Methane (CH_4) sources in Krakow, Poland: insights from isotope analysis

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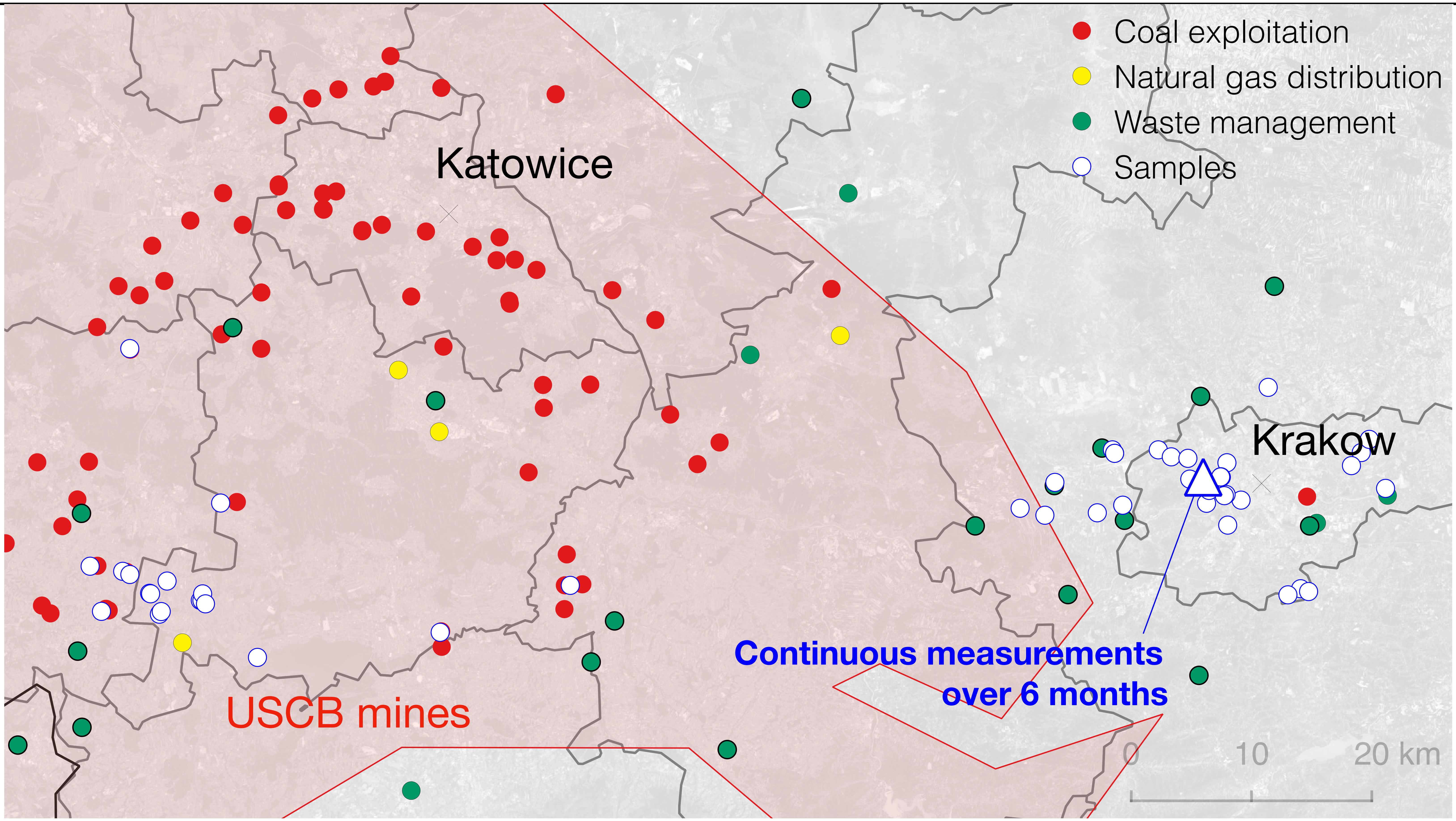


Context: CH_4 emissions from coal mines

The **Upper Silesia Coal Basin** (USCB): 72.5% of European methane emissions related to underground mining and related operations (https://prtr.eea.europa.eu)

Measurements of CH_4 isotopes

Continuously in Krakow

Discrete samples

-> Source attribution

Modelling of CH_4 isotopes

Use of emission inventory

-> Evaluation of the reported source contributions

All key findings

Utrecht University

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 722479.

CH_4 mole fractions and wind directions during the continuous measurements period

$\delta^{13}C$ and $\delta^{2}H$ time series using a continuous flow mass spectrometry system (IRMS)

High precision data obtained at ~1h- resolution over 6.5 months in Krakow

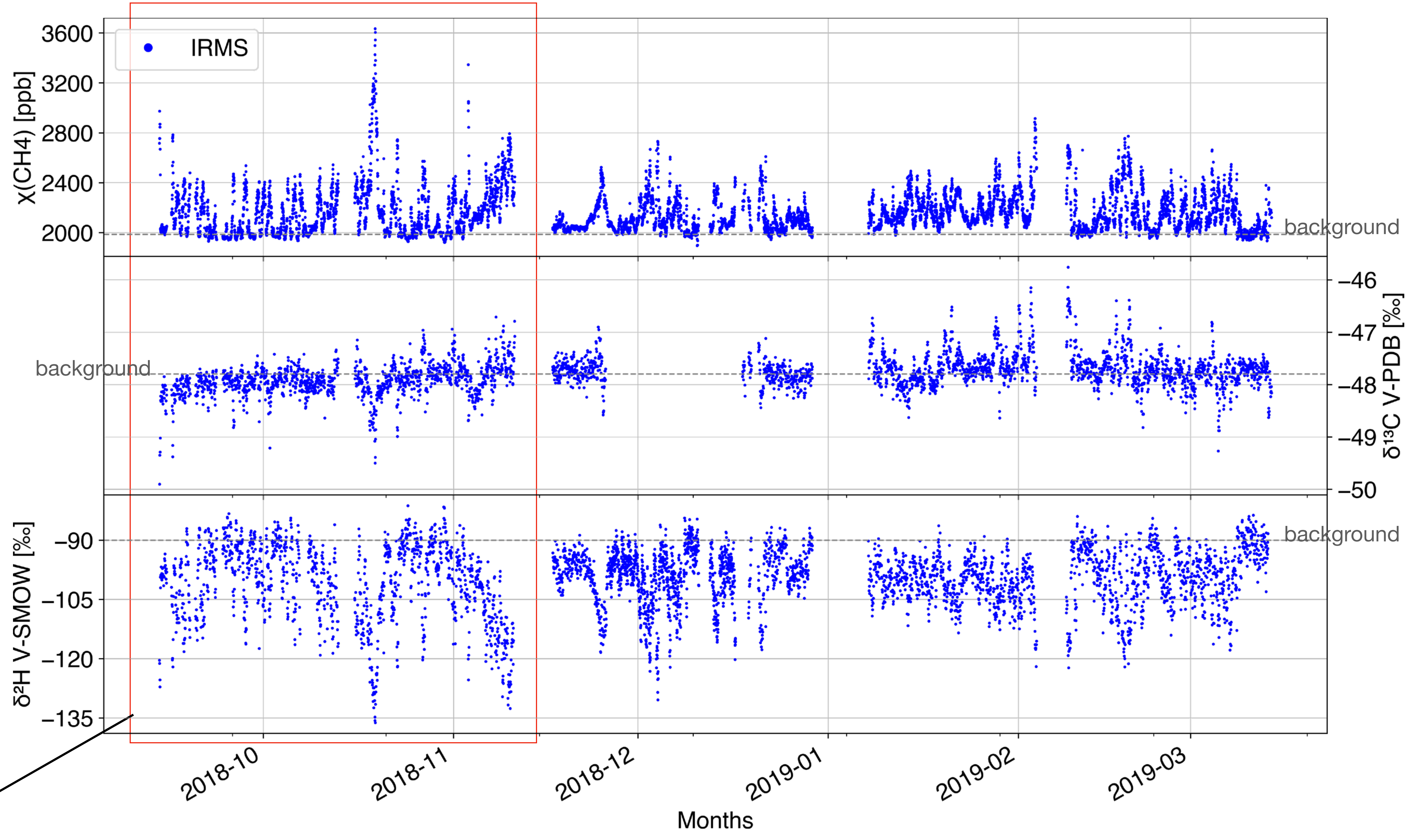
Background:

