Isotopic characterization of coal mine methane in the Upper Silesian Coal Basin, Poland

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Overview of isotopic signatures of different methane sources

I. Levin, pers. comm.

Sherwood et al., 2017

Upper Silesian Coal Basin signatures from literature

Reference	$\delta^{13}\text{C CH}_4$ [‰]	$\delta\text{D CH}_4$ [‰]	Comment
Kotarba et al., 2001	-79.9 to -44.5	-202 to -153	Samples from boreholes inside the coal seam
Kotarba et al., 2004	-72.8 to -47.8	-196 to -153	Samples from boreholes inside the coal seam
Necki et al., 2017	-49.0	n.a.	Samples from inside ventilation shafts
Galkowski et al., 2021	-50.9 ± 1.1	-224.7 ± 6.6	CoMet 1.0 HALO aircraft observations, entire USCB (2 flights)
Stanisavljevic et al., in prep.	-50.2 ± 9.2	-180.1 ± 38.2	Weighted average of single mine isotopic signatures (weighting by measured fluxes or fluxes reported by E-PRTR)

The CoMet mission overview

Special Issue: [CoMet: a mission to improve our understanding and to better quantify the carbon dioxide and methane cycles](#) (AMT/ACP/GMD inter-journal SI), 2019

Eds. ACP co-editors | Coordinators: Martin Dameris and Christoph Gerbig

CoMet 1.0

Knowledge for Tomorrow

Introduction to the CO₂ and Methane Mission (CoMet)

Realization of **active and passive remote sensing** as well as **in situ** observations of greenhouse gases from satellite, aircraft and ground platforms.

FDLR Cessna Instrumentation

CRDS Picarro G1301-m: CO_2 , CH_4 , H_2O (Klausner et al., 2020)

Aerodyne QCLS: CO , C_2H_6 , CO_2 , CH_4 , N_2O , H_2O (Kostinek et al., 2019)

Flask sampler: Isotopes, Jena Air Sampler (JAS)

MetPod: T , p , H_2O , 3D-wind (Mallaun et al., 2015)

Katowice,
Silesia,
Poland

28.05. –
14.06.2018

Ventilation Shaft, Pniowek Mine

USCB emission estimate from mass balance and comparison with inventories

The CH₄, CO₂, and CO emissions of the entire USCB have been assessed from flights 4 and 5 with an airborne mass balance technique.

CH₄: Airborne estimate in the **lower range** of the six presented emission inventories.

CO₂: Second flight constrains the emissions to the **lower end** of inventory values.

CO: In range of inventories.

published by Fiehn et al., 2020, ACP

Airborne flask samples, analysis with mass spectrometry at MPI-BGC Jena

A Jena Air Sampler (JAS) with 12 glass flasks was installed on the Caravan aircraft. The samples were analyzed for trace gas concentrations and isotopic ratios of methane. JAS and the analysis are described by Galkowski et al. (2021).

Samples are distinguished in three categories according to their location with respect to the sources:

	Sampling location	#
ALL	TOTAL	55
FT	Free Troposphere	15
IN	Inflow (upwind, PBL)	8
PL	Plumes (downwind, PBL)	32

Determination of source signatures from airborne samples

$$c_s + c_{bg} = c_{tot} \quad (s: \text{source}; bg: \text{background})$$

$$c_s * \delta_s + c_{bg} * \delta_{bg} = c_{tot} * \delta_{tot} \rightarrow \delta_{tot} = c_{bg}(\delta_{bg} - \delta_s)(1/c_{tot}) + \delta_s$$

Observed isotopic ratios have to be corrected for the dilution with the background air masses to derive the **source signatures**. We use keeling plots and orthogonal distance regression.

FT and IN samples represent the “clean end member” of the Keeling plot. Here we also made a Keeling plot for these sub-sets separately, because it turns out that there is a good correlation between delta values and CH₄ in these “background” samples.

Upper Silesian Coal Basin signatures per flight

Flight	Wind direction	Target region	# Flasks in PBL	$\delta^{13}\text{C CH}_4$ [‰]	SE $\delta^{13}\text{C}$ [‰]	$\delta\text{D CH}_4$ [‰]	SE δD [‰]
1	S	Southwest	3	-54.7	1.3	-261	53
2	S	Southwest	3	-52.0	2.6	-261	15
3	N	North	7	-49.4	1.3	-219	12
4	NE	Entire	0	-	-	-	-
5	NE	Entire	7	-49.6	2.0	-228	24
6	E	South	3	-52.4	1.8	-223	12
8	SE	South	4	-54.0	1.2	-236	14
9	NW	Entire	7	-49.9	2.4	-235	31
10	NE	Southeast	4	-49.3	7.6	-237	10
PL	-	-	32	-50.9	0.7	-226	9

Sub-regional isotopic signatures

Isotopic signatures vary for different flights and **parts of the USCBA**.

