



## Isotopic characterisation of methane emissions from Krakow, Poland

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Methane (CH<sub>4</sub>) emissions from human activities are a threat to the resilience of our current climate, and to the adherence of the Paris Agreement goals. The stable isotopic composition of methane ( $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ ) allows to distinguish between the different CH<sub>4</sub> origins. A significant part of the European CH<sub>4</sub> emissions, 10 % in 2016, comes from the Upper Silesian Coal Basin (USCB).

Measurements of CH<sub>4</sub> mole fraction ( $\chi(\text{CH}_4)$ ),  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  in CH<sub>4</sub> in ambient air were performed continuously during 6 months in 2018 and 2019 at Krakow, Poland. In addition, CH<sub>4</sub> samples were collected during parallel mobile campaigns, from multiple CH<sub>4</sub> sources in the footprint area of continuous measurements. The resulting isotopic signatures from natural gas leaks, coal mine fugitive emissions, landfill and sewage, and ruminant emissions were statistically different. The use of  $\delta^2\text{H}$  in CH<sub>4</sub> is crucial to distinguish the fossil fuel emissions in the case of Krakow, because their relatively depleted  $\delta^{13}\text{C}$  values overlap with the ones of microbial sources. The observed  $\chi(\text{CH}_4)$  time series showed a regular daily night-time accumulations, sometimes combined with irregular pollution events during the day. The isotopic signatures of each peak were obtained using the Keeling plot method, and generally fall in the range of thermogenic CH<sub>4</sub> formation, with  $\delta^{13}\text{C}$  between -55.3 and -39.4 ‰ V-PDB, and  $\delta^2\text{H}$  between -285 and -124 ‰ V-SMOW. They compare well with the signatures measured for gas leaks in Krakow and USCB mines.

The CHIMERE transport model was used to compute the CH<sub>4</sub> time series at the study location, based on two emission inventories. The  $\chi(\text{CH}_4)$  are generally under-estimated in the model. The isotopic signatures of all pollution events over the entire time periods were extracted from Keeling plots applied on each peaks, for both observed and modelled time series using the EDGAR v5.0 inventory. The results indicate that a higher contribution from fuel combustion sources in the inventory would lead to a better agreement. The isotopic mismatches between model and observations are mainly caused by uncertainties in the assigned isotopic signatures for each source category, and how they are classified in the inventory. These uncertainties are larger for emissions close to the study site, which are more heterogenous than the ones advected from the USCB coal mines. Our isotope approach proves here to be very sensitive in this region, thus helping to improve emission estimates.

