Evaluation of continuous $\delta^{13}CH_4$ measurements in Heidelberg and at Schauinsland, Germany

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Measurement sites Heidelberg & Schauinsland

In **Heidelberg** (116m a.s.l.), south-west Germany, a CRDS G2201-i analyser has been used to continuously measure CH_4 and its $^{13}C/^{12}C$ ratio in ambient air at the Institute of Environmental Physics (IUP) since 2014. Heidelberg is in the North of the Upper Rhine valley, east of the low mountain range Odenwald and in the west of agricultural areas. The industrial cities Mannheim and Ludwigshafen are 15-20 km north-west.

At the mountain station **Schauinsland** (1205m a.s.l.), operated by the German Environment Agency (UBA), the CH_4 mole fraction is measured since 1992. Schauinsland is on the edge of the black forest to the Rhine valley, south-east of the city Freiburg im Breisgau. Two measurement campaigns were performed at Schauinsland with the CRDS G2201-i analyser to monitor continuous $\delta^{13}CH_4$ measurements at a semi-rural station.
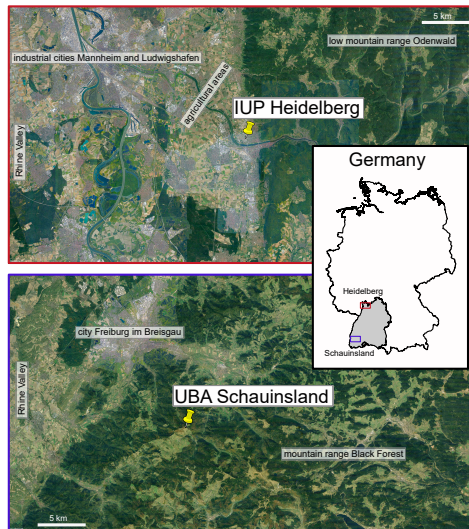
Map data: Google Earth, 2020 Google, Image Landsat/Copernicus, 2020 GeoBasis-DE/BKG.

# Isotopic composition of methane

The isotopic composition can be described using the δ-notation. The CH_4 mole fractions were calibrated against the WMO scale (Dlugokencky et al., 2005) and the $\delta^{13}CH_4$ values of calibration gases were analysed at Max-Planck-Institute for Biogeochemistry (MPI-BGC) in Jena (Sperlich et al., 2016). These analyses connect our Heidelberg measurements to the VPDB (Vienna Pee Dee Belemnite) isotope scale.

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \cdot 1000\ ‰ \qquad \text{with} \qquad {}^{13}R = \frac{\left[{}^{13}CH_4 \right]}{\left[{}^{12}CH_4 \right]}$$

Analyses of the isotopic composition of CH_4 in ambient air can potentially be used to differentiate between different CH_4 source categories. Isotopic signatures of CH_4 sources in the surrounding of Heidelberg were characterised (Hoheisel et al. 2019) and shown in the right figure.

CH_4 emission enhancements measured in Heidelberg can origin from biogenic sources like dairy cows in the nearby farms and waste water treatment plants, thermogenic sources from the natural gas distribution system and even pyrogenic sources like traffic.
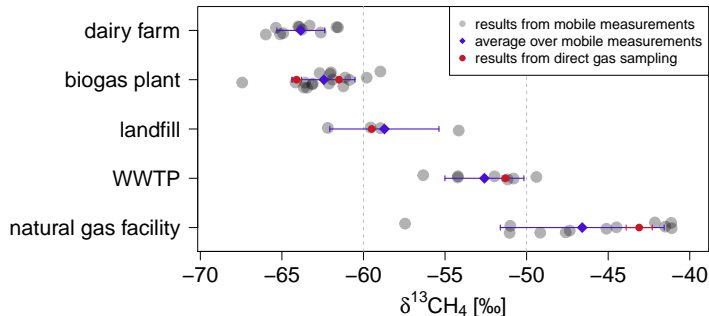
Continuous CH_4 and $\delta^{13}CH_4$ measurements in Heidelberg

Since April 2014 CH_4 and $\delta^{13}CH_4$ are measured continuously with a CRDS analyser in Heidelberg. The daily mean CH_4 mole fraction varies between 1890 and 2310 ppb with higher spikes in winter than in summer.

