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Short communication

Monitoring radionuclides in subsurface drinking water sources near unconventional drilling operations: a pilot study

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ABSTRACT

Unconventional drilling (the combination of hydraulic fracturing and horizontal drilling) to extract oil and natural gas is expanding rapidly around the world. The rate of expansion challenges scientists and regulators to assess the risks of the new technologies on drinking water resources. One concern is the potential for subsurface drinking water resource contamination by naturally occurring radioactive materials co-extracted during unconventional drilling activities. Given the rate of expansion, opportunities to test drinking water resources in the pre- and post-fracturing setting are rare. This pilot study investigated the levels of natural uranium, lead-210, and polonium-210 in private drinking wells within 2000 m of a large-volume hydraulic fracturing operation – before and approximately one-year following the fracturing activities. Observed radionuclide concentrations in well waters tested did not exceed maximum contaminant levels recommended by state and federal agencies. No statistically-significant differences in radionuclide concentrations were observed in well-water samples collected before and after the hydraulic fracturing activities. Expanded monitoring of private drinking wells before and after hydraulic fracturing activities is needed to develop understanding of the potential for drinking water resource contamination from unconventional drilling and gas extraction activities.

1. Introduction

The application of unconventional drilling (i.e., the combination of hydraulic fracturing and horizontal drilling) techniques to extract natural gas and oil is rapidly expanding throughout the world (Kerr, 2010; USEIA 2014). Although the current political and economic landscape is favorable for expanded natural gas exploration, many have voiced concerns for potential environmental and public health impacts (Howarth et al., 2011a, 2011b; Goldstein et al., 2012). One of the most important issues to be considered is the impact of unconventional drilling on local and regional water resources (Gregory et al., 2011; Vidic et al., 2013). Within this context, concern about potential contamination of drinking water resources by naturally occurring radioactive materials (NORM) liberated by unconventional drilling activities is on the rise (Brown, 2014).

Emerging reports indicate that unconventional drilling activities may contaminate ground water, as evidenced by increased levels of methane gas and other geologic signatures apparently originating from the natural gas-bearing formations (Osborn et al., 2011; Warner et al., 2012). Similarly, NORM have the potential to contaminate ground water by numerous mechanisms, including, but not limited to: flowback water spills on the surface, leakage of flowback from containment ponds, well casing failure, and introduction of new/larger fractures to the subsurface (USEPA 2012a). Through any of these processes, NORM contained either within the formation or in wastes removed from the formation (bit cuttings, brine, gas streams), have the potential to partition into groundwater. The potential for migration through the formation depends on the physical-geochemical (redox state, pH sensitivity, gas/solid)

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and radiochemical properties (half-life, decay products) (Nelson et al., in review).

Studying the impacts of unconventional drilling on NORM levels in private drinking is challenging for several reasons. In the United States (US), landowners are not required to monitor private drinking water wells for radionuclides (USEPA 2012b). Consequently, there are no large publically-accessible databases of NORM levels in private drinking wells in regions with drilling activities. Although the need to monitor private drinking water wells is recognized (DeSimone 2009), access to wells can be difficult and requires explicit permission from landowners. Another challenge is that scientific studies often lack critical temporal perspective (i.e. pre- and post- drilling), as drilling activities often outpace the ability for scientists to commence a well-controlled study. Thus, given that NORM is present in most groundwater, source-term attribution of NORM found in drinking water wells can be challenging. Taken together, these observations and the paucity of well-controlled studies complicates a scientific assessment of the relationship between unconventional drilling activities and NORM mobilization into ground water.

An opportunity for a small pilot study arose to investigate the potential for mobilization of NORM into groundwater due to unconventional drilling activities. Based on our experience with produced fluids from the Marcellus Shale region of the US, we focused our pilot study on levels of natural uranium (^{nat}U: ^{238}U, $t_{1/2} = 4.5 \times 10^9$ years; ^{235}U, $t_{1/2} = 7.0 \times 10^8$ years; ^{234}U, $t_{1/2} = 2.5 \times 10^5$ years), lead-210 (^{210}Pb, $t_{1/2} = 22.2$ years), and polonium-210 (^{210}Po, $t_{1/2} = 138$ days) in private drinking wells (with permission) in the north San Juan Basin of southwestern Colorado, USA (Nelson et al., in review). This area was chosen because we were able to obtain a sample of water that was collected weeks before a hydraulic fracture that occurred in January, 2012. Additionally, the San Juan Basin is a unique location to study the connection between drilling and NORM, as the region is renowned for fossil fuel resources and natural uranium (^{nat}U) deposits (Finch et al., 1989). In 2000 over 80% of the US coalbed methane was extracted from the San Juan Basin, mostly from the Fruitland formation (late Cretaceous) (Ayers, 2002). Most (90%) of this gas is extracted from an area termed the "Fairway," which is hydrostatically over-pressured (US EPA, 2004). In addition to large volumes of natural gas, wells in this area produce large volumes of water with 1000–4000 mg/L total dissolved solids (TDS) (US EPA 2004). Like many oil and gas rich regions in the world, the San Juan Basin is experiencing a boom in unconventional drilling, as operators seek to extract oil and natural gas from deeper shale formations (Sakelaris, 2014). Many landowners are concerned that these expanded unconventional drilling operations may introduce contaminants into drinking water resources. Thus, the goal of this pilot project was to determine if levels of ^{nat}U, ^{210}Pb, and/or ^{210}Po significantly changed in the year following a hydraulic fracture in a relatively small sub-geographical area within an area of intensive unconventional drilling activity.

