Review of Darrah et al, 2014

This is a remarkable and important paper which shows how noble gases and carbon isotopes can be used to determine whether gas in an aquifer is from natural background sources or from a leaking well, and furthermore tell, in many cases, the kind of well flaw that allowed the gas to escape into the drinking water aquifer.

The paper points out that gases which have migrated through the stratigraphy in brines expelled eons ago are enriched in crustal $^4$He and CH$_4$ and depleted in atmospheric gases like $^{36}$Ar and $^{20}$Ne. When circulating water interacts with these methane-rich brines the noble gas chemistry falls on their mixing line in which CH$_4$ and $^4$He increase with the salinity of the drinking water sample. In strong contrast, drinking water samples that short circuit through a well from shale sources have high methane concentrations that are independent of salinity and are stripped of the atmospheric gases while at the same time enriched in CH$_4$. It is thus very clear when a methane-rich drinking water acquired its methane from “natural” methane concentration in the subsurface or from a leaking gas well.

Furthermore, the carbon isotopic signature of the gas can identify whether the gas came up the annulus of the well from sources above the Marcellus, or and Marcellus gas that escaped from the production casing. The authors targeted drinking water wells in northeastern Pennsylvania which had elevated methane.

The authors find that 93 out of 113 of their methane-rich drinking water samples derived their methane from natural sources, and 20 derived their methane from production well leaks. In about half the cases, the leaks were from gas shale above the Marcellus that leaked into and up the well annulus. In about half the cases, the leaks were from the Marcellus (the target formation) and leaked from faulty production casing. In one case a packer failure is indicated. In no cases was there evidence of gas migration up through the stratigraphy form the hydrofractured portions of the Marcellus. The authors state strongly: “Noble gas data appear to rule out gas contamination by upward migration from depth through the overlying geological strata triggered by horizontal drilling or hydraulic fracturing.”

This paper is an excellent example of what good science can contribute to the leakage discussion.

Detailed discussion and figures
As of October 28$^{th}$ there are 7109 active shale wells in Pennsylvania. To understand the mechanisms of gas contamination of drinking water 113 domestic water wells that had elevated concentrations of dissolved methane were sampled and analyzed for hydrocarbon abundance, water chemistry, noble gas concentrations, and isotopic composition. Pennsylvania water wells are 35 to 90 m deep. Wells selected were both close to and far from drill sites as shown in Figure 1. One natural methane seep was
also sampled. For comparison, 20 domestic water well samples from the Barnett area of Texas were analyzed in a similar fashion.

Figure 1. Figure S2 from Darrah et al (2014). Red dots show unconventional shale wells. Circles indicate domestic water well samples closer than 1 km to a shale gas well. Triangles samples further than 1 km from a shale gas well. Shading indicates the methane concentration in the collected samples.

Figure 2 shows that the water well chemistry are of two distinct kinds: (1) A “normal” population of samples in which the ratios of crustally-sourced CH₄ and ^4^He to atmospherically-sourced ^36^Ar and ^20^Ne increase with sample salinity. And (2) an “anomalous” population of samples where these ratios are very high, there is no dependence on sample salinity, and the samples are all within 1 km of a shale gas well (green-rimmed circles). The methane in the “normal” samples was acquired when circulating meteoric waters (sourced by rainfall) interacted with pockets of CH₄-rich brines that had migrated from deeper source strata in the geologic past. The methane in the “anomalous” samples came from a nearby gas production well.
Figure 2. The ratios crustally-sourced CH$_4$ and $^4$He to atmospherically-sourced $^{36}$Ar and $^{20}$Ne in domestic water well samples plotted against the chlorinity of the sample define two distinct populations: (1) a “normal” population in which the ratios increase with chlorinity indicating methane was derived from methane-rich brine pockets that migrated into the shallow stratigraphy in the geologic past, and (2) an “anomalous” population of water wells samples (green rimmed) whose elevated CH$_4$ levels came from leaks in nearby shale gas production wells.

