Environmental monitoring of coal mining area: insights from stable isotope measurements of methane excess

Monitoring środowiska na obszarach wydobycia węgla kamiennego: zastosowanie badań izotopowych strumieni metanu

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Stable isotopic signatures of methane sources



Global GHG budget

Increase in global CO₂ and CH₄ concentrations in the atmosphere



What ¹³C Tells Us

Recall that the Suess Effect is the observed decrease in δ^{13} C and Δ^{14} C values due to *fossil fuel emissions*, which are **depleted** in ¹³C and do not contain ¹⁴C.

February 2024:	424.55 ppm CO ₂
February 2023:	420.30 ppm CO ₂
November 2023: November 2022:	1934.16 ppb CH ₄ 1923.63 ppb CH ₄



Global GHG budget

Global methane emissions from the energy sector over time, 2000-2021



• Global CH₄ emissions from the coal sector, according to the IEA, were estimated to be 43.6 Mt in 2021.

- Coal mining is the second main source of methane emissions in Poland (37.1% in 2021), according NIR.
- The application of a coal mine monitoring system implies large uncertainty of methane emissions.
- The broad discussion by the EU Council (EU Methane Action Plan).

Source: <u>https://www.iea.org/data-and-statistics/charts/global-methane-</u> emissions-from-the-energy-sector-over-time-2000-2021

Methane emissions in Poland

Methane emissions from coal mining, 2018 – 2020



Source: https://www.esa.int/Applications/Observing_the_Earth/Copernicus/Sentinel-5P/Methane_detected_over_Poland_s_coal_mines

Methane emissions in Poland

Methane emissions from coal mining, 2018 – 2020



Tendency:

- increase the value of methane content in the deposit with a depth of coal-bearing strata;

- deeper the coal mines go into exploitation (coal is extracted at depth of 800 m below m.s.l., even exceeding 1000 m).

- the specific methane emission – *release of CH₄ per 1 t of extracted coal* (reached 15 m³·t⁻¹ in 2020).

Source: WUG (State Mining AuthorityOcena stanu bezpieczeństwa pracy, ratownictwa górniczego oraz bezpieczeństwa powszechnego w związku z działalnością górniczo-geologiczną w 2022 roku, Wyższy Urząd Górniczy w Katowicach, 2023.

Research background

Stable isotopes as environmental tracers





$$\delta^{13}\mathrm{C} = \left(rac{\left(rac{13}{\mathrm{C}\mathrm{C}}
ight)_{\mathrm{sample}}}{\left(rac{13}{\mathrm{C}\mathrm{C}\mathrm{C}}
ight)_{\mathrm{standard}}} - 1
ight) imes 1000$$

Isotopic source identification: linear mixing model Keeling Plot Approach

C_s + C_{bg} = C_{mix} (s: source; bg: background; mix: measured sample)

$$\delta_m c_m = \delta_{bg} c_{bg} + \delta_s c_s$$

$$\delta_m = rac{c_{bg}}{c_m} (\delta_{bg} - \delta_s) + \delta_s$$

Source: Keeling, 1958; Pataki et al., 2006

Research background



Stable isotopes as environmental tracers

Overview of methane source signatures (δ^{13} C, δ^{2} H) M: microbial; T: thermogenic; A: abiotic;

MCR: microbial CO₂ reduction; MAF: microbial acetate fermentation; ME: microbial in evaporitic environment;

Source: Sherwood et al. 2017; Way et al., 1950; Pierson, 1993.

Methane emissions from coal mining

Stable isotope geochemistry of coalbed methane



Methane migration in coal seam

The pattern of methane release from the coal seam and surrounding strata



Coalbed gas exists in forms:

- **adsorbed gas** (80–90 % of the total CH_4 content in coal seams)
- free gas (10–20 %)
 presented in the pores
 and cracks within the
 coal structure,
- < 1 % of *dissolved gas* content in the coal containing water.

