Measurements of carbon and hydrogen isotopes of methane in archived CARIBIC air samples

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Introduction and motivation

Methane (CH_4) is the second important greenhouse gas that also plays an important role in atmospheric chemistry via reaction with hydroxyl radical (OH). Uncertainties in quantitative estimates of individual CH_4 sources are still large on both global and regional scales. Asia is important CH_4 source regions in terms of both anthropogenic and natural sources, but atmospheric observations in the region to improve source estimates are very limited. Carbon and hydrogen isotopic ratios of CH_4 are useful to disentangle relative contributions of different types of CH_4 sources, because individual CH_4 sources have characteristic isotopic signatures. CARIBIC is a long-term atmospheric observation project using passenger aircraft that have regularly collected whole air samples (Ref. 1). Air samples that were collected by CARIBIC in the upper troposphere over South Asia were archived for future measurements. Part of the CARIBIC air samples was already analyzed for CH_4 isotopes, but additional measurements are needed to reveal seasonal changes of isotopic ratios. At the same time, it is important to connect new measurements to existing datasets. Recent studies have indicated that there are significant biases in CH_4 isotopic ratio measurements among laboratories, which should be carefully taken into account in comparing datasets from different laboratories (Ref. 2).

Scientific objectives

Scientific objectives of this study are as follows:
Organize data of carbon and hydrogen isotopic ratios of CH_4 for CARIBIC air samples
Describe seasonal variations of CH_4 concentration and isotopic ratios over South Asia
Clarify biases in CH_4 isotopic ratio measurements between laboratories

Method and experimental set-up

Sets of CARIBIC air samples archived at Max Planck Institute for Chemistry (MPIC) were sent to the Institute for Marine and Atmospheric Research Utrecht (IMAU), where measurements of carbon and hydrogen isotopic ratios were carried out (Ref. 3). Since the laboratory where the early data were measured is no longer available (Ref. 4), air samples once analyzed in the laboratory were also sent to IMAU in order to clarify possible laboratory biases. To compare with external dataset, air samples were also sent from Tohoku University (TU), Japan to IMAU. TU has made extensive CH_4 isotopic ratio measurements for air samples collected in the upper troposphere (Ref. 5).

Preliminary results and conclusions

Sets of CH_4 isotopic measurements for the CARIBIC air samples were made at IMAU. The new data were combined with the original dataset, but we found obvious biases of the early data with

the recent IMAU measurements. The following measurements for intercomparison indicated likely offset values between the laboratories, enabling us to harmonize both datasets. The intercomparison with TU has not been finalized yet. However, as soon as the final measurement values are delivered, the CARIBIC dataset can be compared to the TU data, which allows us deeper discussions.

Outcome and future studies

The harmonized dataset now illustrate seasonal variations of CH_4 concentration and carbon and hydrogen isotopic ratios in the upper troposphere over South Asia. Together with describing the observed variations in detail, isotopic signatures of contributing sources are inferred. These observation-based implications for CH_4 source types will be compared to CH_4 emission database employed in atmospheric chemistry transport models. Intercomparison carried out in this study will allow future data users to combine existing data from different laboratories for extensive data analysis and modeling studies in a consistent way.

References

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