

gas wells drilled in that time period (Brantley et al. 2014). Management practices appear to be improving as well; the rate of problems has decreased since 2010 (Figure 1).

Apparently, however, the public responds not only to the number of problems per gas well or per unit of gas produced but rather to the number of problems per unit time and per unit area. Thus, even though the rate of problems with shale gas wells has remained small on a per well basis, pushback has grown in areas of increasing density of drilling and fracking. This may be especially true when consequences are fearsome such as flaming tapwater, toxic contamination, or earthquakes.

It is natural that the social license for shale gas development is influenced by short-term, local thinking. But, such thinking may not be helpful given that Marcellus Shale gas wells generate one third the waste per unit volume of gas as compared to conventional shallow gas wells (Vidic et al. 2013). In addition, the release of pollutants such as carbon dioxide, particulates, mercury, nitrogen, and sulfur generated per unit of heat energy is lower for unconventional shale gas than for fuels such as coal (Heath et al. 2014).

Public pushback could nonetheless be a blessing. After all, pushback represents intensified interest in environmental issues. This interest may be seen in the PA DEP data for the rate of well integrity issues in conventional oil and gas wells—the increase in problem rate from 2008 to 2012 (Figure 1) is more likely due to heightened public attention and inspector scrutiny rather than a sudden deterioration in the management practices of the drilling companies (Brantley et al. 2014).

During the next decades, the rate of hydraulic fracturing in PA will eventually slow. At some point, the use of produced brines to hydrofracture new wells will cease. Once recycling of brine to frack new wells stops, hundreds of gallons of brine will accumulate as waste at each well per day (Rahm et al. 2013). Disposal of this slightly radioactive brine will then become increasingly problematic. Interest on the part of the public for such issues is warranted. Public engagement today is needed to develop sustainable waste management and sustainable energy practices for the future.

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Noble Gases: A New Technique for Fugitive Gas Investigation in Groundwater

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Introduction

Few issues have captured the attention of the public, political, media, and scientific communities more than the prospect of groundwater contamination of drinking-water wells in areas of unconventional energy development. Along with a substantial increase in domestic energy production from unconventional reservoirs in the last decade (Kerr 2010), the environmental implications of energy production, including elevated hydrocarbon gas levels in drinking-water wells, remain highly controversial (e.g., Osborn et al. 2011; Warner et al. 2012; Jackson et al. 2013; Molofsky et al. 2013; Brantley et al. 2014; Vengosh et al. 2014; Warner et al. 2014). Several studies suggest that shale gas drilling leads to fugitive gas contamination in a subset of drinking-water wells near drill sites (Osborn et al. 2011; Jackson et al. 2013; Darrah et al. 2014), while others suggest that methane is natural and unrelated to shale gas development (Kornacki and McCaffrey 2011; Molofsky et al. 2013; Baldassare et al. 2014).

Much of this debate results from a lack of pre-drill data, complex hydrogeological histories for natural migration of hydrocarbons, and a lack of geochemical tracers that can constrain simultaneously the source, timing, and mechanism of hydrocarbon migration into shallow aquifers. The need for pre-drill data in basins targeted for shale gas development is clear. However, the latter two factors which are more challenging and subject to different viewpoints by researchers and other stakeholders (Schwartz 2013), are critical for distinguishing between natural and anthropogenic sources of hydrocarbons in shallow aquifers and determining the source and mechanisms of anthropogenic gas contamination. Here, we highlight the use of noble gases as a new set of tracers for identifying the cause of hydrocarbon contamination in groundwater. We examine case studies from the Marcellus and Barnett shales to demonstrate the utility of gas geochemistry for characterizing hydrocarbon sources in shallow aquifers (Darrah et al. 2014).

Noble Gases as a Geochemical Tracer for Fugitive Gas Investigations

Traditionally, fugitive gas investigations have used the molecular ($\text{CH}_4/\text{C}_2\text{H}_6^+$) and stable isotopic (e.g.,

$\delta^{13}\text{C}-\text{CH}_4$ and $\delta^2\text{H}-\text{CH}_4$) compositions of hydrocarbons to determine the source of gas in shallow aquifers (Rowe and Muehlenbachs 1999; Kornacki and McCaffrey 2011; Osborn et al. 2011; Tilley and Muehlenbachs 2012; Jackson et al. 2013; Molofsky et al. 2013; Baldassare et al. 2014). These tracers are routinely used to resolve thermogenic and biogenic hydrocarbon contributions (Schoell 1980, 1983; Whiticar et al. 1986; Martini et al. 1998) and to differentiate between hydrocarbon sources of differing thermal maturity (Jenden et al. 1993; Burruss and Laughrey 2010; Tilley and Muehlenbachs 2013). Data from two study areas (Marcellus and Barnett) reveal that the majority of groundwaters contain naturally occurring hydrocarbons with thermogenic contributions (Osborn et al. 2011; Jackson et al. 2013; Molofsky et al. 2013; Baldassare et al. 2014; Darrah et al. 2014).