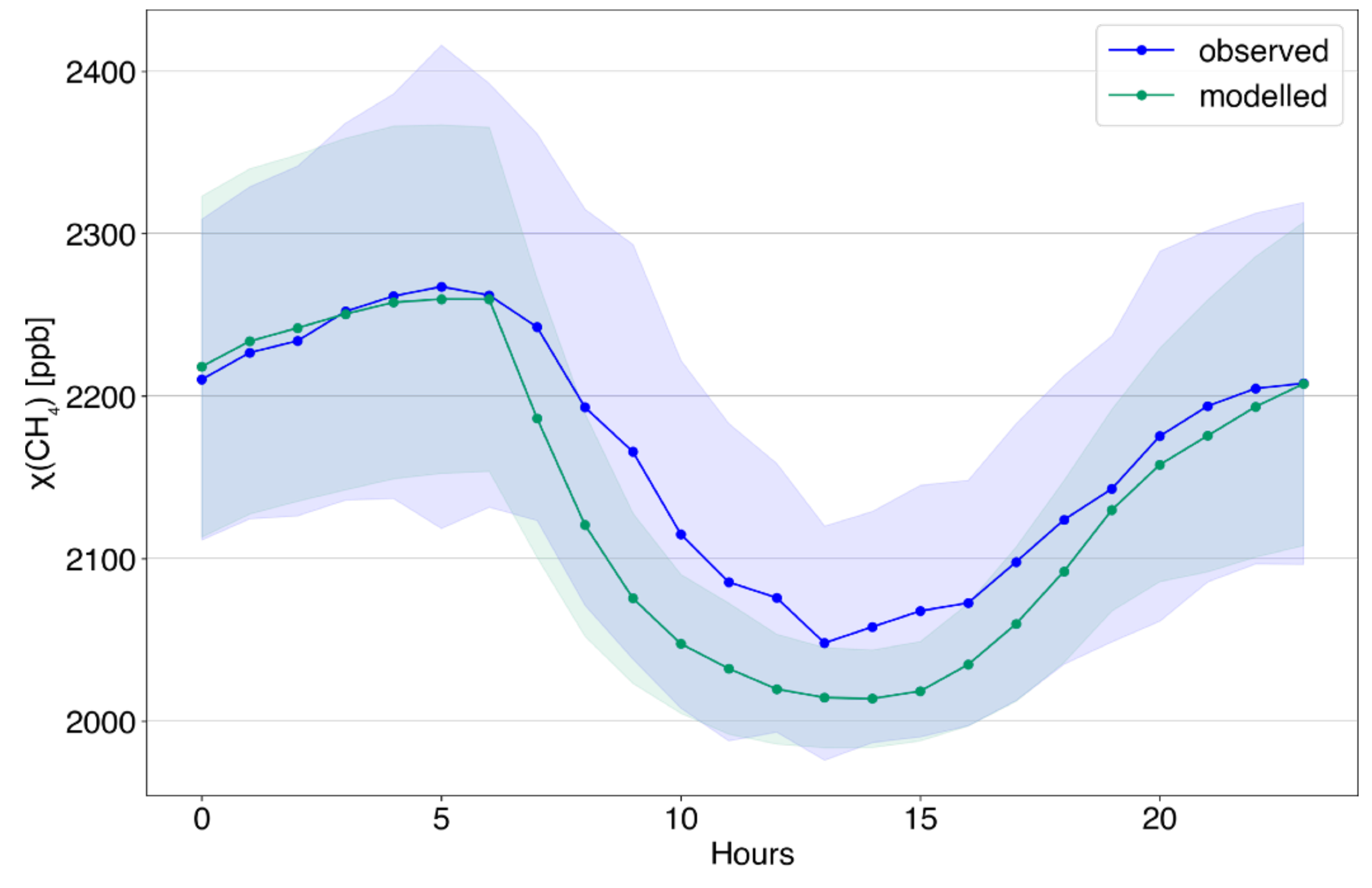
$\chi(CH_4)$ < 1986.0 ppb (10th lower perc.)

$\delta^{13}C$ = -47.8 ± 0.16 ‰ VPDB

$\delta^{2}H$ = -90.0 ± 3.0 ‰ VSMOW

CH$_4$ enhancements occurring every night

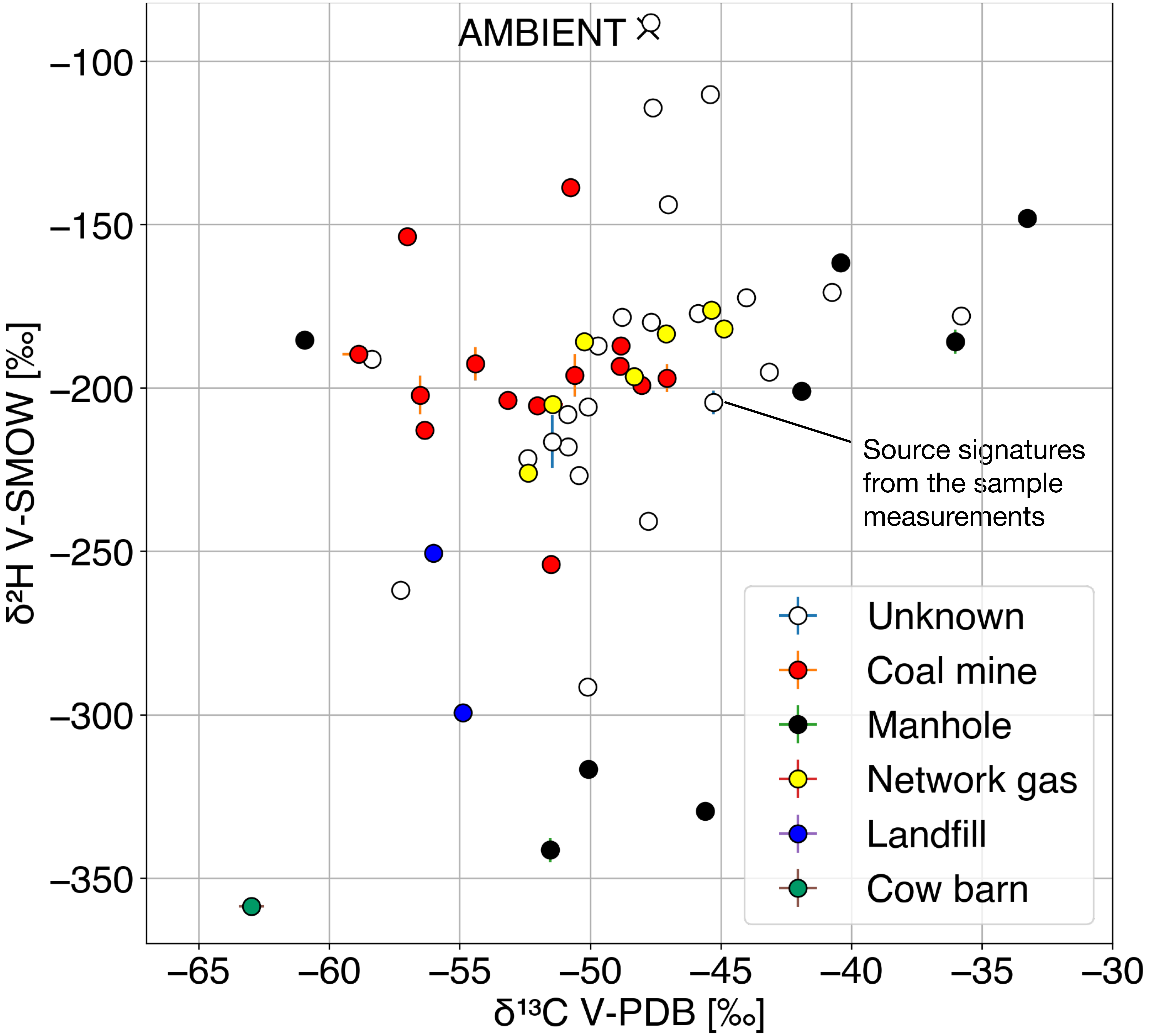




Diurnal cycle: CH$_4$ accumulation during the night

How was this modelled?

