Validation of Boreas: an instrument for simultaneous measurement of amount fraction and stable isotope ratios in methane

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Introduction

Methane (CH_4) is the second most important anthropogenic greenhouse gas in terms of its impact on climate and current rates of emissions.

- It is integral to quantify emissions for the validation of CH_4 inventories.
- Each source of CH_4 is identified by distinct isotopic ratios which proves useful in attributing source sectors.
- **Boreas** is an automated preconcentrator system coupled to an infrared laser spectrometer
  - Continuous, high-frequency hourly $\delta^{13}C(CH_4)$ and $\delta^2H(CH_4)$ measurements of ambient air.

Objectives

- Develop a **method of validation** of Boreas measurements;
- Compare CH_4 amount fraction measurements against high-precision reference instrument (Picarro G2401) to evaluate Boreas measurement precision;
- Analyse source signatures of local pollution events using **Miller-Tans analysis** while developing a **method for background determination**.

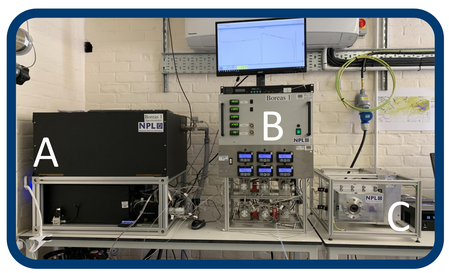

Figure 1: The Boreas methane (CH_4) preconcentration system (B-C) is coupled to a dual-laser spectrometer (A) for making simultaneous measurements of $\delta^{13}C(CH_4)$ and $\delta^2H(CH_4)$ in ambient air.

Measurement site

- Boreas measured at National Physical Laboratory (NPL), Teddington, U.K., (Dec 2020 – Feb 2021) → relocated to the tall tower site in Heathfield, East Sussex, U.K. (HFD) (Jun 2021-present).
- Boreas samples ambient air from 100m in hourly intervals. The Picarro G2401 measures from 50m and 100m at one-minute intervals.
- The regional characterisation of HFD is **semi-rural** with expected **agricultural and waste sources** and **minimal fossil fuel influence.**
- NPL is an **urban** area with expected **fossil-fuel and waste sources**.

Data and Methodology

Miller-Tans analysis

- Assumption of **single source mixed into background & non-constant background**:

$$\delta_a C_a - \delta_b C_b = \delta_s (C_a - C_b)$$

where a = atmosphere, s = source, b = background

Background method

- HFD site receives minimally polluted background air under certain conditions;
- Selected low points in amount fraction measurements before & after peak and applied an average;
- Confirmed as baseline conditions using the NAME back trajectory footprint (clean, westerly air).

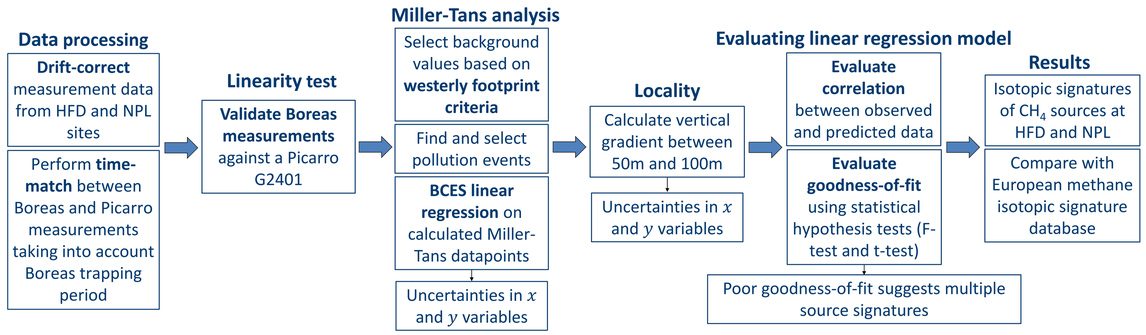

Figure 2: Diagram presenting the steps in data processing and analysis of the Boreas dataset.

Results

- Fig. 5 is the result of applying Miller-Tans analysis to an identified pollution peak with BCES (Y|X) linear regression.
- F- and t-tests on R^2 for both Fig. 5A and 5B concludes the correlation between the linear regression model and the dependent variable is **statistically significant** ($\boldsymbol{p < 0.05}$).