The observed CH_4 variability in the **inflow** and **free troposphere** originates from biogenic sources.

Ground-based samples

A total of 58 signatures from ventilation shafts and other sources were gathered in the USCB in cooperation with MEMO².

<https://h2020-memo2.eu/>

Ground samples from individual ventilation shafts

For **each signature** several air samples were taken outside of the ventilation facilities, analyzed via mass spectrometry and corrected for dilution processes. Pniowek samples from inside the shaft show that signatures of inside and outside sampling agree. A **spread in signatures** of one shaft is usually associated with temporal changes of the source signature caused by different sections of the mine being ventilated on different days. A mean signature for each shaft was determined for comparison to airborne signatures.

Airborne and shaft signature

The $\delta^{13}\text{C}$ signatures of **individual shafts** are in the upper range and higher than previous signatures found by Kotarba et al. (2004), while δD signatures are in the range of previous signatures.

Compared to the **aircraft observations**, the ground studies show more positive signatures in δD . The methane emissions sampled from the aircraft contain **60% coal mine methane and 40% biogenic methane** assuming the following signatures:

$$\delta\text{D}_{\text{aircraft}} = -226 \text{ ‰}$$

$$\delta\text{D}_{\text{coal}} = -180 \text{ ‰}$$

$$\delta\text{D}_{\text{biogenic}} = -300 \text{ ‰}$$

EDGAR v5.0 gives a ratio of 92% fossil methane sources and only 8% from biogenic sources (waste + cows) for the USCB.

MECO(n) global/regional model

“MESSyified ECHAM and COSMO models nested n times”

Global model with 3 regional nests at 50km, 7km and 2.8 km horizontal resolution

Nudging

- Analysis simulation started 1st of April 2018 and is nudged towards ECMWF operational analysis data towards divergence, vorticity, temperature and the logarithm of surface pressure. SST and SIC are prescribed as boundary conditions.

Emission inventory combination

- Anthropogenic includ. Rice : EDGAR5 ($0.1^\circ \times 0.1^\circ$), year 2012, indiv. Sectors
- Natural: EMPA inventory ($1^\circ \times 1^\circ$) (Frank et al., 2018), 2012

Initial conditions

- Methane isotopologues and a posteriori emissions from Frank et al., (2018), (Restart 31.03.2012)

Isotopic source signatures used in the MECO(n) model

	$\delta^{13}\text{C CH}_4$ [‰]	$\delta\text{D CH}_4$ [‰]
Biomass burning	-23	-213
Wetlands	-59.4	-336.2
Termites	-63.3	-390
Wild animals	-61.5	-319
Rice	-63	-324.3
Volcanoes	-40.9	-253.4
Ocean	-59	-220.0
Anthropogenic	-46.8	-223.5

(from Frank et al., 2018)

Refinement of
anthropogenic
source
signatures
→

	$\delta^{13}\text{C CH}_4$ [‰]	$\delta\text{D CH}_4$ [‰]
Livestock	-60.2	-317.5
Landfills	-51.7	-304.3
Fossil fuels	-41.7	-164

Analysis simulations to check plume representation

Published by Nickl et al., (2020)

- Plume **positions** match
- **Enhancements** are higher in the model (here with EDGARv4.2)

Comparison of model and aircraft in situ and flask samples

The regional model reflects the **changes** in methane isotopic composition caused by the methane emission from coal mining ventilation.

A comparison with airborne **in situ and flask data** confirms the changes.

The curtain plot in the lowest panel shows that the isotopic composition varies only **within the boundary layer** and not in the free troposphere.

Comparison of model and aircraft isotopic signatures

a) CH_4 mixing ratio and $\delta^{13}\text{C}$ of three simulations with different assumptions on the coal isotopic source signatures compared to those of the observation

b) Best fit with isotopic source sig for fossil fuel emission = -50 ‰

The comparison shows three discrepancies:

- Model bias in the background CH_4 mixing ratio
- Model bias in the background isotopic composition
- Small discrepancy in $\delta^{13}\text{C}$ source signature

PhD thesis A. Nickl

Conclusions

- Isotopic **signatures** of methane derived from the aircraft **vary** for different parts of the USCB.
- The observed CH₄ variability in the **inflow and free troposphere** originates from biogenic sources.
- **Coal mine methane** signatures vary strongly from mine to mine and shaft to shaft and also over time.
- δD signatures indicate that methane emissions sampled from the aircraft contain about **60% coal mine** methane and **40% biogenic** methane from the waste sector.
- The regional model reflects the **changes** in methane isotopic composition caused by the methane emission from coal mining ventilation.

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