Regional source characterisation using $\delta^{13}C$ and $\delta^{2}H$ signatures in CH_4



Samples were taken during mobile surveys in:

- USCB[1] in May 2018, around coal mine shafts
- The surroundings of Krakow: urban (residential & industrial) and rural environments

Source signatures are derived from the sampled plumes (n=57) using the Keeling plot method.

The use of δ^{2}H allows us to distinguish fossil fuel and biogenic related sources

δ^{13}C allows us to distinguish between the types of fossil fuel sources

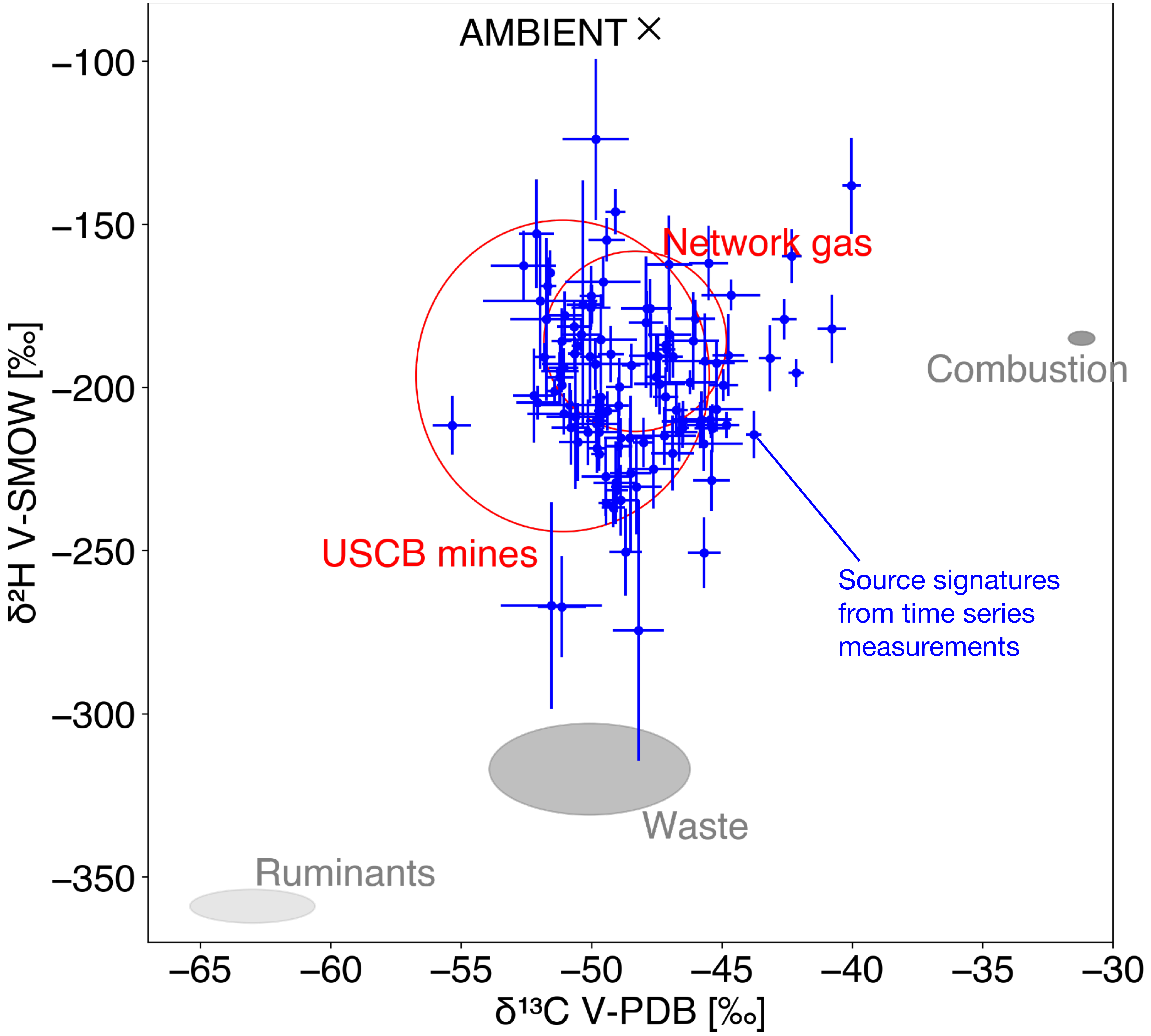
Coal mines average δ^{13}C = -51 ‰

Natural gas average δ^{13}C = -48.5 ‰

Compare with time series

[1]Upper Silesia Coal Basin

Source attribution using $\delta^{13}C$ and $\delta^{2}H$ signatures in CH_4



Source signatures are derived from the **time series measurements** (n=114 peaks), applying the Keeling plot method.

Average **$\delta^{13}C$ = -48.3 ± 2.9 ‰ VPDB**

$\delta^{2}H$ = -204 ± 27 ‰ VSMOW

They are compared with ranges of values for the different sources **sampled in the surroundings**, and verified by literature values.

Fossil fuel related CH_4 emissions were the main contributor

-> Wind directions point at Silesian coal mines, but the use of natural gas in the urban area of Krakow is also an important source.

