Measurements of stable carbon isotope ratio of methane at Hateruma Station, Japan

Taku Umezawa (umezawa.taku@nies.go.jp), Yukio Terao, Yasunori Tohjima, Takuya Saito, Motoki Sasakawa and Hitoshi Mukai

National Institute for Environmental Studies

Abstract

Hateruma island is the southernmost inhabited island of Japan. As the place is in the downwind of the continental East Asia in winter, arrivals of air masses of continental origin cause synoptic-scale variations (i.e., high-concentration events in CO_2, CH_4 etc.). We have collected air samples so as to coincide with such high-CH_4 events, and those air samples have been analyzed for stable carbon isotope ratio of CH_4 (δ^{13}C-CH_4) since December 2017 by using a continuous-flow preconcentration and isotope ratio mass spectrometry system. In this study, we present our experimental method for δ^{13}C-CH_4 analysis including our attempts to assure data quality. We prepared a compressed dry air as a working standard as well as a set of three surveillance cylinders (CH_4 in synthetic air) that cover a wide range of δ^{13}C-CH_4 values (from -68 to -26 per mil VPDB). Two-year measurement records show that the three surveillance cylinders have indicated no significant drifts. and that the standard deviations of the measured values for the individual cylinders are about 0.1 per mil. It is also observed that the span of our δ^{13}C-CH_4 measurement (difference of the measured values of the cylinders with high and low δ^{13}C-CH_4) has been constant over time. Although temporal drift needs to be monitored for a longer period, we consider that performance of our system is satisfactory to identify synoptic-scale variations at Hateruma island and to infer δ^{13}C-CH_4 signatures of the continental CH_4 sources.

Table 1. Cylinder gases used for long-term quality assurance of δ^{13}C-CH_4 measurements at NIES.

Gas Name	Cylinder ID	Composition	δ^{13}C-CH_4 (‰)
Work	CPB03323	Compressed dry air	-47.49±0.13
LOW	CC706220	2-ppm CH_4 + 1-ppm Kr in synthetic air (manufactured by Air Liquid)	-68.23±0.11
HIGH	EB0132294	2-ppm CH_4 + 1-ppm Kr in synthetic air (manufactured by Air Liquid)	-26.88±0.09
MID	EB0129050	2-ppm CH_4 + 1-ppm Kr in synthetic air (manufactured by Air Liquid)	-45.15±0.06