We know the methane in the “normal” water migrated from deeper source strata because the 4He/CH$_4$ ratio of these samples is much greater an their 36Ar much lower than un-migrated hydrocarbons in the area. For example, Figure 3 shows that the “normal” water well samples the 4He/CH$_4$ ratio is much
higher than it is in gases in the Marcellus or Upper Devonian shales (black- and pink-hatched boxes, respectively). Uranium decay in the sediments produced $^4\text{He}$ which was picked up by the migrating brines along with Cl and CH$_4$. At the same time the more water soluble atmospheric gases $^{36}\text{Ar}$ and $^{20}\text{Ne}$ were lost. Thus, the higher-than-source ratios of $^4\text{He}/\text{CH}_4$ indicate migration. The increase in CH$_4$/$^{36}\text{Ar}$ and $^4\text{He}/^{20}\text{Ne}$ with increasing salinity ([Cl-]) reflects the mixing of meteoric water rich in atmospheric gases with the pockets of CH$_4$-rich brine.

Figure 3. The normal water well samples (triangles and non-green-rimmed circles) were enriched in $^4\text{He}/\text{CH}_4$ compared to shale gases (pink and black hatched boxes) when these gases migrated (dissolved in brine) upward and acquired $^4\text{He}$ produced in the sediments by radioactive decay of uranium in the sediments. Most of the green-rimmed “anomalous” samples are not enriched in $^4\text{He}/\text{CH}_4$ and thus did not migrate through $^4\text{He}$-rich sediments, but short circuited up the well annulus or production tubing. The exception is the “migrated” gases which are probably from a packer failure.

Figure 4 shows furthermore that the green-rimmed “anomalous” water well samples have been stripped of their atmospheric gases. For this to happen the gas from the annulus or production string must have been injected into the aquifer rapidly (faster than ground water flow) and in substantial quantity. This
gas injection will remove atmospheric gases (like any gas-stripping sparge system) while increasing dissolved CH₄).

Figure 4. The “anomalous” green-rimmed samples are stripped of atmospheric ²⁰Ne and N₂, while at the same time being enriched (supersaturated) in CH₄. The cyan line shows the temperature-dependent water compositions of water equilibrated with the atmosphere. The green-rimmed samples are below the end of this line. Gas from the nearby production wells stripped out the atmospheric gases.

The rapidity with which methane from a gas production well can change the chemistry of aquifer waters is illustrated from changes observed in Barnett drinking water well that were sampled several times by the arrows in Figure 5.
Figure 5. Two water wells changed composition between initial sampling (1) in December 2012 and resampling in August and November 2013 (2 and 3). Initially along the “normal trend”, methane from the nearby gas production well added methane and stripped the atmospheric gases (N$_2$ and $^{20}$Ne) as shown by the arrows on the diagrams.

Finally, the “anomalous” gases from the shale gas production wells retain composition of their gas-rich reservoir source, and therefore it is possible to tell where the gases came from and the location and nature of the flaw in the production well that methane to escape into the aquifers. Figure 3B (above) and Figure 6 below shows that the green-rimed “anomalous” gases from the Marcellus water well
samples came both from Upper Devonian strata (mid way down through the stratigraphy to the Marcellus) and from the Marcellus.

Figure 6. The composition of the “anomalous” green-rimmed water samples indicate the gases came from both Upper Devonian shale and Marcellus shale sources.

Figure 7 summarizes the conclusions of the Darrah et al (2014) paper. Most waters in Pennsylvania do not contain anomalous methane. The study concentrated on those water well samples that contained anomalous methane and found that the vast majority of these water well samples (93 of 113) derived their methane from their interaction with Cl- and CH4 rich brines that had migrated eons ago into what is now the shallow stratigraphy (scenario 2 in Figure 7). Twenty of the 113 water well samples contained methane that came from a shale gas production well which, in all cases, was <1 km away. The gas was introduced to the drinking water aquifer by migration up the annulus of the well from Upper Devonian strata (scenario 4), from escape from faulty production casing (scenario 5), and from a packer failure. In no case did the methane come from the hydrofractured parts of the Marcellus.
This paper shows that gas leakage into aquifers from shale gas production wells is rare (20 instances from 113 water well samples screened for having anomalous methane); most methane in drinking water is from natural sources (93 of 113 instances). All shale gas production leaks were from well casing, cementing, or operating flaws. None were from the fracked formation. This means that the leaks are under engineering control and their risk can be minimized. The analysis shows how isotopic and noble gas analyses can distinguish methane contamination from shale gas production and natural contamination, and in many cases can identify the kind of well flaw responsible for leakage from a well into the aquifer.