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Inter-laboratory comparison of δ13C and δD measurements of atmospheric CH4 for combined use of datasets from different laboratories

Taku Umezawa (1,2) and the Laboratories measuring isotopic composition of atmospheric methane

(1) Max Planck Institute for Chemistry, Mainz, Germany, (2) National Institute for Environmental Studies, Tsukuba, Japan (umezawa.taku@nies.go.jp)

Many studies have shown that isotope measurements are useful to constrain the global methane budget. However, in history of isotope measurements of atmospheric methane, there have been no widely accepted standards and calibration methods, which has caused significant measurement offsets among laboratories. The lack of knowledge on such inter-laboratory offsets has hampered synthesis analysis of the methane budget based on a merged datasets contributed from different laboratories. In this study, we present results from a worldwide inter-laboratory comparison of samples among laboratories that measure (or measured in the past) stable carbon and hydrogen isotope ratios of atmospheric CH4 (δ13C-CH4 and δD-CH4). The offsets among the laboratories are larger than the measurement reproducibility of individual laboratories. To estimate measurement offsets among laboratories, we evaluated and critically assessed a large number of intercomparison results, some of which have been documented previously in the literature. The results indicate significant offsets among datasets reported from different laboratories; the differences among laboratories at modern atmospheric methane level spread over ranges of 0.5 ‰ for δ13C-CH4 and 13 ‰ for δD-CH4. The intercomparison results summarized in this study may be of help for future attempts to harmonize datasets from different laboratories in order to jointly incorporate them into modeling studies. However, establishing such a merged dataset, which includes δ13C-CH4 and δD-CH4 data from multiple laboratories with desirable compatibility, is still challenging due to differences among laboratories in instrument settings, correction methods, traceability to reference materials and long-term data management. Further efforts are needed to identify causes of the inter-laboratory measurement offsets and to decrease those towards the best use of available δ13C-CH4 and δD-CH4 datasets.