2. Materials and methods

2.1. General

All reagents were ACS reagent grade or higher. NIST-traceable certified reference materials (CRM's, Eckert Ziegler Radioisotopes, Atlanta, GA USA) were used to prepare ^{232}U tracer (92403) and ^{209}Po tracer (92565), as previously described (Knight et al., 2014). All half-lives and alpha-emission energies, with the exception of ^{209}Po, were extracted from the United States National Nuclear Data Center (NNDC Brookhaven National Laboratory, US Department of Energy). Emission energy of ^{209}Po was extracted from NNDC; however, we chose to use a half-live of 128.3 years for ^{209}Po based on reports from the literature (Collé et al., 2007). All uncertainties are "standard uncertainties" with a coverage factor $k = 1$, unless stated otherwise (Currie, 1968). For all laboratory experiments, the analyst was blinded from the source of samples. Unless otherwise explicitly stated, all reported radioactivity concentrations were decay corrected to 2 January, 2013, 8:00 AM CST using standard differential equations (Bateman, 1910).

2.2. Sampling description

Duplicate groundwater samples from three private residences in the "Fairway" of the San Juan Basin in southwestern Colorado, USA; one surface water sample; and one municipal water sample were collected on 2 January, 2013 – based on standard collection methods (US Geologic Survey 2006). For all water samples, 1 L was collected and acidified (pH 2 using concentrated HNO_3), at least one week prior to analysis. An additional groundwater sample from residence A was collected by the owner on 22 January, 2012. Private drinking water wells ranged from approximately 40-100 m in depth according to information obtained from Colorado Division of Water Resources (http://www.dwr.state.co.us/WellPermitSearch/). Wells were approximately 2000 m from an unconventional well that was hydraulically fractured in January 2012 with ~750,000 L of hydraulic fracturing fluid at a depth of ~2400 m, according to information from FracFocus Chemical Disclosure Registry (http://fracfocus.org/). Additionally, within a 3 km radius of the homes, there are approximately 131 natural gas wells (12 of which were horizontally drilled) and 28 natural-gas/produced-water storage pits according to publically available information from the Colorado Oil and Gas Conservation Commission (COGCC, http://cogcc.state.co.us/Home/gismain.cfm). Municipal water (purified from surface water) was collected from a city recreation center. Surface water was collected downstream of the site of a former U smelter. Note that surface and municipal water samples were collected upstream of any drilling activity in the region.

2.3. Determination radionuclide activities

250 to 500 mL aliquots of acidified samples were analyzed for activities of ^{nat}U, ^{226}Ra, ^{210}Po, and ^{210}Pb using established methods (Knight et al., 2014; Eichrom 2009, Nelson et al., 2014). Briefly, ^{238}U, ^{235}U, and ^{234}U were determined by preconcentration with $FeOH_3$, separation on TRU resin (Eichrom Technologies, USA) and TEVA resin (Eichrom), and prepared by CeF_3 microprecipitation, as previously described (Knight et al., 2014). 250 mL glass vials were hermetically sealed and stored for 30 days prior to quantitation of ^{226}Ra by ^{222}Rn emanation using a RAD7 as recommended by the manufacturer (Durridge Company, Inc., USA). ^{210}Po activities were determined by preconcentration with $FeOH_3$, separation on Eichrom SR-Resin, and autodeposition on Ag disks (Eichrom, 2009). ^{210}Pb was determined by holding samples for 467 days and measuring ^{210}Po as previously described (Vesterbacka and Ikäheimonen, 2005). Approximately 3.5 half-lives of ^{210}Po had elapsed, suggesting that if modeled by secular equilibrium, the ^{210}Po had grown in to ~90% of the supporting ^{210}Pb activity. Alpha spectra of U and Po isotopes were collected on vacuum-controlled alpha spectrometers (Alpha Analyst, Canberra Industries, USA) employing passivated ion-implanted silicon detectors (PIPS, Canberra) with a source to detector distance of approximately 10 mm as described by us previously (Knight et al., 2014). Contamination of detectors was prevented by use of thin-films (Inn et al., 2008). Activities were determined using standard isotope dilution techniques (Makarova et al., 1983).