See sample signatures

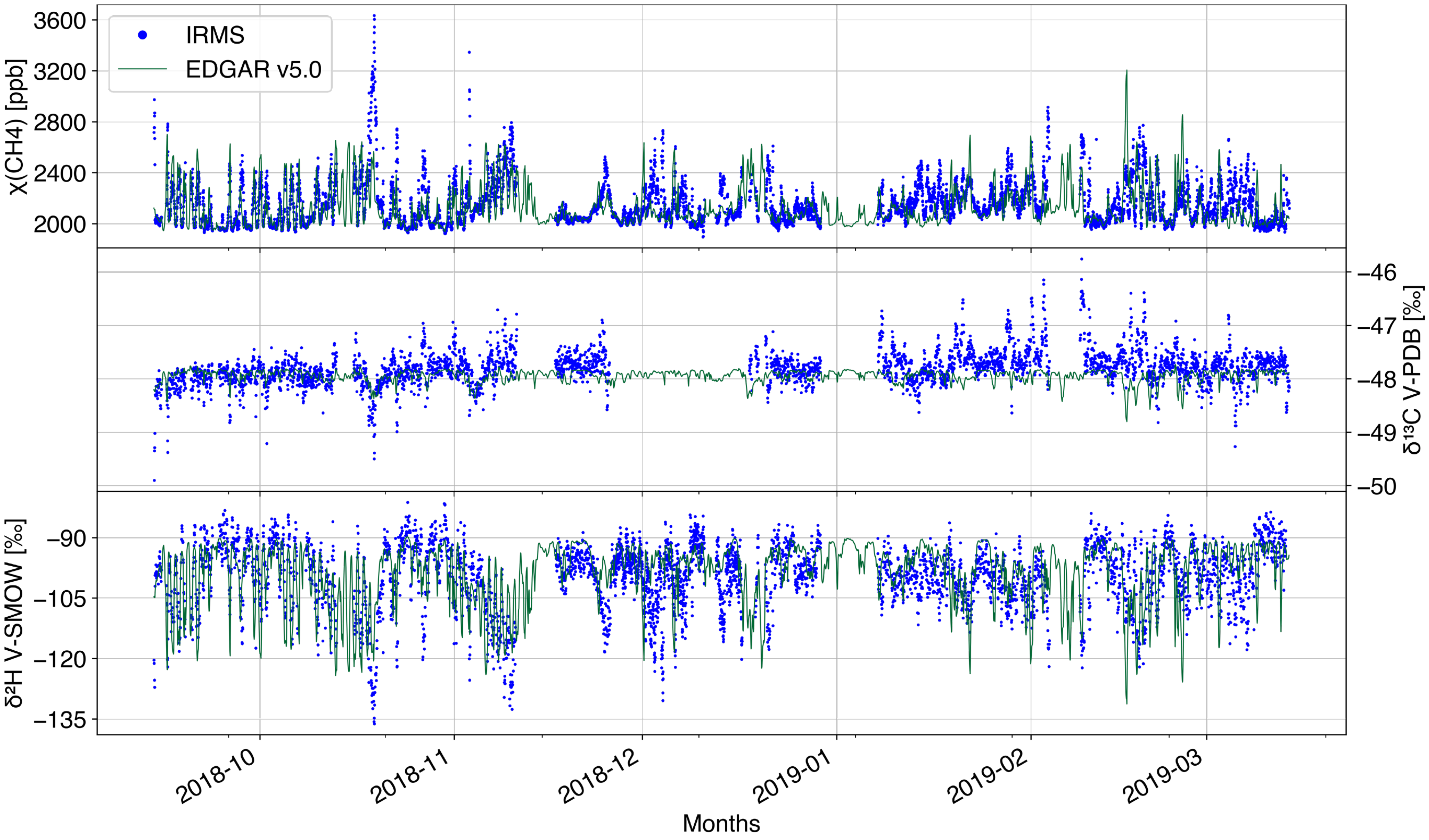
Modelling of $\delta^{13}C$ and $\delta^{2}H$ using the CHIMERE atmospheric transport model

Horizontal resolution of 0.1° x 0.1° in a domain covering Poland and nearby countries.

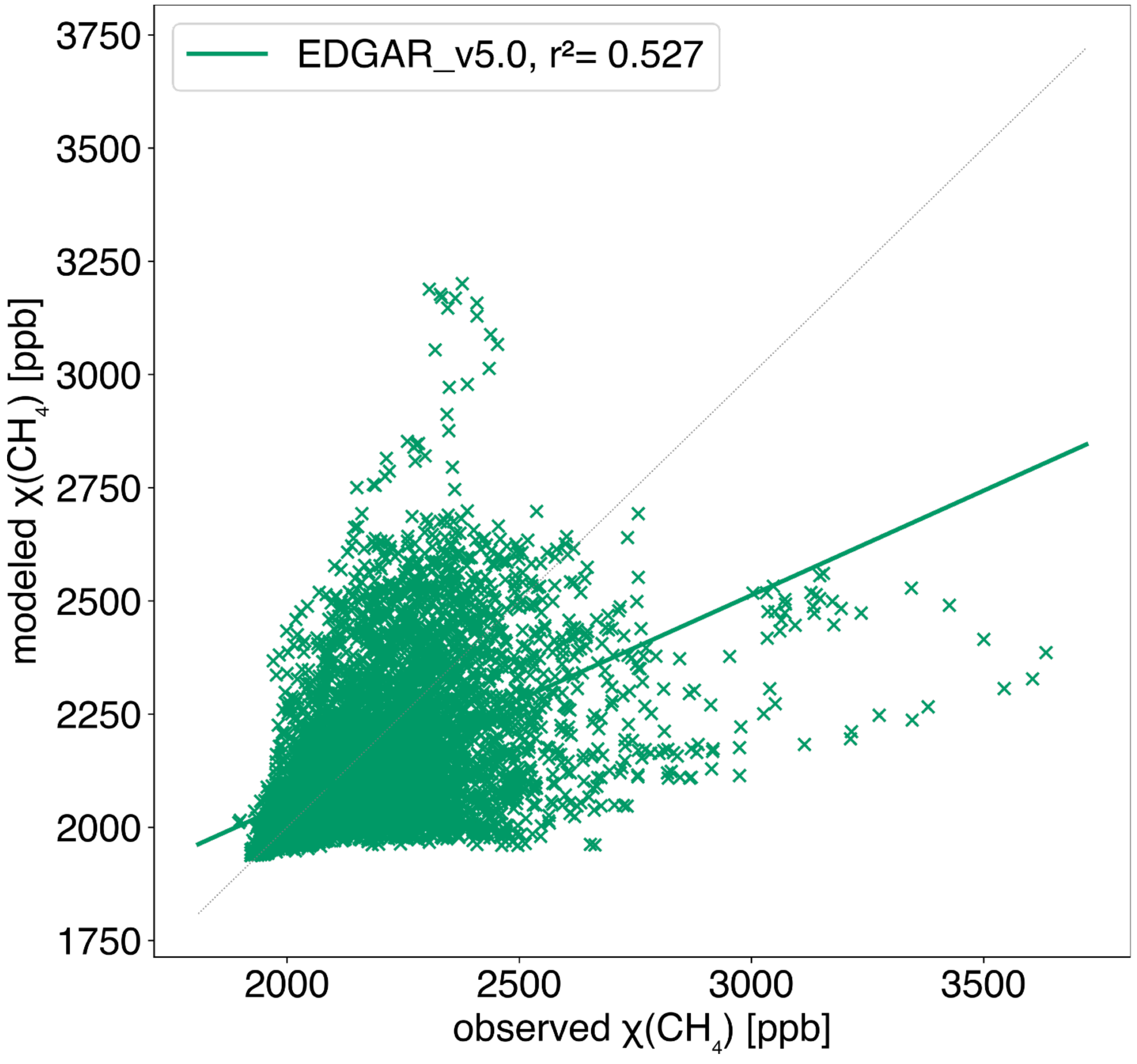
Use of EDGAR (Emission Database for Global Atmospheric Research) v5.0. With source isotopic signatures assigned to 7 source categories:

