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Interactive comment

Interactive comment on "Is Shale Gas a Major Driver of Recent Increase in Global Atmospheric Methane?" *by* Robert W. Howarth et al.

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UPDATED RESPONSE BY AUTHOR TO REVIEWER #1 (3 June 2019):

Please see my first response (dated 9 May 2019) for specific responses to the reviewer's comments. Since writing that response, I have spent considerable time scouring the literature for additional appropriate data on the 13C content of shale gas, and I have substantially changed the value I use in my analysis (from - 51.4 o/oo to – 46.9 o/oo).

In addition to the original sources I used in the "discussion" submission (which were reviewed in Golding et al. 2013), I followed the leads in the Tilley and Muehlenbachs (2013) review suggested by the reviewer, as well as those in the Sherwood et al. (2017)

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Discussion paper

data set. With regard to the work cited by Tilley and Muehlenbach (2013), some of these studies refer to methane that has migrated from the original shale formation, and not to methane that would be released from shale through high-volume hydraulic fracturing (which is how I and most others define "shale gas"). Since my argument is that the methane would be subject to fractionation by partial oxidation during migration, it would not be appropriate to include data on these migrated gases. Included in the Tilley and Muehlenbach (2013) paper are data from Tilley et al. (2011): note that Hao and Zou (2013) specifically decided not to include those data in their modeling, noting that fractionation during migration seemed likely. Similarly, many of the samples listed by Sherwood et al. (2017) as "shale" are not in fact not for shale gas that is released through high-volume hydraulic fracturing, but rather again for methane that has migrated from shales. In some cases, it is possible to determine from the original papers cited whether or not the samples are truly for shale gas, but in many cases this is not possible.

My response is to only use data for samples that unambiguously came from shale gases, and that clearly were not from migrated gases. One such set of data come from Botner et al. (2018), which reviewer #1 specifically suggested I consider. Further, I have decided not to use the organic-rich shales from the Golding et al. (2013) review – as I had done in the "discussion" submission – as I now feel these are unlikely to reflect the major shale gas plays of the past decade. In rewriting, I am now including additional papers on 13C fractionation from partial oxidation of migrating methane.

I have extensively revised two paragraphs in my revised submission. The new language follows:

"Several studies have suggested that the δ13C signal of methane from shale gas can often be lighter (more depleted in 13C) than that from conventional natural gas (Golding et al. 2013; Hao and Zou 2013; Turner et al. 2017; Botner et al. 2018). This should not be surprising. In the case of conventional gas, the methane has migrated over geological time frames from the shale and other source rocks through permeable rocks until trapped below a seal (Fig. 2-A). During this migration, some of the methane is can be oxidized both by bacteria, perhaps using iron (III) or sulfate as the source of the oxidizing power, and by thermochemical sulfate reduction (Whelan et al. 1986; Burruss and Laughrey 2010; Rooze et al. 2016). This partial oxidation fractionates the methane by preferentially consuming the lighter 12C isotope, gradually enriching the remaining methane in 13C (Hao and Zou 2013; Baldassare et al. 2014), resulting in a δ13C signal that is less negative. The methane in shales, on the other hand, is tightly held in the highly reducing rock formation and therefore very unlikely to have been subject to bacterial oxidation and the resulting fractionation. The expectation, therefore, is that methane in conventional natural gas should be heavier and less depleted in 13C than is the methane in shale gas."

and

"Although our expectation is that the methane in shale gas is depleted in 13C relative to conventional natural gas, the δ13C ratios for the methane in both conventional gas reservoirs and in shale gas vary substantially, changing with the maturity of the gas and several other factors (Golding et al. 2013; Hao and Zou 2013; Tilley and Muehlenbachs 2013). The large data set of Sherwood et al. (2017) suggests no systematic difference between the average ratio for shale gas and the average for conventional gas. However, some of the data listed as shale gas in that data set are actually for methane that has migrated from shale to reservoirs (Tilley et al. 2011) and therefore may have been partially oxidized and fractionated (Hao and Zou 2013). In other cases, the data appear to come both from conventional vertical wells and shale-gas horizontal wells in the same region, making interpretation ambiguous (Rodriguez and Philp 2010; Zumberge et al. 2012). Note that in the Barnett shale region, Texas, the δ13C ratio for methane emitted to the atmosphere (- 46.5 o/oo; Townsend-Small et al. 2015) is more depleted than the average for wells reported in the Sherwood et al. (2017) data set: -44.8 o/oo for "group 2A and 2B" wells and - 38.5 o/oo for "group 1" wells (Rodriguez and Philp 2010) and -41.1 o/oo (Zumberge et al. 2012). For our analysis, we use the mean of the δ13C ratio (- 46.9 o/oo) from three studies where the methane clearly came from horizontal, high-volume fractured shale wells: - 47.0 o/oo for Bakken shale, North Dakota (Schoell et al. 2011), -46.5 o/oo for Barnett shale, Texas (Townsend-Small et al. 2015), and - 47.3 o/oo for Utica shale, Ohio (Botner et al. 2018). Note that several studies have reported mean δ13C ratios for methane from organic-rich shales that are more depleted in 13C (more negative) than this: -50.7 (Martini et al. 1998) for Antrim shale, Michigan; - 53.3 (McIntosh et al. 2002) and – 51.1 (Schlegel et al. 2011) for New Albany shale, Illinois; - 49.3 (Osborn and McIntosh 2010) for a Devonian shale in Ohio. However, these shales are not typical of the major shale plays supporting the huge increase in gas production over the past decade. “

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