A seasonal cycle can be noticed. The maximum mean CH_4 mole fraction occurs in late autumn (October-December). During winter and spring the mole fraction decreases slightly to the minimum in late summer (June-August). The high CH_4 mole fractions in winter occur especially due to climatological conditions like long lasting inversions, a much lower boundary height and longer continental residence times of air masses due to high pressure systems.

$\delta^{13}CH_4$ shows more depleted values in autumn (Sep-Nov) and more enriched ones in spring (Mar-May).
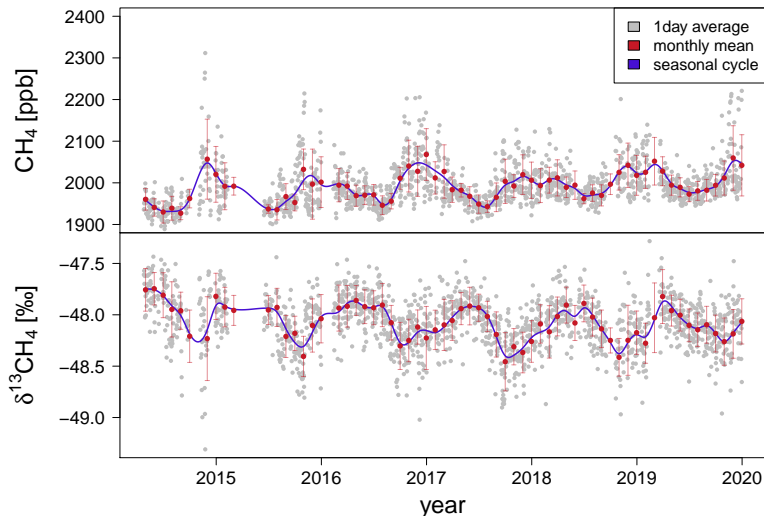
Comparison of CH_4 and $\delta^{13}CH_4$ at different sites

The CH_4 mole fractions measured in Heidelberg (HD) and Schauinsland (SSL) are higher than at the background station MaceHead (MHD). As Heidelberg is an urban station located in the Rhine Valley, the seasonal variations of the measured CH_4 mole fraction at Heidelberg vary much stronger than at the mountain station Schauinsland.

Similar to Heidelberg, the CH_4 mole fraction at Schauinsland is lowest in summer, increases in autumn and decreases in spring. However, in winter the CH_4 mole fraction at Schauinsland is lower again as the mountain station is often above the boundary layer during this season. The orange data points show the mean mole fraction and isotopic composition of CH_4 measured at Schauinsland during two measuring campaigns. The mean CH_4 mole fraction measured during these campaigns was lower than the mean of the corresponding months. However, the $\delta^{13}CH_4$ values follow well the ones measured in Heidelberg.

The $\delta^{13}CH_4$ values at Heidelberg showed clearly more depleted values than in Mace Head. An offset of 0.28‰ is subtracted from the MaceHead data (White et al. 2018) to take into account the measurement offsets among the laboratories INSTAAR and MPI-BGC (Umezawa et al. 2018).
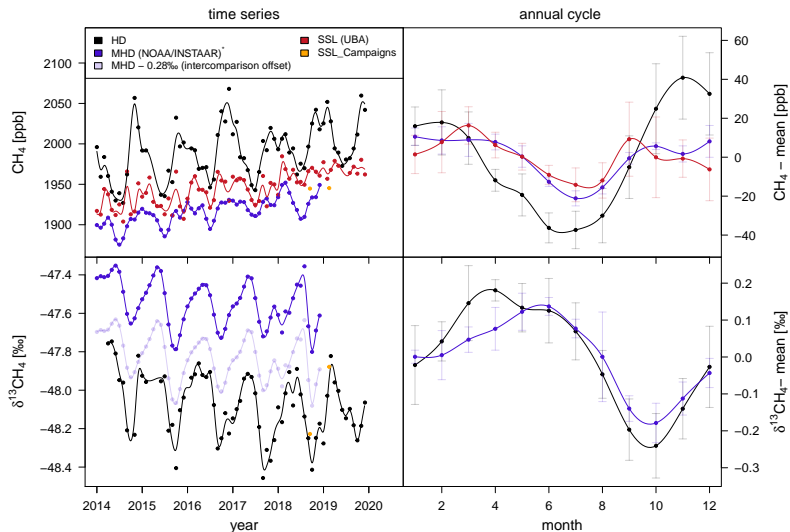

