Real-time analysis of δ^{13}C- and δD-CH$_4$ by high precision laser spectroscopy

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Methane (CH$_4$) is the most important non-CO$_2$ greenhouse gas (GHG) contributing 18% to total radiative forcing. Anthropogenic sources (e.g. ruminants, landfills) contribute 60% to total emissions and led to an increase in its atmospheric mixing ratio from 700 ppb in pre-industrial times to 1819 ± 1 ppb in 2012 [1]. Analysis of the most abundant methane isotopologues ^{12}CH$_4$, ^{13}CH$_4$ and ^{12}CH$_3$D can be used to disentangle the various source/sink processes [2] and to develop target oriented reduction strategies. High precision isotopic analysis of CH$_4$ can be accomplished by isotope-ratio mass-spectrometry (IRMS) [2] and more recently by mid-infrared laser-based spectroscopic techniques. For high precision measurements in ambient air, however, both techniques rely on preconcentration of the target gas [3].

In an on-going project, we developed a fully-automated, field-deployable CH$_4$ preconcentration unit coupled to a dual quantum cascade laser absorption spectrometer (QCLAS) for real-time analysis of CH$_4$ isotopologues. The core part of the rack-mounted (19 inch) device is a highly-efficient adsorbent trap attached to a motorized linear drive system and enclosed in a vacuum chamber. Thereby, the adsorbent trap can be decoupled from the Stirling cooler during desorption for fast desorption and optimal heat management. A wide variety of adsorbents, including: HayeSep D, molecular sieves as well as the novel metal-organic frameworks and carbon nanotubes were characterized regarding their surface area, isosteric enthalpy of adsorption and selectivity for methane over nitrogen. The most promising candidates were tested on the preconcentration device and a preconcentration by a factor > 500 was obtained. Furthermore analytical interferants (e.g. N$_2$O, CO$_2$) are separated by step-wise desorption of trace gases.

A QCL absorption spectrometer previously described by Tuzson et al. (2010) for CH$_4$ flux measurements was modified to obtain a platform for high precision and simultaneous analysis of CH$_4$ isotopologues. The infrared radiation emitted by the two cw-QC laser sources are combined and coupled into a 0.5 L astigmatic multipass absorption cell with an optical path length of 76 m. An Allan variance minimum of the isotope ratio time-series of 0.1 ‰ for δ^{13}C-CH$_4$ and 0.3 ‰ for δD-CH$_4$ has been achieved using 300 s integration time. First experiments of the developed analytical technique demonstrate its potential with respect to field-applicability and temporal resolving power.

References:

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