The occurrence of thermogenic gas in shallow aquifers in the two study areas is consistent with water chemistry data that suggest paired migration and dilution of oil-field brines and hydrocarbons in these basins (Warner et al. 2012; Darrah et al. 2014). At a first glance, the coherent behavior of dense salts and buoyant gases might seem surprising based on a rudimentary consideration of fluid flow dynamics. However, petroleum geologists have known for more than a century that the distribution and migration of hydrocarbons and “oil-field brines” in the Earth’s crust, specifically in aquifers, result from the complex interplay between the tectonic and hydrologic cycles (e.g., Bethke and Marshak 1990; Cathles 1990).

Since before the birth of anticlinal theory in the 1880s, researchers have known that the geological migration of hydrocarbons is paired with oil-field brines in two sequential processes: 1) primary migration of hydrocarbons out of source rocks (e.g., black shales) and 2) secondary migration where groundwater flow and buoyancy forces emplace hydrocarbons in stratigraphic or tectonically induced structural traps (Oliver 1986; Allen and Allen 1990; Cathles 1990; Selley 1998; Lollar and Ballentine 2009). This knowledge has allowed people to successfully exploit hydrocarbon traps for generations.

The story of hydrocarbon migration does not end there. Tertiary migration (Selley 1998) over geological time allows hydrocarbons to escape from stratigraphic and structural traps, which allows the hydrologic cycle to redistribute thermogenic hydrocarbons in the crust, specifically within shallow aquifers. The remnants of these three successive processes generate a suite of distinctive geochemical tracers that help distinguish hydrocarbons that migrated naturally from those that migrated as anthropogenic fugitive gases associated with shale gas development.

The crucial first step in any fugitive gas investigation should involve characterizing the source and natural history of hydrocarbon (and brine) migration in a basin. By understanding these processes, scientists can develop a geochemical framework on which to distinguish natural processes from fugitive gas contamination.

Noble gases provide a new and informative set of stable tracers to complement hydrocarbon geochemistry because: (1) they are non-reactive (e.g., unaffected by microbial activity); (2) have distinct compositions in the crust, hydrosphere, atmosphere, and mantle; and (3) they are useful for discerning the scale, conditions, and physical mechanism (e.g., one- or two-phase advection, diffusion, gas-phase migration) (Ballentine et al. 1991; Onions and Ballentine 1993; Ballentine et al. 2002; Lollar and Ballentine 2009; Darrah et al. 2014) of hydrocarbon migration in the Earth's crust. Noble gases adeptly quantify hydrocarbon migration because each of the inert tracers (He, Ne, Ar, Kr, Xe) has a unique solubility and diffusion constants that are fractionated during fluid migration.

The noble gas composition of most aquifers is a binary mixture of: (1) air-saturated water, containing ^{20}Ne , ^{36}Ar , ^{84}Kr (and N_2) derived from solubility equilibrium with the atmosphere during groundwater recharge and (2) radiogenic production of noble gases such as ^4He , ^{21}Ne , and $^{40}\text{Ar}^*$ (sourced from U, Th, and ^{40}K decay) within minerals in the Earth's crust (Ballentine et al. 2002).

When we combined noble gas and hydrocarbon techniques in our case studies, we found that samples located >1 km from drilling, including natural methane seeps (Salt Spring in Montrose, PA), consistently revealed a positive relationship between hydrocarbon gases (e.g., methane, ethane), brine-like salts (e.g., chlorine, bromine, strontium, barium), and elevated, low-solubility noble gases (i.e., ^4He and ^{20}Ne). These samples had normal levels of atmospheric gases (Darrah et al. 2014).

Extreme enrichments of He and Ne suggest that primary and secondary migration occurred naturally over geological time, followed by tertiary migration. When natural gas slowly migrates buoyantly through the water-saturated crust (low ratios of gas to water), He and Ne are strongly enriched in the migrating gas-phase because of their low solubility in water (Ballentine et al. 2002). Importantly, all groundwater samples with thermogenic methane located >1 km from drilling in both study areas show clear and strong enrichments in He and Ne following a complex history of migration from source rocks to modern aquifers (Darrah et al. 2014).

In contrast, groundwater <1 km from drill sites in both study areas show clear evidence of two populations: (a) a subset with enrichments of He and Ne that is statistically indistinguishable from those collected >1 km from drill sites, and (b) wells with super-saturated levels of thermogenic methane and no relationship to the crustal tracers (i.e., $[\text{Cl}^-]$, $[\text{Br}^-]$, and $[\text{He}]$), including low concentrations Ne, Ar, and other atmospheric gases (e.g., N_2 , Kr) (Darrah et al. 2014).