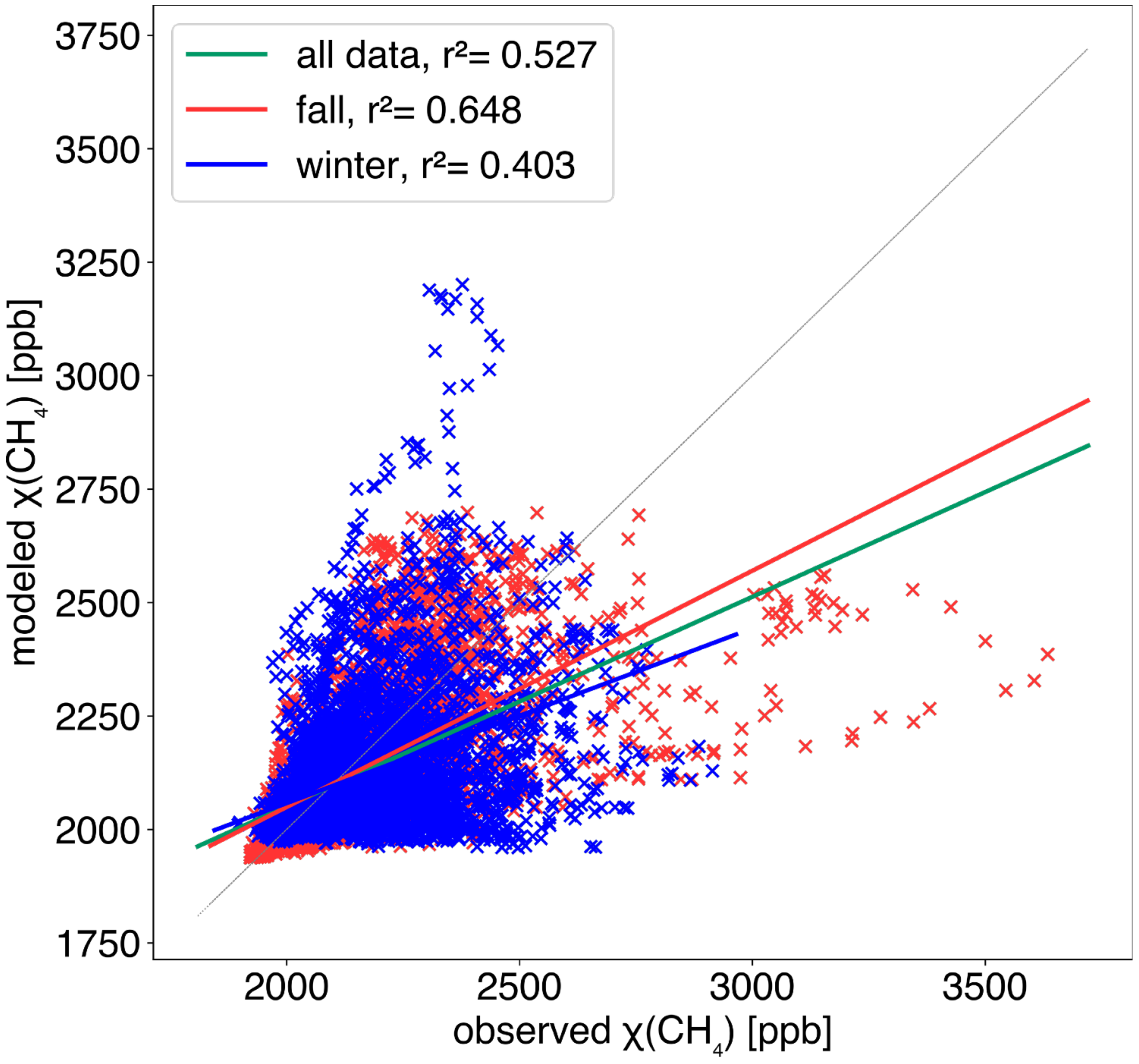
	d13C [‰]	d2H [‰]
Agriculture	-63	-359
Waste	-51.6	-299
Fossil fuels -coal	-51	-192
Fossil fuels -gas	-48.5	-194
Non-industrial combustion	-32.1	-185
Other anthropogenic*	-49.3	-193
Wetlands	-73.2	-323

* Mainly industry & transport



Model performances for time series of CH_4 mole fractions





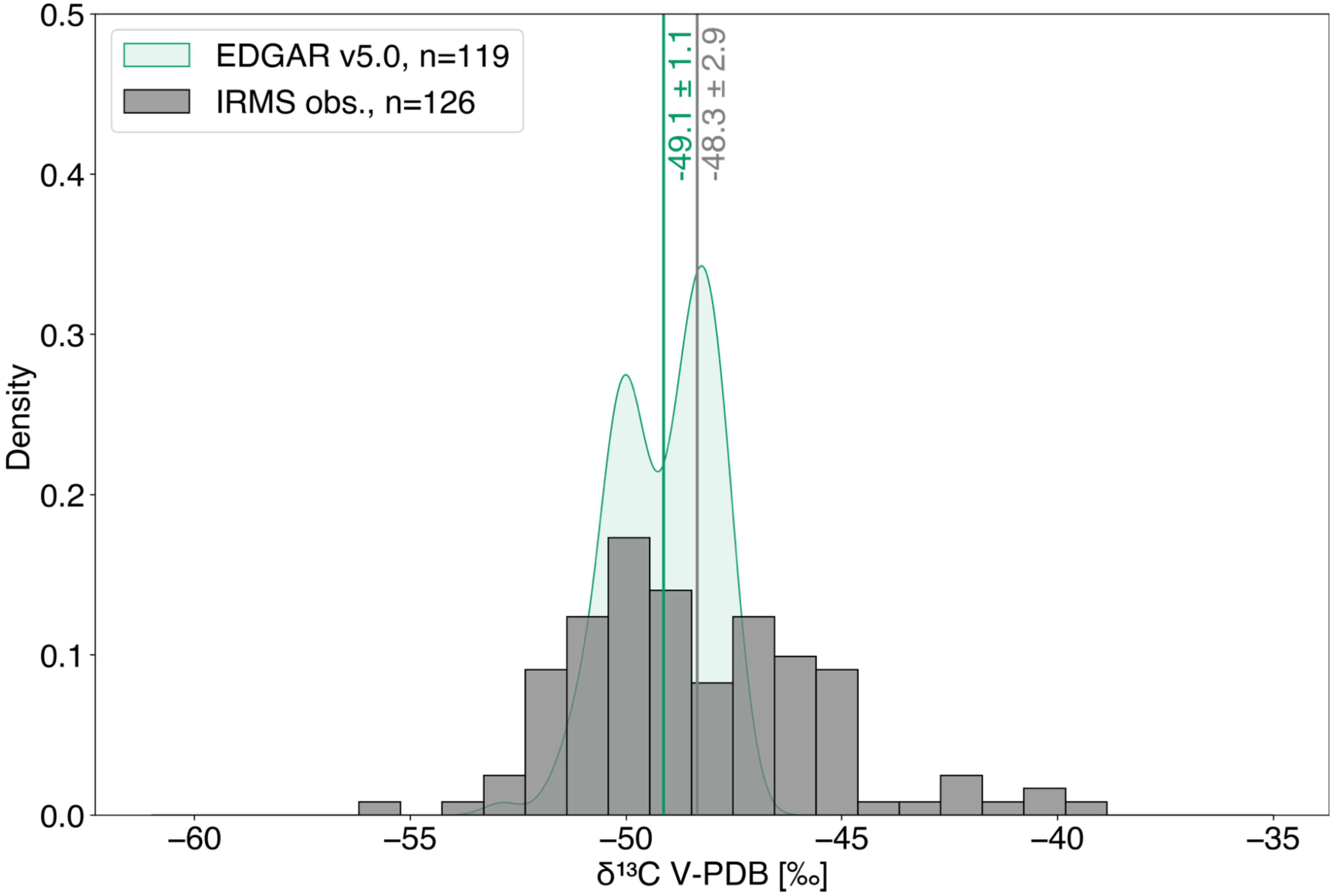
Before Nov. 15th, 2018 (fall):
Better agreement because of the more regular pattern in CH_4 enhancements.