* Dlugokencky et al. 2019 (https://doi.org/10.15138/VNCZ–M766), White et al. 2018 (ftp://aftp.cmdl.noaa.gov/data/trace_gases/ch4c13/flask/)

Diurnal cycle at Heidelberg and Schauinsland

The mean diurnal CH_4 cycle in Heidelberg shows a 10 times larger amplitude than at the mountain station Schauinsland. The daily variations of CH_4 in Heidelberg show large seasonal differences whereas the diurnal variations in $\delta^{13}CH_4$ are comparable during the year.

At Schauinsland, no mean diurnal variation can be noticed in $\delta^{13}CH_4$ for both measurement campaigns.

The evaluation of the mean source signature at Schauinsland is even more challenging than for Heidelberg due to the much lower diurnal variability.


diurnal cycle at Heidelberg (2014–2019)

diurnal cycle at Schauinsland (2014–2019)
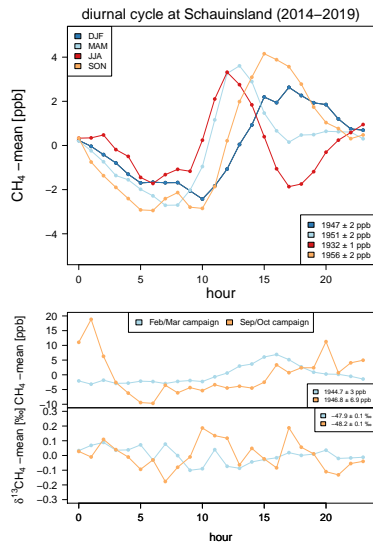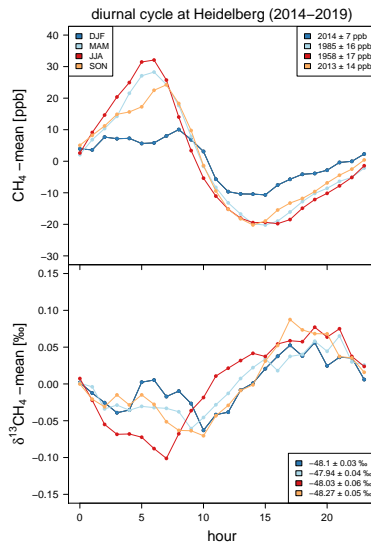
Determination of the mean isotopic source signature

In the Heidelberg CH_4 record, we can identify three typical dependencies of CH_4 and $\delta^{13}CH_4$.

1. CH_4 increase and $\delta^{13}CH_4$ decrease (black)
   $\rightarrow$ added CH_4 is less enriched (e.g. dairy farms)

2. CH_4 increase and $\delta^{13}CH_4$ increase (blue)
   $\rightarrow$ added CH_4 is more enriched (e.g. natural gas facilities)

3. CH_4 increase and $\delta^{13}CH_4$ constant (red)
   $\rightarrow$ added CH_4 is nearly the same than the background CH_4

However, in the last case, the added CH_4 is most likely a gas mixture of different sources.

The precision of the isotopic source signature calculation using the Keeling or Miller-Tans approach strongly depends on the CH_4 peak height and instrumental precision. Therefore, we use only Miller-Tans approach with CH_4 enhancements larger than 50ppb. Different methods such as monthly/daily interval evaluations and moving Miller-Tans approaches (Röckmann et al. 2016) have been used to calculate the isotopic source signature in ambient air.
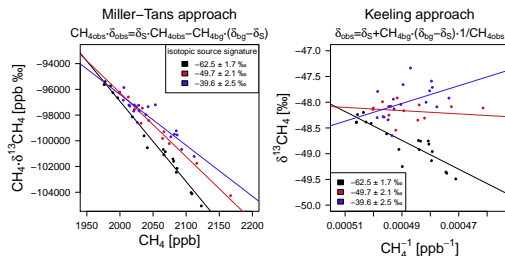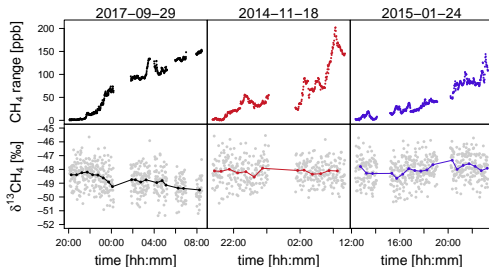
Mean isotopic source signature in Heidelberg