Methane is being emitted into the mine workings from:

- active/fresh face on the *longwall and goaf zone* (overlying strata collapsed into the void left by longwall mining);
- *mined coal itself* being taken to the surface on the conveyor belts;
- *surrounding strata* (geologic discontinuities, such as faults, fractures, fissures in walls, roof and floor) as a result of lower pressures in the mining area;

Active mining methane emissions

Compaction of strata after removal of the mined coal seam



The properties of the strata and CH_4 emission potential:

- Strata (overlying rock mass) disturbance created by longwall mining;
- creating tensional stress and enhancing permeability;

Source: Karacan, C. Özgen; Warwick, Peter D. (2019). Assessment of coal mine methane (CMM) and abandoned mine methane (AMM) resource potential of longwall mine panels: Example from Northern Appalachian Basin, USA. International Journal of Coal Geology, 208(), 37–53. doi:10.1016/j.coal.2019.04.005

Parameters related to longwall coal extraction

Longwall coal mining operations

Machines included in the longwall complex:

(I) longwall shearer;

(II) bottom scraper conveyor;

(III) powered roof support in the longwall;

(IV) section of the powered roof supports.



(To panel end) Panel length Coal seam Panel width (To panel start) Shields Sheare Stage Gob loader Face Cutting depth: conveyor Entries Methane drainage of longwalls intake air return air

Source: Szurgacz, D.; Tutak, M.; Brodny, J.; Sobik, L.; Zhironkina, O. The Method of Combating Coal Spontaneous Combustion Hazard in Goafs—A Case Study. *Energies* 2020, *13*, 4538. https://doi.org/10.3390/en13174538 Obracaj, D.; Korzec, M.; Deszcz, P. Study on Methane Distribution in the Face Zone of the Fully Mechanized Roadway with Overlap Auxiliary Ventilation System. *Energies* 2021, *14*, 6379. https://doi.org/10.3390/en14196379 Karacan, 2008a

Parameters related to longwall coal extraction

Vhirl-flow air duct COAL EAM

Depending on the specific coal seam, the **gas occurring in coal beds contains**:

- 80–95 % of CH₄,
- < 3 % of CO₂, N2,
- proportions of hydrocarbons (ethane, propane, ethylene, acetylene).

Methane-air mixture is drained out by the underground mine ventilation system, becomes considerably diluted (*less than 1 % CH_4*) and is discharged through the exhaust ventilation shafts into the atmosphere.



Source: Szurgacz, D.; Tutak, M.; Brodny, J.; Sobik, L.; Zhironkina, O. The Method of Combating Coal Spontaneous Combustion Hazard in Goafs—A Case Study. *Energies* 2020, *13*, 4538. https://doi.org/10.3390/en13174538 Obracaj, D.; Korzec, M.; Deszcz, P. Study on Methane Distribution in the Face Zone of the Fully Mechanized Roadway with Overlap Auxiliary Ventilation System. *Energies* 2021, *14*, 6379. https://doi.org/10.3390/en14196379 Wierzbicki, M., Skoczylas, N., & Kudasik, M. (2017). *The Use of a Unipore Diffusion Model to Describe the Kinetics of Methane Release from Coal Spoil in the Longwall*

Environment. Studia Geotechnica et Mechanica, 39(2), 81-89. doi:10.1515/sgem-2017-0018

Ventilation system in methane-rich coal seams

Ventilation of active longwall coal face

Discharging methane emissions into the mine ventilation air



U-type ventilation system

discharges the air through the tailgate that runs along the body of coal

Advantages:

- limits heating and spontaneous combustion of coal left in the goaf zone;

Disadvantages:

- risks of high CH₄ accumulations and its spontaneous combustion hazards;

Y-type ventilation system

air through the tailgate that runs along the goafs

Advantages:

- substantially higher velocity of airflow decrease CH₄ level along the longwall;

Disadvantages:

- flow of air rich in oxygen intensified process of coal oxidation, heating in the goaf zone;

Source: Tutak, M.; Brodny, J.; Szurgacz, D.; Sobik, L.; Zhironkin, S. The Impact of the Ventilation System on the Methane Release Hazard and Spontaneous Combustion of Coal in the Area of Exploitation—A Case Study. Energies 2020, 13, 4891. https://doi.org/10.3390/en13184891

The explosive potential for CH₄ and air mixtures

The state of methane hazard in coal mines



Explosive gas regions:

- explosive region (red),
- fuel-rich inert region that can become explosive when fresh air or oxygen is added (yellow);
- inert region where no explosive composition is possible (green and dark green;
- *fuel-lean inert region* (blue).

Source: J. Marts, R. Gilmore, J. Brune, G. Bogin Jr., J. Grubb & S. Saki. Accumulations of Explosive Gases in Longwall Gobsand Mitigation through Nitrogen Injection and Face Ventilation Method. Colorado School of Mines , USA, 2014.

System for monitoring ventilation parameters



Source: Brodny, J.; Felka, D.; Tutak, M.; Applying an Automatic Gasometry System and a Fuzzy Set Theory to Assess the State of Gas Hazard during the Coal Mining Production Process. Engineered Science, 2023, 23, 891. <u>http://dx.doi.org/10.30919/es891</u>

Mróz J., Felka D., Broja A., Małachowski A. Devices for measuring ventilation parameters and methane concentration as well as concept of complex monitoring of methane hazard in longwall area. Mining – informatics, automation and electrical engineering. No. 1 (529) 2017. <u>http://dx.doi.org/10.7494/miag.2017.1.529.7</u>

System for monitoring environmental parameters

Online measurement of airflow velocity and CH₄ concentration



CX:095 CMC-4-475 Tel.6647 An010 m/s Chod.taśm.2/Vz pokł.407/3, 10-50m od skrzyż. z przek.poch.19/IVz pk.407/3

🐼 CA:221 CMC-3/I-221 Tel.6878 SMP/SWuP MM2 %CH4 chod.1a/Vz 407/3 zab. na ociosie przeciwległym od wyrobiska śc.na wysokosci okna

SEMP.0221:%CH4 Limity %CH4	^	CD:252 CD:253 CT:126 CL:002 CD:254 CX:095 CD:250 CA:221 CD:028 CD
Min $08:44$ 0.4 Ostrzeż >= 1.5		010 %CH4
Max 19:20 8 Ostrzeż.<= Alarm <=		
Czasy pomiarów,ostrzeżeń i alarmów		
Pomiary 1439 (480, 479, 480)		
Ostrzeż. 60 (6, 53, 1)		06 07/28 07 07/28 08 07/28 09 07/28 10 07/28 11 07/28 12 07/28 13 07/28 14
Alarmy 28(4, 21, 3)		
Pomiary beznośrednie		
		14 07/28 15 07/28 16 07/28 17 07/28 18 07/28 19 07/28 20 07/28 21 07/28 22
Kartoteka czujnika Łączność		
Zakres 0÷100 %CH4 🗖 6878		
Adres SEMP.0221>		
Mapa Śc.2/Vz pokł.407/3 🔁 CAO		
✓ Bilans czasu	~	
		22 07/28 23 07/28 00 07/29 01 07/29 02 07/29 03 07/29 04 07/29 05 07/29 06

thermocatalytic methanometer

Current statement and preliminary results



Experimental set-up

Instrumentation

Picarro CRDS (Cavity Ring-Down Spectroscope, **G2201-i**) for measuring concentrations of δ^{13} C in CO₂ and CH₄. (precision: CO₂: 210 ppb; δ^{13} C: 0.16‰; CH₄: 50 ppb; δ^{13} C: 0.55‰).