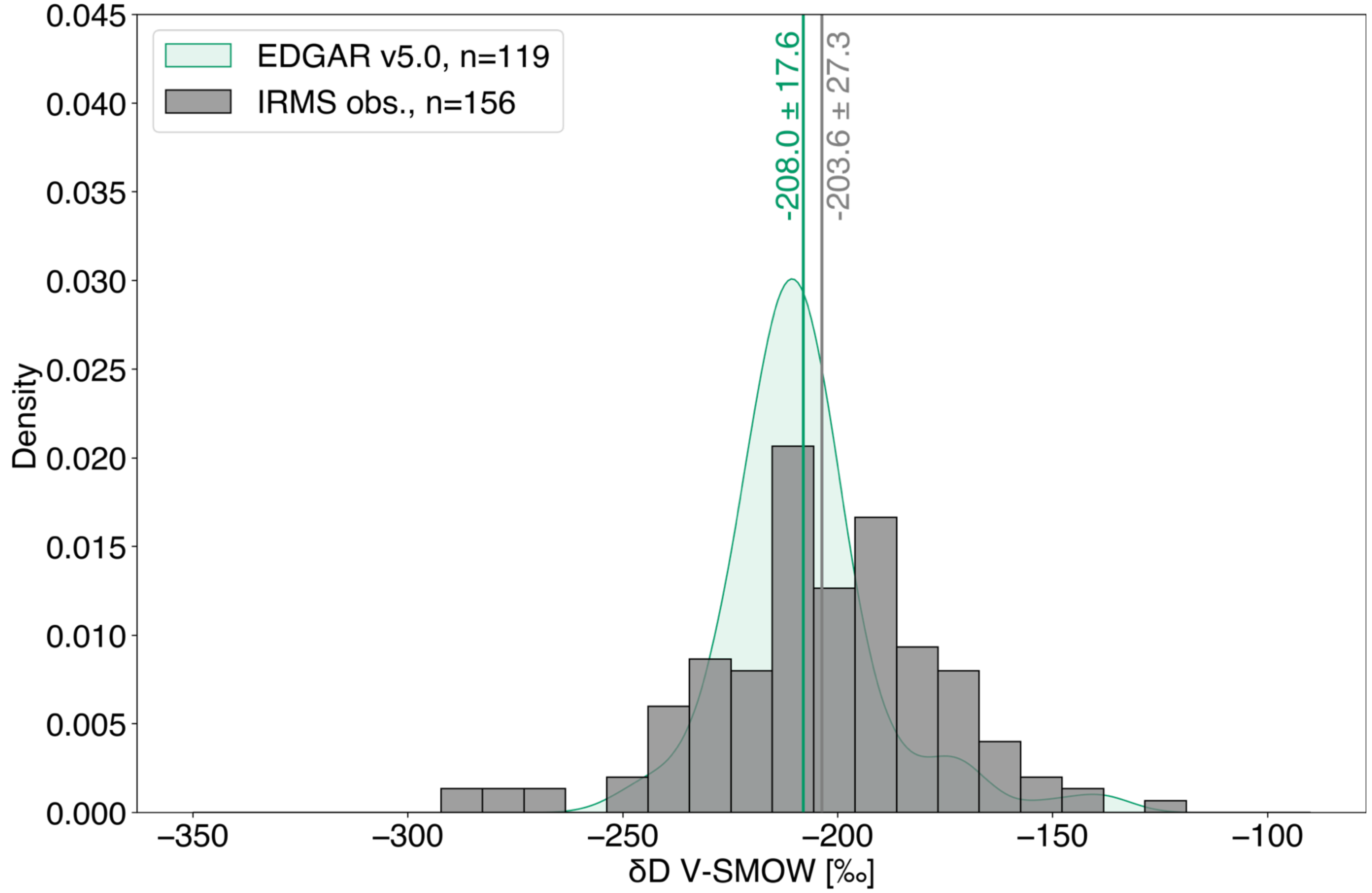
After Nov. 15th (winter):
Mismatches in the timing of CH_4 enhancements

Overall $\chi(CH_4)$ are under-estimated in the model

Root mean square error (RMSE)
= 164.4 ppb

$\delta^{13}C$ and $\delta^{2}H$ isotopic signatures in CH_4, for all peaks derived from both observed and modelled time series



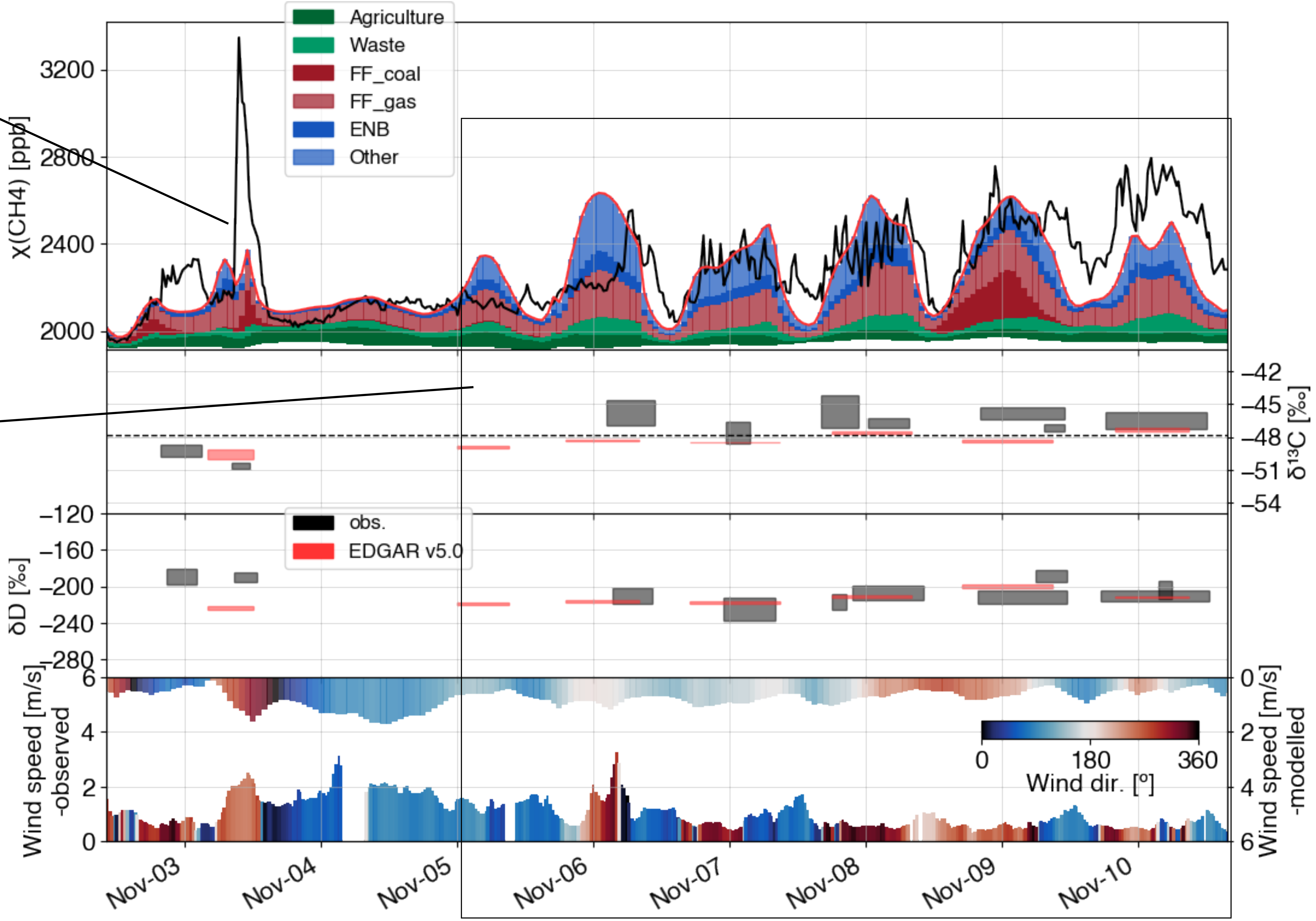


- The model does not fully reproduce the observed variability of isotopic signatures, caused by secondary processes related to transport (diffusion, oxidation, …). To assign one fixed signature value to a reduced number of source categories is the main cause for this discrepancy.
- The under-estimated emissions must be of relatively enriched sources in both $\delta^{13}C$ and $\delta^{2}H$.