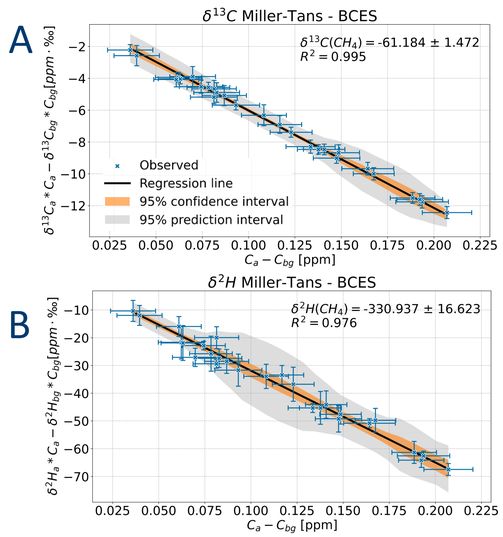

Figure 5: Application of the Miller-Tans method to an identified pollution event (27th June 2021) for A) $\delta^{13}C$ and B) δ^2H. Confidence and prediction bands and the error on the y-intercept are at a 95% confidence interval.

- HFD source signatures most align to **microbial** with sub-groups of **agriculture** and **waste** → expected for HFD's regional characterisation.
- NPL source signatures mostly align with **fossil fuel exploitation** with overlap into **microbial waste** sources.
  - Measurements are single source due to passing of statistical tests → Source signature could be fossil fuel **OR** microbial.

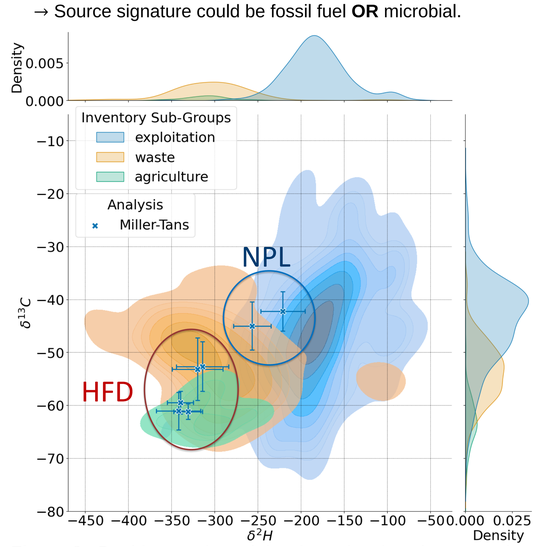

Figure 6: Dual-isotope kernel density estimation plot presenting the European Methane Database from Menoud et al. (2022) with the addition of the Miller-Tans analysis results datapoints from HFD and NPL monitoring sites.

Linearity Test

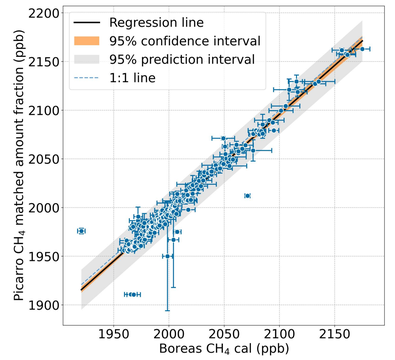

Figure 3: Measurements of Boreas amount fraction against a Picarro G2401 located at Heathfield.

Ensuring that Boreas amount fraction measurements are accurate by comparison to a Picarro G2401.

- Data from June 2021.
- Matched the time period of the measurements made in Boreas trapping period to those made by Picarro G2401.
- Measurements were found to be **strongly correlated** to the regression line, $\boldsymbol{r(221) = 0.974, p < 0.00001}$.
- **The degree of concordance is strong** between the variables, $\boldsymbol{r_c = 0.968}$

Time-series Data

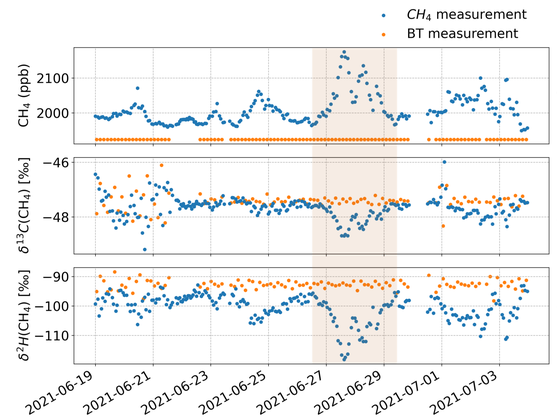

Figure 4: Sample of the Boreas dataset where BT refers to the standard atmospheric air tank retrieved from the background site in Mace Head, Ireland (MHD)

- Identified local pollution event used in this analysis is highlighted.
- Three consecutive peaks → all were found to be from same source.

Conclusion

- **Boreas has been validated against a Picarro G2401 and is shown to be capable of making high-frequency, high-precisions measurements of CH_4 suitable of source sector attribution.**
- **The Miller-Tans analysis method used in conjunction with the background method and BCES (Y|X) regression is capable of extracting source signatures with quantified uncertainties as in Fig. 6.**
- **Fig. 6 highlights the need for more continuous measurements to contribute to higher frequency modelling in order to disentangle the source signature overlap.**

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