We applied several methods to determine the isotopic CH_4 source signature in Heidelberg. For the left panel a Miller-Tans approach is applied for each month. For the middle panel a Miller-Tans approach is used for each diurnal cycle. And on the right side moving Miller-Tans plots with time spans of 6,8,10 and 12h were applied. For each of these three methods (monthly, daily and moving) the isotopic signatures are calculated in two different ways. First we apply the York fit to the data without assuming a background (black). The red data corresponds to isotopic source signatures calculated using a simple OLS fit with fixed intercept at 0 and determined background data (mean of a 48h interval using only daytime data).

All methods show similar results. The monthly isotopic methane source signatures of ambient air in Heidelberg was found to be between -63‰ and -41‰, with an average value of (-53 ± 2)‰. An annual cycle can be noticed with more depleted values (-56‰) in summer and more enriched values (-51‰) in winter. This indicates a larger contribution of biogenic sources in summer and thermogenic sources (e.g. natural gas) in winter.
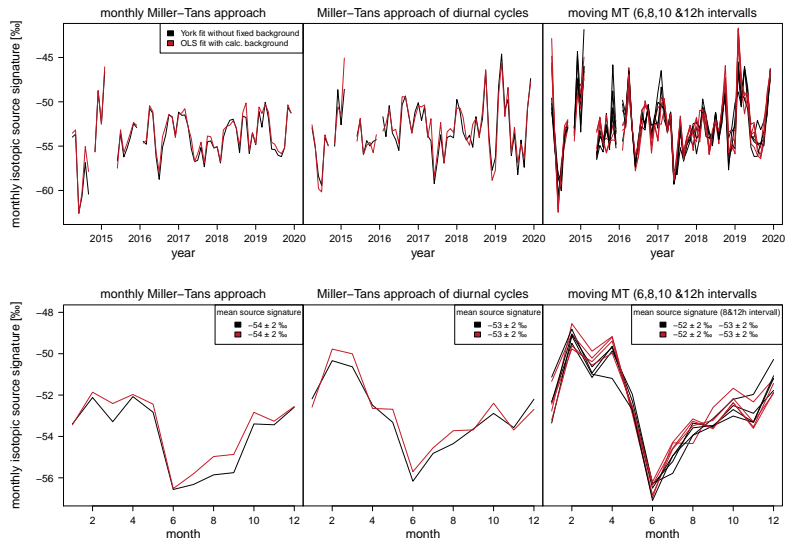
Mean isotopic source signature at Schauinsland