Use of fossil fuel (distribution/combustion) might be under-estimated in the inventory

Zoom-in: November 2018

Single pollution event, different from the diurnal cycle
-> Isotopes suggest **coal mining emissions**



<u>Eastern winds</u>, at low speeds, reflects **CH_4 emissions** within the urban area of Krakow

-> Relatively enriched $\delta^{13}C$ in CH_4

Local emissions likely dominated by the use of fossil fuel (natural gas network, power generation, industries)

Zoom-in: February 2019

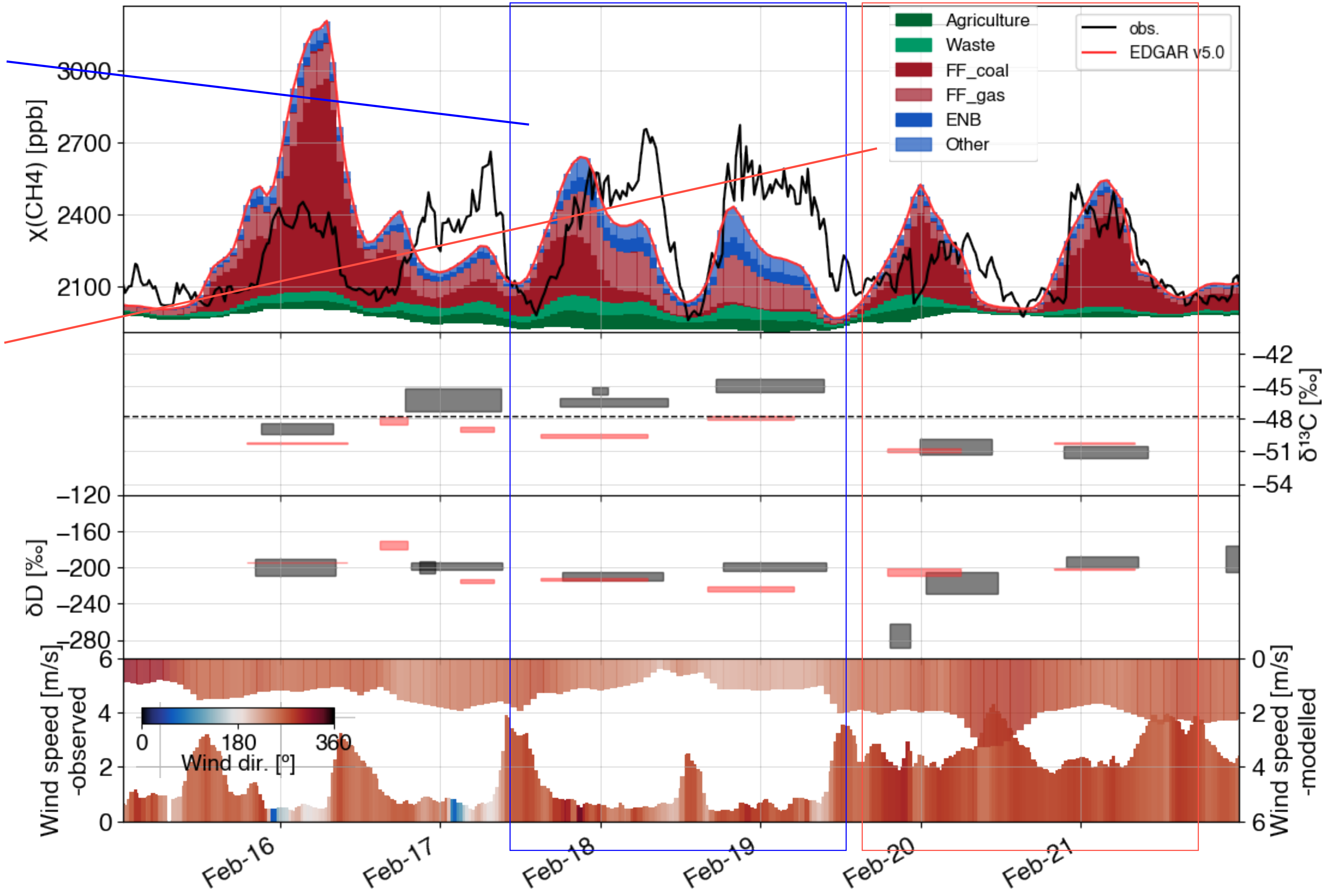
- Low wind speeds reflects **local CH_4 emissions** (see Nov. 2018)

-> the isotopic signature of local sources are less precisely defined in the model

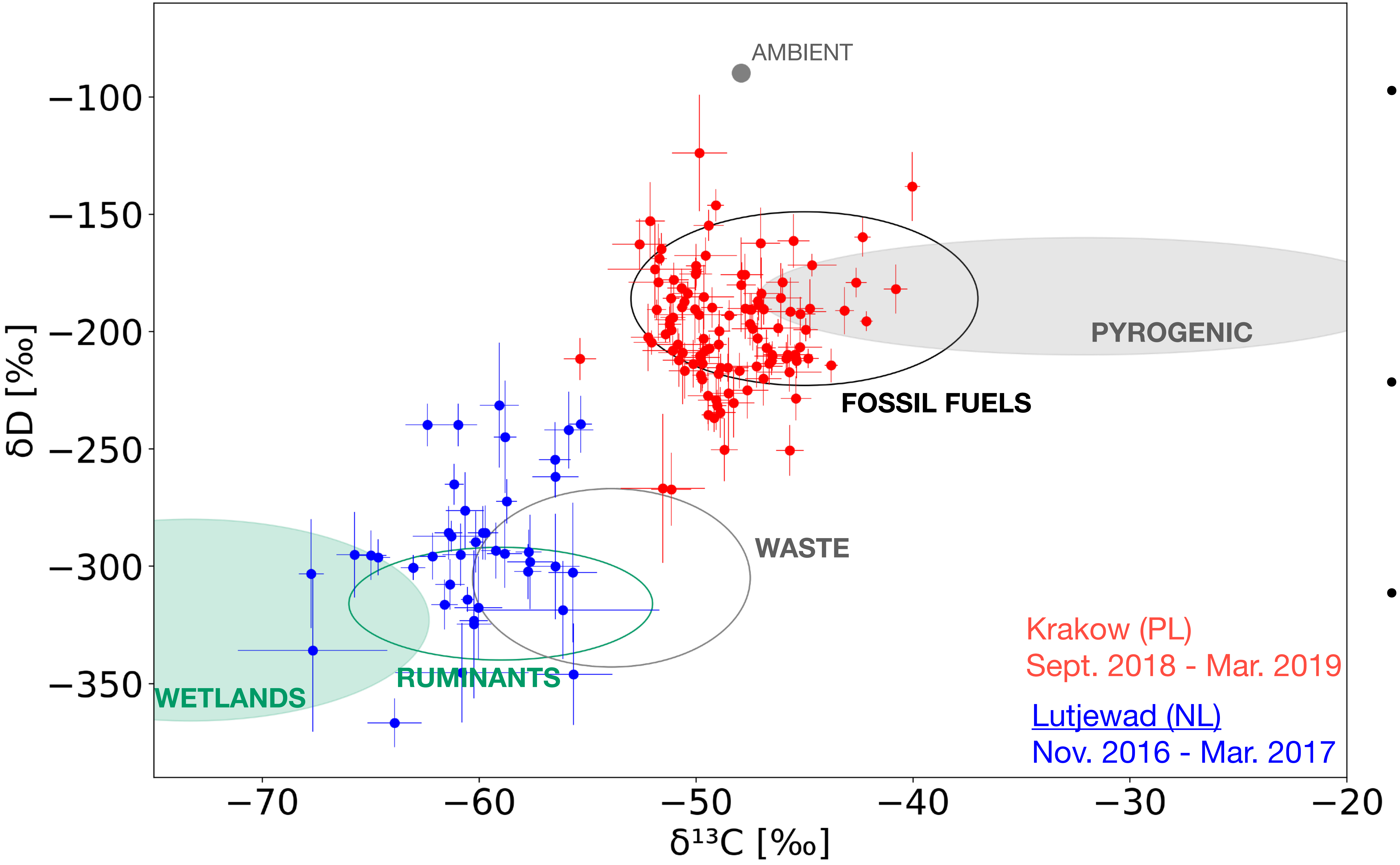
- Strong winds from the west reflect emissions from **coal mining activities**