Continuously Flow Isotope Ratio Mass Spectrometry (**CF-IRMS**) at **Utrecht University** for determining CH_4 isotopes ($\delta^{13}C$, $\delta^{2}H$). (precision: $\delta^{13}C$ - CH_4 : 0.07‰; $\delta^{2}H$ - CH_4 : 1.7‰).

Trace gas analyzer **mGA-918 OA-ICOS** (Off-axis integrated cavity output spectroscopy) **Los Gatos** for analysis of CH_4 and CO_2 (precision 1s, 1 sec: CH_4 : 1 ppb; CO_4 : 0.4 ppm).





Study area and study site

South-western part of USCB – Rybnik Mining District



PGG KWK ROW Ruch *Chwałowice*

The mining area covers 21.76 km², with extractable resources amount to 144,643 thousand tons of coal.

Source: Państwowy Instytut Geologiczny: https://cbdgportal.pgi.gov.pl/haldy/

Geology and mine operating conditions

Lithostratigraphic column of coal seam



The total thickness of the coal seams is in the ~6–8 m range, with a depth in the **~450–700 m range**, and the **thickness of the coal bed ranges from 1.6 to 2.0 m**.

Source: Tutak, Magdalena; Brodny, JarosÅaw; Szurgacz, Dawid; Sobik, Leszek; Zhironkin, Sergey (2020). The Impact of the Ventilation System on the Methane Release Hazard and Spontaneous Combustion of Coal in the Area of Exploitation. Case Study. Energies, 13(18), 4891–. doi:10.3390/en13184891

The number of coalbed gas samples was collected in relation to the distance from:

- the longwall face, where mining activities had been performed (670 m deep),
- across walkways of mine workings (650-390 m deep),
- towards the ventilation shaft (390 m deep).
- inside of the exhaust ventilation shaft (surface channel).

Samples of *raw bituminous coals and coal-bearing rocks* were collected.



Measurements and sampling procedure

Schematic cross-section of sampling points in the underground coal mine workings



CH₄ concentration in ventilation air of mine workings corresponding to the depth of exploitation



S1-S2 – samples collected along longwall coal face (tailgate);
P1-P9 – samples of ventilation air in mine workings;

Methane content in coal (*daf) seam *increases with depth*;

CH₄ *being diluted* with the rise of ventilating air stream;

Accumulation (high-methane zone) occurring in areas of bends and obstructions in the airway.

*coaldaf – dry ash free coal substance the pure coal substance, without moisture and ash

Variation in methane content in mine workings

CH₄ concentration in mine workings in relation to the ventilation airflow rate and distance from the longwall coal face



Decrease in CH₄ content is associated with a *dilution effect with the distance from the exploitation longwall* towards the ventilation shaft.

The higher velocity of the ventilation air stream has **a pronounced dilution effect on gas content**.

Accumulation of CH₄ occurring in areas of bends and obstructions in the airway.

Methane δ^{13} C vs δ^{2} H for coalbed and coal mine CH₄ in USCB



Empirical compositional and isotopic classifications from *Whiticar, 1999* was applied for discrimination of different origins of coalbed gases.

shaft VII

B1 – free gas samples taken from the borehole;
S1-S11 – samples collected along longwall coal face;
P1-P9 – samples of ventilation air in mine workings;
Shafts – samples collected inside of the exhaust ventilation shaft (surface channel).

shaft V – depth 399.77 m;
shaft VII – depth 543.25 m (flooded in 420 m);

A major share of CH₄ emissions from mining activities is represented by *thermogenic gas origin*.

CH₄ depleted in ¹³C from ventilation shafts confirmed the presence of *secondary microbial gas sources* (as result of invasion of meteoric water with nutrients for methanogens).

 Δ^{13} C(CO₂-CH₄) values from 40.3 to 49.6 – *acetate fermentation pathway of CH₄* α CO₂-CH₄ values from 1.042 to 1.053 – acetate fermentation.