NIES δ^{13}C-CH_4 measurement system

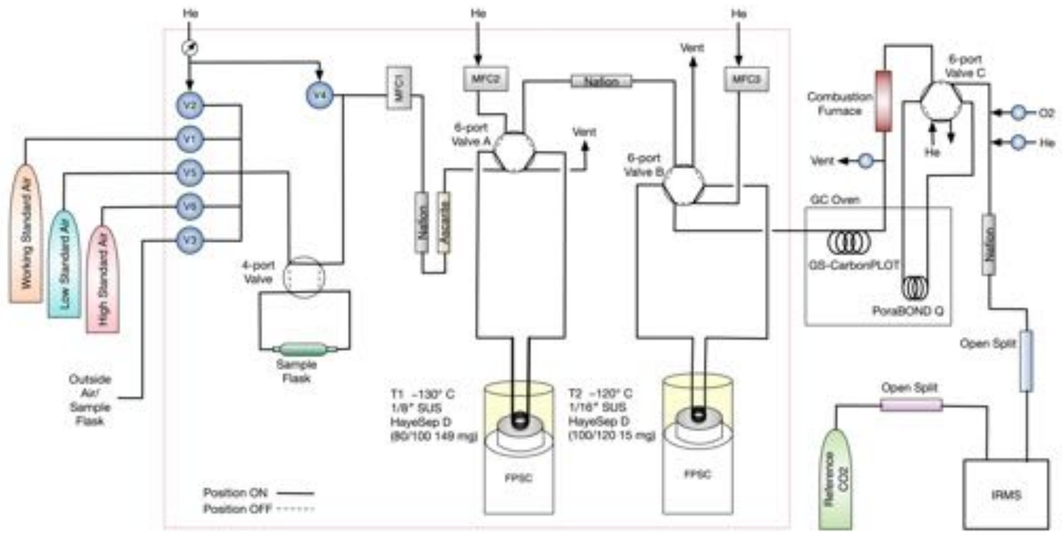

Figure 1. A schematic overview of the NIES CPR-GC-IRMS system. The sub-system CPR (Continuous-flow Preconcentration and Refocusing) is surrounded by the dotted square. The on/off valves V1 to V6, 4-port Valve and 6-port Valves A and B are controlled pneumatically by CPR. MFC: mass flow controller, IRMS: isotope ratio mass spectrometer. The figure has been modified after Umezawa et al. (2020).

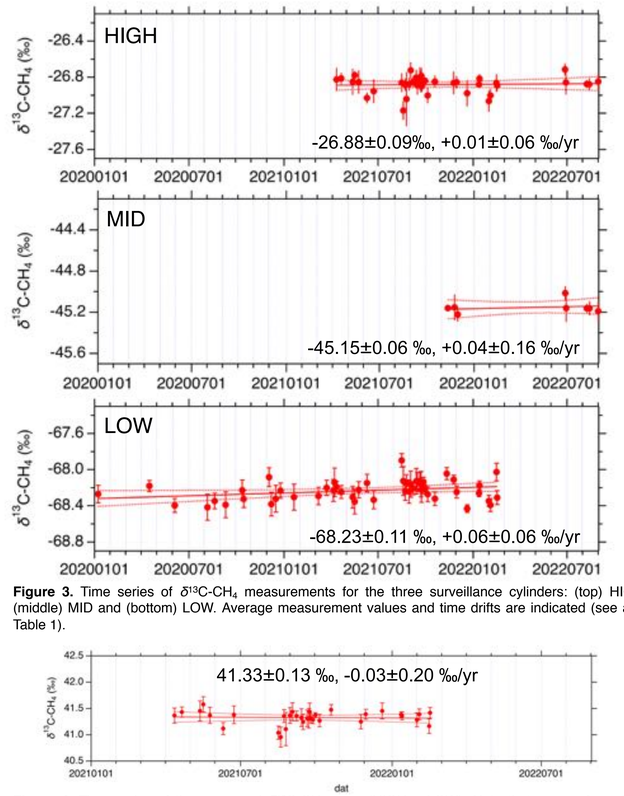

Figure 3. Time series of δ^{13}C-CH_4 measurements for the three surveillance cylinders: (top) HIGH, (middle) MID and (bottom) LOW. Average measurement values and time drifts are indicated (see also Table 1).

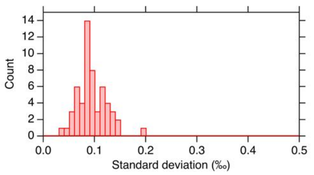

Figure 2. A histogram of standard deviation of the Work measurements on each measurement day during the periodic surveillance measurement series.

Figure 4. Time series of the measured δ^{13}C-CH_4 span (HIGH – LOW). Note that range of x-axis is different from Figure 3.

Measurement traceability

The δ^{13}C-CH_4 value of the working standard air (Work, **Table 1**) was determined based on replicated measurements during 9 November 2018–21 January 2019 (N=158) against the reference CO_2 cylinder with δ^{13}C-CO_2 value of -32.460‰ (NIES VPDB). Work has been measured on every sample measurement day. Its δ^{13}C-CH_4 value has been assumed to be stable and sample measurements have been corrected accordingly.

Long-term quality assurance

Work and the three surveillance cylinders with wide range of δ^{13}C-CH_4 values (**Table 1**) are measured periodically in a replicate way (typically 10 times for each cylinder). Standard deviations of the Work measurements during those surveillance series are generally ~0.1‰ or better (**Figure 2**).
The three surveillance cylinders did not show significant time drifts over the last two years (**Figure 3**). These measurements also indicate insignificant temporal change of the measurement span over the last years (**Figure 4**).

