Atmospheric Measurements of Methane, Isotopic Methane, and Ethane Using a Cavity Ring-down Spectrometer

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Atmospheric methane (CH_4) has a powerful short-term global warming impact, and comes from a variety of natural and anthropogenic sources. Methane sources include wetlands, landfills, oil/gas/coal extraction activities, and urban emissions from leaks in the natural gas distribution system. Constraining the magnitude and distribution of these emissions spatially and temporally is critical to understanding the present and future climate impacts of CH_4. There are two tracer molecules that are often employed to investigate relative importance of various methane sources (and sinks): delta 13 carbon ($\delta^{13}C$) in CH_4 and ethane (C_2H_6). Biogenic sources of methane have lighter isotope ratios relative to thermogenic sources, although the ranges for each type of source are fairly broad and can overlap with each other. Atmospheric ethane is primarily a product of fossil fuel extraction, transport, or consumption. The ethane-to-methane ratio from these sources can vary dramatically, depending on the source C2/C1 signature in the geologic formation, and where in the extraction process the emissions originated. In combination, these two tracers can provide a wealth of information about the sources of methane contributing to the emissions.

Generally, measurements of these two tracers are made via off-line analysis of flask samples. In this study we present a novel, field-deployable instrument based on Cavity Ring-Down Spectrometer (CRDS) that is capable of real-time atmospheric measurements of mixing ratios of CH_4, C_2H_6, and $\delta^{13}C$ in CH_4, along with water vapor and carbon dioxide. This instrument is capable not only of Global Atmosphere Watch-quality methane measurements, but this highly sensitive analyzer can provide sub-permil measurements of $\delta^{13}C$ in CH_4 and sub-ppb measurements of ethane. The spectrometer is based on rugged near-infrared optical technology that is as well-suited regional monitoring networks as it is to making mobile measurements for real-time attribution of fugitive methane emissions.

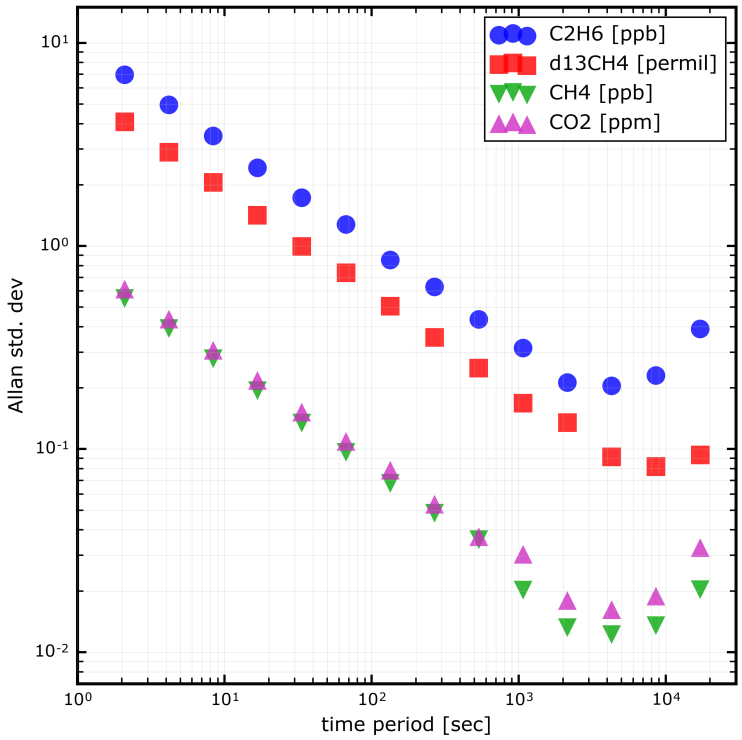

Figure 1. Allan standard deviation from the CRDS analyzer for key analyte species. Units are in the legend for each species.