Concentration and isotopic composition (δ^{13} C) of CH₄ sampled in single sections of the longwall face



S1-S11 – samples collected along longwall coal face;

The decrease in CH₄ level downwards from the tailgate (S1) (return airflow) towards maingate (S11) (intake airflow) *being diluted with the rise of ventilating air stream* supplied to the longwall.

Concentration and isotopic composition (δ^2 H) of CH₄ sampled in single sections of the longwall face



The decrease in CH₄ level downwards from the tailgate (S1) (return airflow) towards maingate (S11) (intake airflow) *being diluted with the rise of ventilating air stream* supplied to the longwall.

Cross-plot of CH_4 isotopic compositions ($\delta^{13}C$, $\delta^{2}H$) of coalbed gas samples collected in single sections of the longwall face



The arrow represents **trend for enrichment in** ¹³**C** during primary desorption from longwall face exploitation.

The concentration of CH_4 decreases in the maingate (S11) being diluted with fresh air from ventilating airflow.

The *dilution effect is not proportional* along the longwall face and CH_4 concentration increases towards the tailgate side (S1).

Ventilation air does **not have a pronounced dilution effect** as CH_4 becomes progressively more enriched in ¹³C with slight ²H depletion.

Mass balance of methane in the area of the longwall coal face

Longwall section / End-member 27/07/2023	S1	S2	S 3	S 4	S5	S 6	S 7	S 8	S 9	S10	S11
$\delta^2 H_{coal \ borehole}$	-192.4±2.8‰										
$\delta^2 H_{ventilation air}$	-93.3±1.5‰										
$\delta^2 H_{total longwall}$	-192.36	-189.35	-192.12	-191.40	-187.33	-178.12	-180.14	-184.79	-187.59	-184.30	-188.79
Q _{coal} / Q _{total}	98%	95%	98%	97%	93%	84%	86%	91%	93%	90%	95%
Q _{vent. air} /Q _{total}	2%	5%	2%	3%	7%	16%	14%	9%	7%	10%	5%

Two End Member Mixing Model

Longwall gases as a *mixture of borehole CH*₄ and *ventilation air* from the surface background.



Isotopic mass balance calculations



Cross-plot of carbon isotopic compositions (δ^{13} C) of CH₄ vs CO₂ of coalbed gas samples collected in single sections of the longwall face



Primary CO₂ (occurs in 1.2–2.3 % v/v) in the seam borehole mostly enriched in ¹³C (–2.6±0.4‰) implies the **gas generation from underlying carbonates derived from metamorphism**.

Typically, **CO**₂ in thermogenic gases has δ^{13} C values in a range from -20 to -18 ‰ (Smith and Pallasser, 1996).

Residual CO₂ from coalbed progressively evolves towards ¹³C isotope enrichment.

Cross-plot of CH_4 isotopic compositions ($\delta^{13}C$, $\delta^{2}H$) of coalbed gas samples collected in ventilation air of mine workings



¹³C-enrichment in methane mixture flowing through the mine workings generally arises from the diffusion and desorption processes.

During **gas migration** to the upper levels **and mixing** desorbed CH₄ from the exposed body of coal **undergoes underground fractionation** with corresponding isotopic offsets.

Sampling points from the surface plumes are on a *mixing line between the ventilation shafts and the ambient air*.

Airflow-normalized CH_4 concentration and its $\delta^{13}C$ in ventilation air of mine workings corresponding to the distance from the longwall coal face



Airflow-normalized CH_4 concentration and its $\delta^2 H$ in ventilation air of mine workings corresponding to the distance from the longwall coal face



In practice, it can be migration and possible *admixture of gas sources*:

- CBM from *different sections of the coal face*;
- gases generated from different intersected coal seams;
- generated from different source rocks.

Different trend recorded for stable hydrogen isotopes (²H) in CH₄, showing different fractionation effects, possibly due to the **lower natural abundance** compared to carbon.