Measurement results for air samples from the Hateruma Station (HAT), Japan

Figure 5. (Left top) A picture of the Hateruma Station (HAT), Japan (https://esd.nies.go.jp/ja/about/facilities/). (Left bottom) Location of HAT (red icon, https://db.cger.nies.go.jp/ged/). (Right top) A picture of the Hateruma event sampler (HEV). This sampler collects sample air into series of ~2.5 L glass flasks at pre-scheduled timings. (Right bottom) A picture of the compact air sampler (CASPER). This sampler houses series of ~0.1 L glass flasks. The sampler switches automatically and post-decision samplings are made, referring to in-situ CH_4 measurement.

Air samples collected at HAT (24.06° N, 123.81° E, see **Figure 5**) have been measured by the CPR-GC-IRMS system. HAT is frequently in downwind of the Asian continent during winter, which causes elevated concentrations of trace gases (Tohjima et al., 2014). The air sample collections have been made by two types of air samplers (HEV and CASPER, **Figure 5**) in conicident with such high-CH_4 events. In total, 42 high-CH_4 events have been captured during December 2017–February 2022 (5 winter seasons). The HEV samples were analysed three times for each flask, and the standard deviations from those replicate analyses indicate that the repeatability of the measurement system is in general better than 0.1‰ (**Figure 6**).

Variations of δ^{13}C-CH_4 associated with CH_4 elevations were examined (**Figure 7**) and δ^{13}C-CH_4 source signatures contributing to the observed high-CH_4 events were estimated based on the Keeling plot approach (**Figure 8**). The events with high correlation between CH_4 mole fraction and δ^{13}C-CH_4 frequently indicated source signatures of about -40‰.

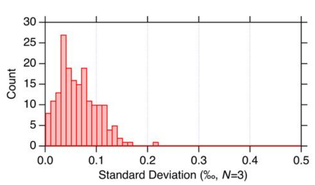

Figure 6. A histogram of the standard deviation from the three-times analyses of the HEV samples (183 samples in total). More than 80% of the sample measurements showed standard deviations of < 0.1‰.

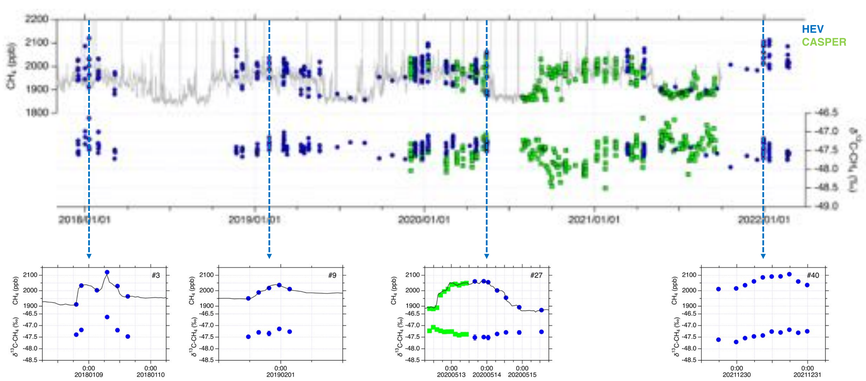

Figure 7. Time series of the CH_4 mole fraction (top panel, left axis) and δ^{13}C-CH_4 (top panel, right axis) at HAT. Grey line shows the in-situ CH_4 measurements at 1-hour intervals (Tohjima et al., 2002). The measurement results from the two samplers HEV and CASPER (see Figure 5) are shown by blue and green symbols, respectively. Zoom-in figures for selected high-CH_4 events are also shown (bottom panels).

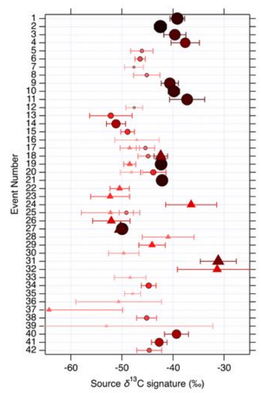

Figure 8. The δ^{13}C-CH_4 source signatures inferred from Keeling plots for high-CH_4 events at HAT. Dark and large symbols indicate high correlation coefficients between CH_4 mole fraction and δ^{13}C-CH_4. Circles and triangles are from HEV and CASPER, respectively.

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