(84-240513-C) **Hydrogen Isotopes as Tracers of Methane Sources**

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Scientists investigating rising CH_4 concentrations regionally and globally have relied on a variety of approaches to estimate sources of excess methane, including inventories of sources, carbon isotopes of CH_4, and methane:ethane ratios. In this presentation, I will give examples from several studies that have measured the hydrogen stable isotopic composition (δD) of CH_4 in both sources (i.e., at the "bottom up" level) and in well mixed air masses (for "top down" source apportionment), and argue that this tracer is a valuable potential tracer of global methane sources. Advantages of hydrogen isotopes include 1), consistent δD ratios of CH_4 within oil and gas basins as compared to $\delta^{13}C$ and CH_4:C_2H_6; 2), most sources have a distinct δD-CH_4 from atmospheric background, which makes it easier to distinguish small enhancements in CH_4, unlike $\delta^{13}C$, where some oil and gas sources have similar signatures to background air; and 3), the ability to use a two-endmember mixing model for source apportionment rather than a one-endmember mixing model, which is the case with CH_4:C_2H_6 (because biogenic sources do not have C_2H_6). Some disadvantages of using δD vs the others include 1), there are no in situ instruments available for measuring δD, as there are for $\delta^{13}C$ and C_2H_6, and fewer laboratories measuring this isotope in CH_4; and 2), currently there are somewhat larger sample volume requirements for δD than $\delta^{13}C$, although still much smaller than in the recent past.

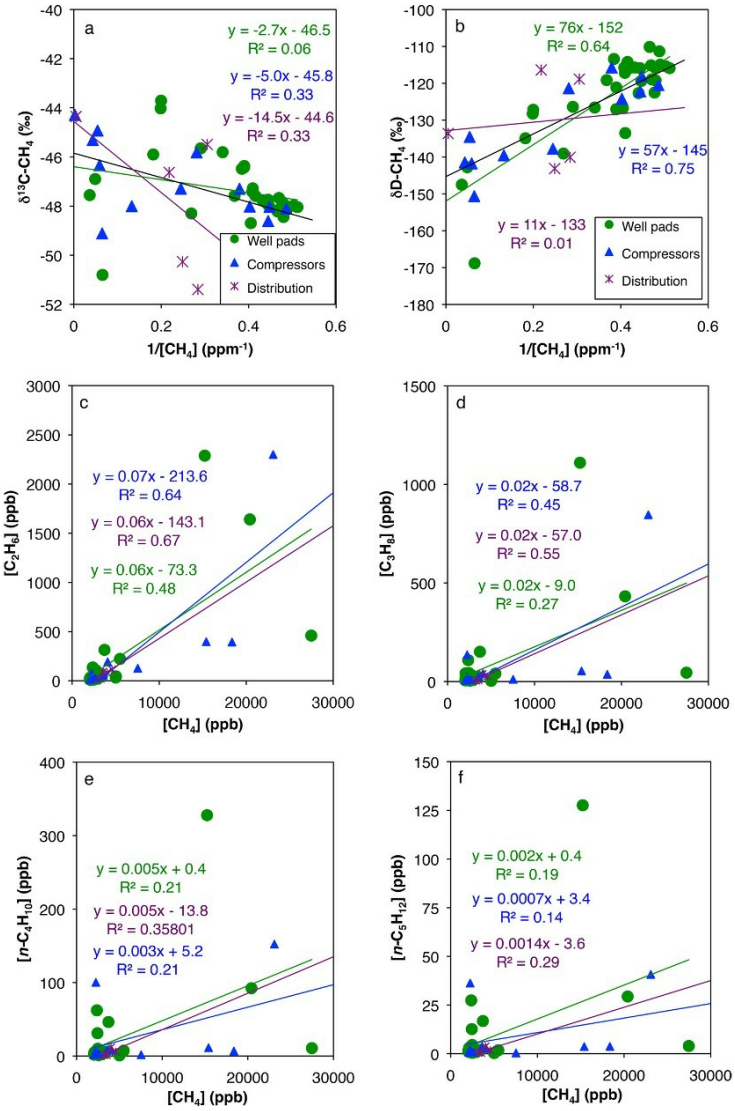

Figure 1. Composition of methane from natural gas sources in the Barnett Shale region. (a) Keeling plot of $\delta^{13}C$-CH_4 vs 1/[CH_4]; (b) δD-CH_4 vs 1/[CH_4]; (c) [C_2H_6] vs [CH_4]; (d) [C_3H_8] vs [CH_4]; (e) [n-C_4H_{10}] vs [CH_4]; and (f) [n-C_5H_{12}] vs [CH_4].