-> can be distinguished by the relatively depleted $\delta^{13}C$ in CH_4

CH_4 from coal mining activities dominate when wind comes from the west, pointing at the USCB



Isotopic variations between different regions in Europe



- CH_4 emissions from different human activities: cattle farming in the Netherlands, exploitation of fossil fuels in Poland
- **Significant difference in average isotopic signatures across Europe**
- Analysis of isotopologues helps constrain local to regional budgets

Key findings

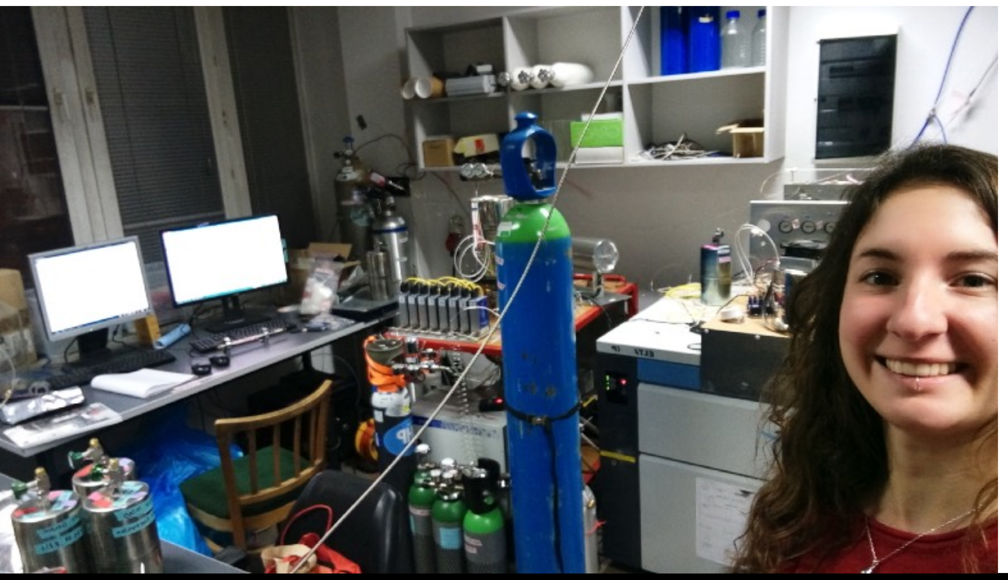
CH_4 enhancements occurring **every night**, larger isolated pollution events also occurred → CH_4 from coal mining activities dominate when wind comes from the west, pointing at the USCB

The use of δ^2H allows us to distinguish fossil fuel and biogenic related sources → Fossil fuel related CH_4 emissions were the main contributor

δ^{13}C allows us to distinguish between the types of fossil fuel sources → Emissions in the Krakow urban area are from the use of fossil fuel (natural gas network, power generation, industries)

↓

They might be under-estimated in the inventory



Interested in the technical aspects? Check out the **blog** on our lab installation.
We've written a **scientific article**, now available for discussion!
Suggestions? Questions? Don't hesitate to contact me: m.menoud@uu.nl

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Method

Determination of an isotopic source signature from air measurements: the Keeling plot

Mass balance equations:

$$c_a = c_b + c_s$$

$$c_a\delta_a = c_b\delta_b + c_s\delta_s$$

Re-arranging:

$$\delta_a = c_b * (\delta_b - \delta_s)(1/c_a) + \delta_s$$

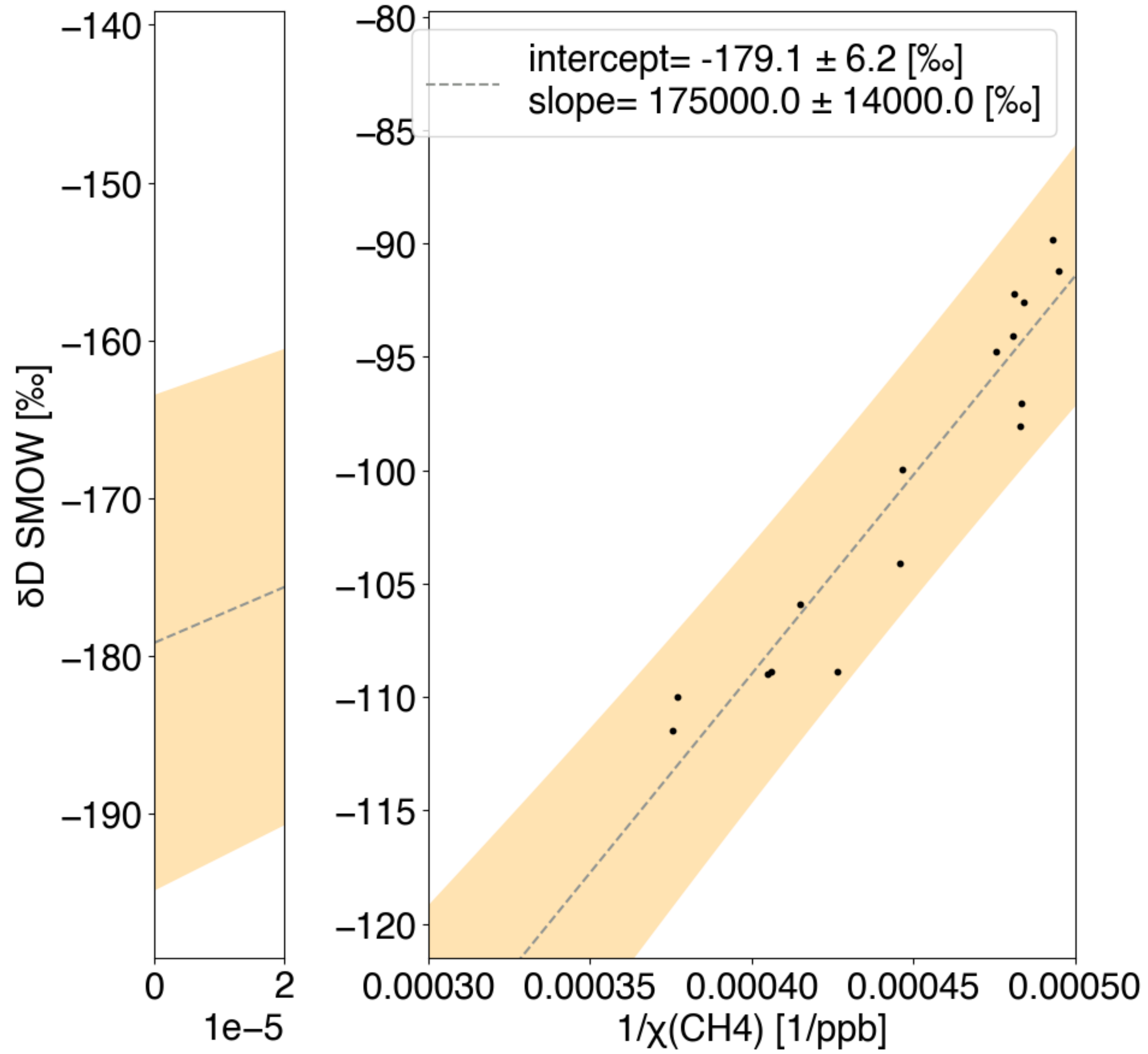
Plot:

x = $1/c_a$ vs y = δ_a

Linear regression
y-intercept = δ_s

-> δ_s gives the isotopic signature of the emission source

Example for $\delta^2 H$ in CH_4



Reference: Keeling, C.D., 1961. The concentration and isotopic abundances of carbon dioxide in rural and marine air. Geochimica et Cosmochimica Acta 24, 277–298.