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Methane Isotopologues of Vehicle Emissions: Added Complexity for Interpreting Urban Air Methane

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Methane clumped isotopologues are thought to be able to better differentiate methane of different origins, indicate certain thermodynamic equilibrium and kinetic processes, and are expected to provide further constraints on the global methane budget. Methane emitted by vehicle exhaust less because it is thought to be a minor part of global methane emissions. However, considering the large number and the high frequency use of internal combustion engines, the possibility that a large proportion of emissions come from a small proportion of episodic high-emitting engines, and the potentially unique isotopic composition, knowing about vehicle methane emissions is of interest

We collected exhaust gas samples from gasoline cars and mower (spark ignition, SI), diesel buses (compression ignition, CI), and wooding burning (WB). The vehicles cover different brands, model years, stroke cycles, ignition methods, operating temperatures, and catalytic converter conditions. The concentration data suggest that older cars emit high amounts of methane, while new cars can also emit gases with methane concentrations several times higher than air. Diesel buses are cleaner in terms of methane emissions, probably because CI allows higher air to fuel. We measured methane isotopes of these samples, as well as air samples from the Washington DC Beltway during morning rush hour.

Exhaust methane from most spark ignition engines is around 0‰ for both $\delta^{13}CH_3D$ and $\delta^{12}CH_2D_2$. These clumped isotopologue signals are consistent with high temperature equilibration. The elevated methane concentration of the Beltway samples (1.15-1.2 times atmospheric concentration) requires air to be mixed with one or more endmember(s). One explanation that fits the relationships between $\delta^{13}C$, δD, $\delta^{13}CH_3D$, and $\delta^{12}CH_2D_2$ signals would be mixing with a natural gas component such as Marcellus that leaks from municipal pipeline. However, an equally plausible explanation is mixing with a component that is predominantly exhaust methane with a small biogenic contribution. It could be important to consider the contributions from car exhaust in addition to those from natural gas to explain the observed fluctuations in methane concentrations and isotopic data in urban areas.