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$^{13}CH_3D$ and $^{12}CH_2D_2$ Clumped Isotopes of Air as A Tool for Understanding Atmospheric Methane Sources and Sinks

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Recent advances in isotope techniques and instrumentation have added high precision measurement of clumped isotopes to the existing toolkit of atmospheric scientists for tracing of methane sources and their geological, biological, and anthropogenic processes of formation. We find CH_4 from urban air samples have $\Delta^{12}CH_2D_2$ of ~46-50‰, which is lower than predicted enrichment by prior published theoretical models. This difference between observation and model reflects an underestimation of sources with negative $\Delta^{12}CH_2D_2$. These measurements also point to negative δ values for the total source composition with negative $\Delta^{12}CH_2D_2$. This negative $\Delta^{12}CH_2D_2$ contrasts with positive $\Delta^{12}CH_2D_2$ equilibrated thermogenic/fossil sources and means that atmospheric $\Delta^{12}CH_2D_2$ will be sensitive to variations in the proportions of biogenic to equilibrated thermogenic/fossil sources. For regional air, we also find that the degree of enrichment of $\Delta^{12}CH_2D_2$ of air samples can be used in combination with other isotopic and concentration information about methane to understand local sources. We focus on early morning air because the night time inversion allows for methane to accumulate and be measured. We find that the $\Delta^{12}CH_2D_2$ of the near surface air collected early in the morning ranged from ~23‰ to ~35‰, relative to the atmospheric reservoir with a value of ~50‰. The mixing behavior is seen in air samples collected from emission sites like wetlands, sites where there are ruminants, and sites where there are other methane sources.

The added information from $\Delta^{12}CH_2D_2$ provides additional ways to fingerprint local contributions of methane and suggest that Δ and δ values for $^{13}CH_3D$ and $^{12}CH_2D_2$ show promise as complementary tracers of atmospheric methane sources and sinks, and provide complementary insights into atmospheric methane.