The atmospheric gases (^{20}Ne , ^{36}Ar , and N_2) are important potential tracers for fugitive gas contamination because they have a consistent source globally and are sensitive tracers to water-gas interactions (Ballentine et al. 2002; Gilfillan et al. 2009). When large volumes of crustal gases migrate through water, the normal levels of atmospheric gases decrease as they partition into the

bubble phase and migrate buoyantly (Aeschbach-Hertig et al. 2008; Gilfillan et al. 2009; Darrah et al. 2013), termed "stripping."

In shallow groundwater, natural "stripping" has been observed only in volcanic and geothermal systems and above rice paddies, while biogenic methane from landfills also induces this phenomenon (Solomon et al. 1992; Dowling et al. 2002; Gilfillan et al. 2009; Darrah et al. 2013). Importantly, even the naturally discharging gas-rich Salt Spring in Montrose, Pennsylvania, retains normal atmospheric gas compositions, suggesting equilibration between shallow meteoric water and a small volume of natural gas and brine following past geological migration (Darrah et al. 2014).

Resolving the mechanism of gas transport to shallow aquifers can help distinguish between natural and anthropogenic sources of hydrocarbons (Figure 1). Because each noble gas (He, Ne, Ar, Kr, Xe) has a unique solubility and diffusion constant, their isotopes fractionate to different extents during their co-transport with hydrocarbons through the water-saturated crust. Any mechanism of migration would enrich diagnostic noble gas tracers (^4He , ^{20}Ne) relative to hydrocarbons (e.g., CH_4) or heavier noble gases (^{36}Ar , ^{84}Kr) in the migrated fluid, but the relative enrichments differ depending on whether the hydrocarbon gas migrates by diffusion (extreme enrichment of helium in the migrated gas-phase), two-phase advection (extreme enrichment of both helium and neon in the migrated gas-phase, such as in samples >1 km from drilling), or as a free gas (progressively less enrichment of the light gases with increasingly higher volumes of gas to water increases).

If hydrocarbon gases were to migrate significant distances from target shale formations to shallow aquifers following hydraulic stimulation, they would experience similar processes of gas fractionation that are observed in gas-rich samples >1 km from drilling in both areas. Instead, in a subset of water wells near drill sites, we recently measured extremely "stripped" atmospheric gas levels in groundwater samples that also displayed minimal fractionation of the trace gases. These patterns identify groundwater samples that experienced recent and rapid introductions of large volumes of gas-phase hydrocarbons into shallow aquifers (Darrah et al. 2014).

The lack of gas fractionation in the majority of samples with "stripping" suggests that extremely large volumes of thermogenic hydrocarbon gases migrated to shallow aquifers without interacting with the water-saturated crust during transport; this finding is inconsistent with large-scale gas migration from depth following hydraulic stimulation. The most likely way that hydrocarbon gas could migrate thousands of feet, even on geological timescales, without interacting with the water-saturated crust, appears to be migration along some pathway in the well bore. These findings suggest that fugitive gas migration occurs either (a) along the well annulus; (b) through faulty or corroded casing; or (c) along legacy or abandoned wells. In these circumstances, the molecular and isotopic fingerprints of hydrocarbon gases and/or

