schroeder, K.; Hammack, R. W. Temperature-dependent Li isotope ratios in Appalachian Plateau and Gulf Coast Sedimentary Basin saline water. *Geofluids* **2014**, DOI: 10.1111/gfl.12084.

(26) Raitzsch, M.; Hönisch, B. Cenozoic boron isotope variations in benthic foraminifers. *Geology* **2013**, DOI: 10.1130/G34031.1 .

(27) Hosterman, J.; Whitlow, S. *Clay Mineralogy of Devonian Shales in the Appalachian Basin*; U.S. Geological Survey, 1983

(28) Williams, L. B.; Hervig, R. L.; Holloway, J. R.; Hutcheon, I. Boron isotope geochemistry during diagenesis. Part I. Experimental determination of fractionation during illitization of smectite. *Geochim. Cosmochim. Acta* **2001**, *65* (11), 1769–1782.

(29) Williams, L. B.; Hervig, R. L.; Wieser, M. E.; Hutcheon, I. The influence of organic matter on the boron isotope geochemistry of the gulf coast sedimentary basin, USA. *Chem. Geol.* **2001**, *174* (4), 445–461.

(30) Hayes, T. *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas*. http://catskillcitizens.org/learnmore/20100916IOGAResponsetoDECChesapeake_IOGAResponsetoDEC.pdf.

(31) Millot, R.; V, N.; Gaillardet, J. Behaviour of lithium and its isotopes during weathering in the Mackenzie Basin, Canada. *Geochim. Cosmochim. Acta* **2010**, *74*, 3897–3912.

(32) Pike, B., Current NETL Water Management R&D Efforts In *Drilling Engineering Association Quarterly Forum*, **2010**; Vol. 2014, <http://dea-global.org/wp-content/uploads/2012/01/DEA-Water-Presentation.pdf>.

(33) Bottomley, D. J.; Katz, A.; Chan, L. H.; Starinsky, A.; Douglas, M.; Clark, I. D.; Raven, K. G. The origin and evolution of Canadian Shield brines: Evaporation or freezing of seawater? New lithium

isotope and geochemical evidence from the Slave craton. *Chem. Geol.* **1999**, *155* (3–4), 295–320.

(34) Stueber, A. M.; Walter, L. M.; Huston, T. J.; Pushkar, P. Formation waters from Mississippian-Pennsylvanian reservoirs, Illinois basin, USA: Chemical and isotopic constraints on evolution and migration. *Geochim. Cosmochim. Acta* **1993**, *57* (4), 763–784.

(35) Son, J.-H.; Carlson, K. Real-time surrogate analysis for potential oil and gas contamination of drinking water resources. *Appl. Water Sci.* **2014**, *1*–7.

(36) Ferrar, K. J.; Michanowicz, D. R.; Christen, C. L.; Mulcahy, N.; Malone, S. L.; Sharma, R. K. Assessments of effluent contaminants from three wastewater treatment plants discharging Marcellus Shale wastewater to surface waters in Pennsylvania. *Environ. Sci. Technol.* **2013**, *47* (7), 3472–3481.

(37) Chapman, E. C.; Capo, R. C.; Stewart, B. W.; Kirby, C. S.; Hammack, R. W.; Schroeder, K. T.; Edenborn, H. M. Geochemical and strontium isotope characterization of produced waters from marcellus shale natural gas extraction. *Environ. Sci. Technol.* **2012**, *46* (6), 3545–3553.

(38) Huh, Y.; Chan, L.-H.; Zhang, L.; Edmond, J. M. Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget. *Geochim. Cosmochim. Acta* **1998**, *62* (12), 2039–2051.

(39) Lemarchand, D.; Gaillardet, J.; Lewin, É.; Allègre, C. J. Boron isotope systematics in large rivers: implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. *Chem. Geol.* **2002**, *190* (1–4), 123–140.

(40) Vengosh, A.; Heumann, K. G.; Juraske, S.; Kasher, R. Boron isotope application for tracing sources of contamination in groundwater. *Environ. Sci. Technol.* **1994**, *28* (11), 1968–1974.

(41) Cluff, M.; Hartsock, A.; MacRae, J.; Carter, K.; Mouser, P. J. Temporal changes in microbial ecology and geochemistry in produced water from hydraulically fractured Marcellus Shale gas wells. *Environ. Sci. Technol.* **2014**, *48* (11), 6508–6517.

(42) Senior, L. A reconnaissance spatial and temporal assessment of methane and inorganic constituents in groundwater in bedrock aquifers, Pike County, Pennsylvania. *Sci. Invest. Rep. (U. S. Geol. Surv.)* **2012–13**, 2014–5117.