The mean isotopic source signature calculated at Schauinsland shows variations, too, with more enriched values (-57‰) in winter and more depleted (-60‰) ones in autumn. The more depleted values in summer/autumn at Schauinsland correspond to more biogenic methane and can be explained by dairy cows grazing near the station especially during this time.
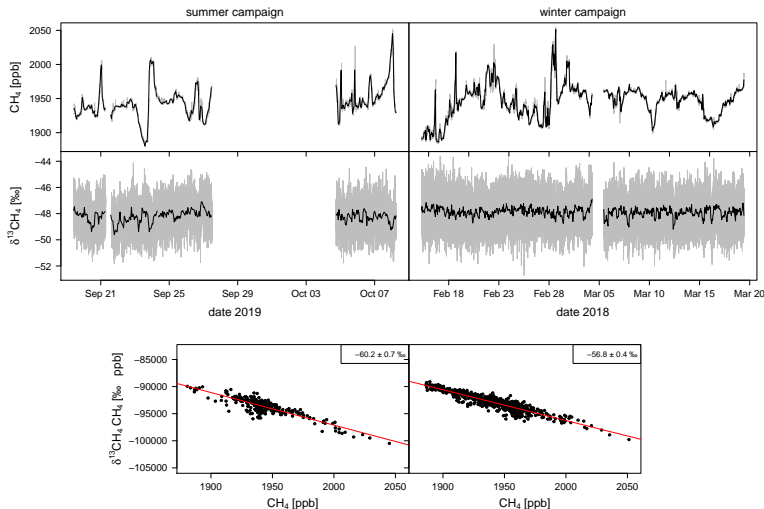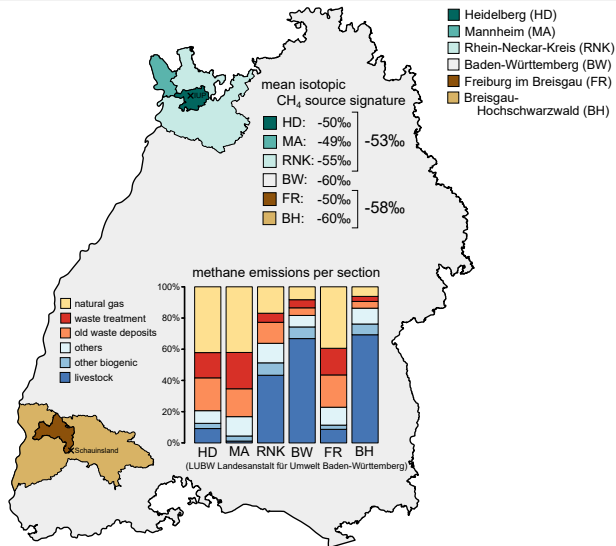
Comparison with emission inventory of LUBW

The generally more enriched values at Schauinsland are caused by the more rural surrounding. Emission estimates of counties provided by the Landesanstalt für Umwelt Baden-Württemberg (LUBW) show that around Schauinsland 60% of the CH_4 emissions are emitted by livestock farming and around Heidelberg only 28%.

The mean isotopic composition of the CH_4 emissions for Heidelberg and Schauinsland are calculated using the inventory provided by the LUBW and isotopic source signatures measured for CH_4 sources in the surrounding (Hoheisel et al. 2019). The determined mean isotopic source signature for Heidelberg is $(-53 \pm 2)‰$ and for Schauinsland $(-58 \pm 2)‰$.

These results agree well with the mean source signatures determined out of continuous isotopic measurements with values between $-41‰$ and $-63‰$ (mean $-53 \pm 2‰$) for Heidelberg as well as $-57‰$ and $-61‰$ for Schauinsland.

Heidelberg (HD)
Mannheim (MA)
Rhein-Neckar-Kreis (RNK)
Baden-Württemberg (BW)
Freiburg im Breisgau (FR)
Breisgau-Hochschwarzwald (BH)

mean isotopic CH_4 source signature

HD:	-50‰	
MA:	-49‰	-53‰
RNK:	-55‰	
BW:	-60‰	
FR:	-50‰	-58‰
BH:	-60‰	

methane emissions per section

natural gas
waste treatment
old waste deposits
others
other biogenic
livestock

HD MA RNK BW FR BH
(LUBW Landesanstalt für Umwelt Baden-Württemberg)

Conclusion and Outlook

Conclusion

- the measured CH_4 mole fraction and $\delta^{13}CH_4$ in Heidelberg show clear annual and diurnal variations
- the measured diurnal variations of the CH_4 mole fraction at Schauinsland are much smaller, which made the determination of the mean source signatures more challenging than in Heidelberg
- the measured $\delta^{13}CH_4$ values at Schauinsland measured during two campaigns followed the seasonal cycle in Heidelberg
- the mean isotopic source signature in Heidelberg shows an annual cycle with more enriched values in winter (-51‰) and more depleted ones in summer (-56‰).
- annual source signatures calculated using county emission inventory provided by LUBW and determined signatures for different sources around Heidelberg (HD: -53±2‰, SSL: -58±2‰) agree well with the values determined out of atmospheric measurements

Outlook

- further improvement of the method and selection criteria to determine the mean isotopic source signature
- analysis of wind pattern and trajectories
- determination of mean isotopic source signature using MaceHead as background

References & Acknowledgements

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