The δ^{13} C-CH₄ and δ^{13} C-CO₂ source signatures calculated based on the Keeling plot approach



Reciprocal of CH₄ mole fraction [ppm⁻¹]

Reciprocal of CO₂ mole fraction [ppm⁻¹]

The CH₄ values determined using the Keeling plot model indicate a source of **desorbed gases** from different coal sections or coal seams enriched in ¹³C.

Isotopic composition of investigated coals

Carbon isotope composition δ^{13} C-TC of hard coal samples





Samples of *fresh/raw bituminous coals* and coalbearing rocks were collected near longwall.

Nearly the same δ^{13} C values (-23.5 ± 0.5‰) in semi-closed underground system confirmed *homogeneity of a coal seam*.



Isotopic composition of investigated coals

Coal haulage system – transport of mined coal from working faces to the surface



Previous studies

Overview of CH₄ isotope signatures from USCB in Poland



A wide range of δ^{13} C, δ^{2} H values (*mixture of thermogenic and microbial origins*) from the underground coal mines is reported in previous studies .

The *aircraft observations* in the area of USCB included a *mixture of CH_4 sources* (e.g. biogenic, coal mine methane, natural gas leaks).

The usage of $\delta^2 H$ as a tracer of CH₄ plume (ground-based surveys) is particularly important, as there is an overlap in the $\delta^{13}C$ from biogenic and fossil fuel sources.

Methane emission rates

Average CH₄ emission from individual ventilation shafts

Shaft	Date	Cross-sct. area [m ²]	Air velocity [m·s ⁻¹]	Airflow rate [m ³ ·min ⁻¹]	CH₄ concentr. [%]	CH₄ Flow rate [m ³ ·min ⁻¹]	Mine reported CH ₄ Flow rate [m ³ ·min ⁻¹]	Emission rate [t·day ⁻¹]
	26/06/2023		13.3	12768	0.15	19.49±0.67	20.52	20.13±0.69
V	28/07/2023	16	13.4	12864	0.36	46.59±1.34	41.20	48.10±1.38
	22/09/2023		13.0	12480	0.42	52.30±2.25	54.79	54.01±2.33
	23/03/2023		3.3	3663	0.02	0.70±0.06	0.37	0.73±0.07
VII	27/07/2023	18.5	3.5	3885	0.02	0.67±0.02	0.77	0.69±0.02
	26/09/2023		4.4	4884	0.12	5.80±0.36	6.31	5.99±0.37

$$\boldsymbol{Q}_{CH_4} = \boldsymbol{C}_{CH_4} \cdot \boldsymbol{60} \cdot \boldsymbol{\nabla}_{ch} \cdot \boldsymbol{A}_{ch} / \boldsymbol{100}$$

Q – methane flow rate $[m^3 \cdot min^{-1}]$ C_{CH₄} – methane concentration [%]

 v_{ch} – air velocity in ventilation channel [m·s⁻¹]

 A_{ch} – cross-section of ventilation channel [m²]

 ρ – methane density (0.717 kg·m⁻³)

The increase in CH₄ in shafts is caused by *changes in mining activities* in coal seams, preparing a new section of the coal deposit for exploration.



Identification of the *genesis, transport process, and migration pathways of coalbed gases* resulting from coal mining activities.

Investigation of the *influence of physical processes, site-specific conditions, and parameters of mine operations* on variations in composition of coalbed methane.

Determination of alterations occurring in the stable isotopic signature to represent the *variety in the origin of the gases in coal seam* in an active underground mine.

Characterizing the origin and volume of CH₄ generation (biogenic – lighter isotopically vs thermogenic – heavier) may help *identify methane-bearing zones*.

Isotopic tracing may *link the mining observations and atmospheric monitoring* perspectives to follow up methane emissions from mining activities in the USCB.

Estimation results in a *lower range of variations in isotopic signatures of methane in the ventilation shaft* than were reported in previous studies.

Thank you for attention!

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