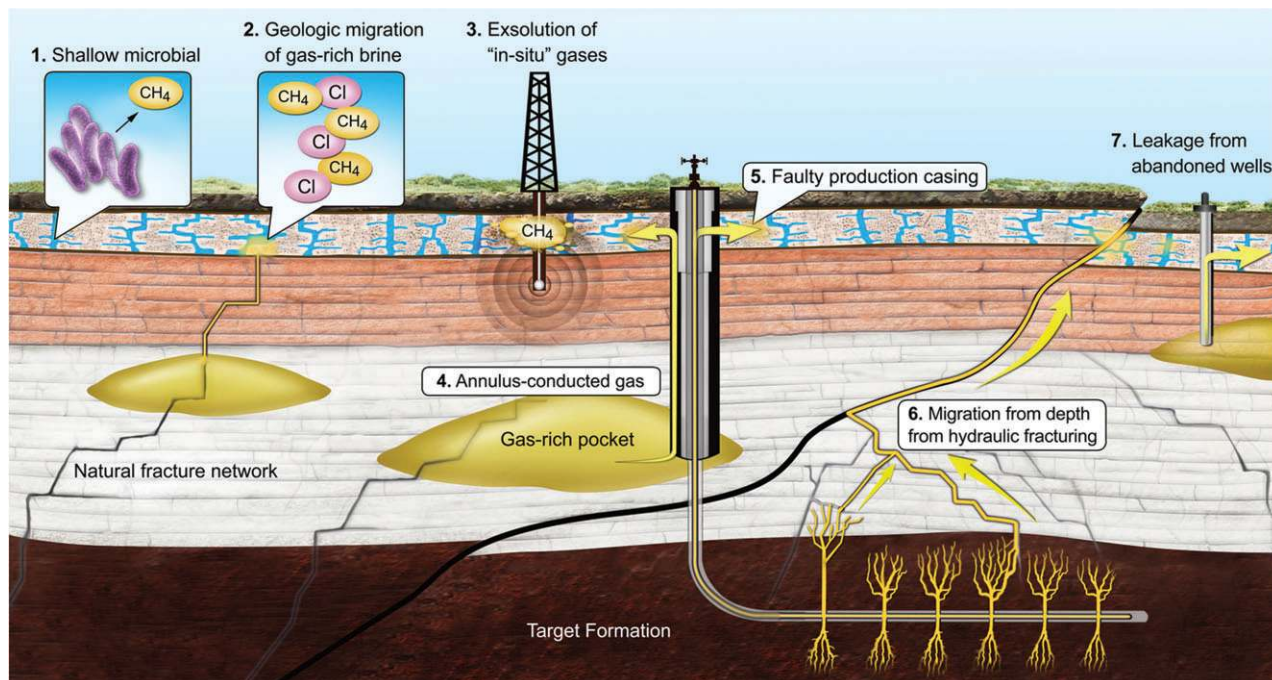


Figure 1. A diagram of seven scenarios that, in addition to coal bed methane, may account for the presence of elevated hydrocarbon gas levels in shallow aquifers. The figure is a conceptualized cross section and not drawn to scale (reprinted from Darrah et al. 2014).

noble gases can distinguish among the plausible sources (Rowe and Muehlenbachs 1999; Kornacki and McCaffrey 2011; Tilley and Muehlenbachs 2012; Molofsky et al. 2013; Baldassare et al. 2014; Darrah et al. 2014).

One unique cluster of drinking-water wells located near a natural-gas production well that experienced an “underground mechanical well failure” in the Marcellus study area prior to our sampling (Kraner 2012; Brantley et al. 2014) showed evidence for stripping and gas fractionation, which is consistent with long-range migration of gas in the crust. These observations provided empirical evidence that noble gases could distinguish this mechanism of gas transport. However, like the other cases discussed above, the fugitive gas contamination is caused by a well integrity issue.

Of the eight clusters of water wells examined in Darrah et al. (2014) where we identified fugitive contamination, all eight were related to well integrity, and not large-scale migration of gas through the water-saturated crust following the hydraulic fracturing process.

Implications of Elevated Levels of Methane in Shallow Aquifers

The conclusions presented above provide both good and bad news about the potential relationship between deep oil and gas drilling and fugitive gas contamination in shallow aquifers. On one hand, the combination of dissolved (e.g., noble gases) and hydrocarbon gas data implicate well integrity as the culprit for fugitive gas contamination in a subset of drinking-water wells. Potential problems with well integrity include corrosion

of steel casing or connections between two strings of casing, deterioration or leaks in the cement that fills the annular space between the steel casing and the formation, and/or pathways between the well bore walls and the outer rings of annular cement (Brufatto 2003; Davies et al. 2014; Ingraffea et al. 2014; Jackson 2014; Jackson et al. 2014). On the other hand, our data also show no evidence that horizontal drilling or hydraulic fracturing deep underground has provided a conduit that connects or transmits natural gas from target formations (e.g., Marcellus or Barnett) directly to surface aquifers, one of the greatest concerns for the public. These findings minimize the potential for the migration of large-scale hydrocarbon gas, brine, or fracturing fluids following drilling.

Well integrity failure has been recognized for decades as the most important factor in environmental stewardship for conventional oil and gas production (Brufatto 2003; Davies et al. 2014). These same factors remain critically important to unconventional oil and gas development (Davies et al. 2014; Jackson 2014).

Conclusions

The broader use of dissolved gas geochemistry, specifically the noble gases, will benefit present and future efforts to determine where fugitive gas contamination exists and how it occurs. In complex hydrogeological systems, noble gases inform us about the source, age, and migration of fluids in the Earth’s crust, whether natural or anthropogenic, specifically when paired with hydrocarbon geochemistry (Poreda et al. 1986; Ballentine

et al. 1991; Lollar et al. 1994; Gilfillan et al. 2009; Lollar and Ballentine 2009; Hunt et al. 2012). Fugitive gas studies provide novel applications for dissolved gas geochemistry. Our new data highlight an old, but critically important problem: the need to improve well integrity.

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