

Supplement of

Direct methane measurements in a coal mine ventilation shaft: instrument intercomparison and emission estimates

Yaroslav Bezyk et al.

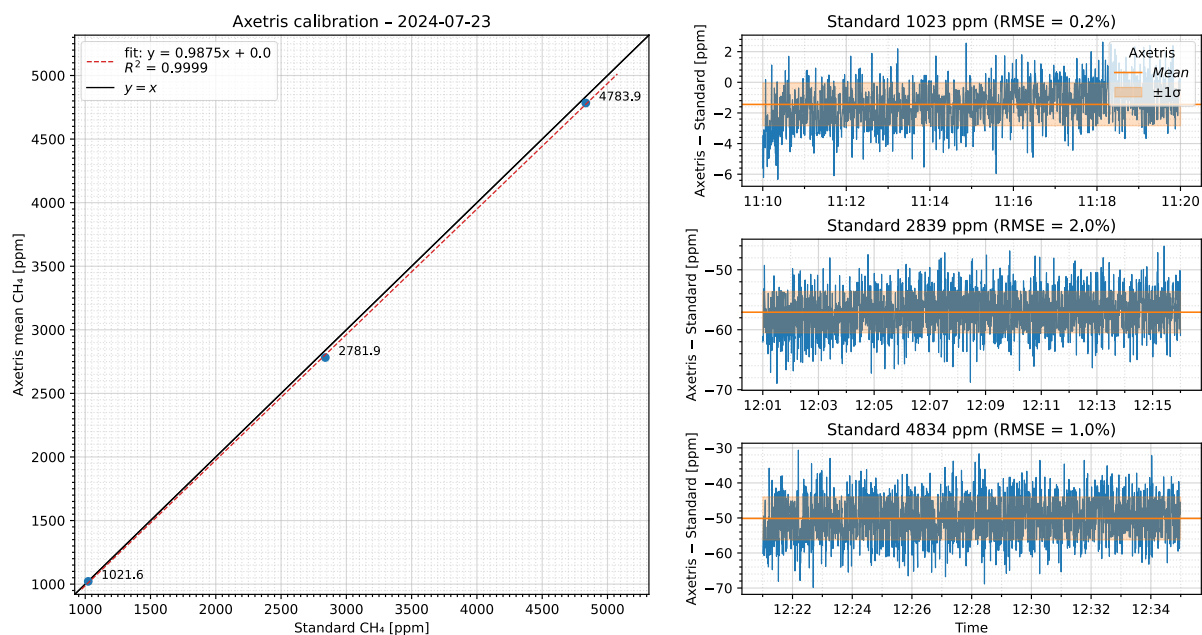
5 Correspondence to: Yaroslav Bezyk (bezyk@agh.edu.pl)

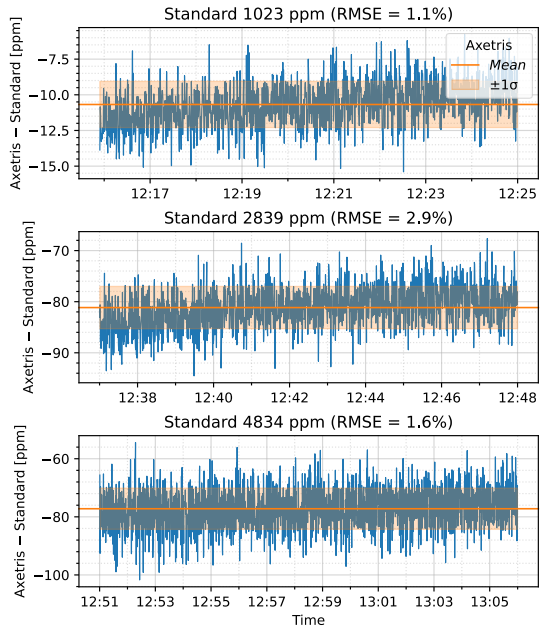
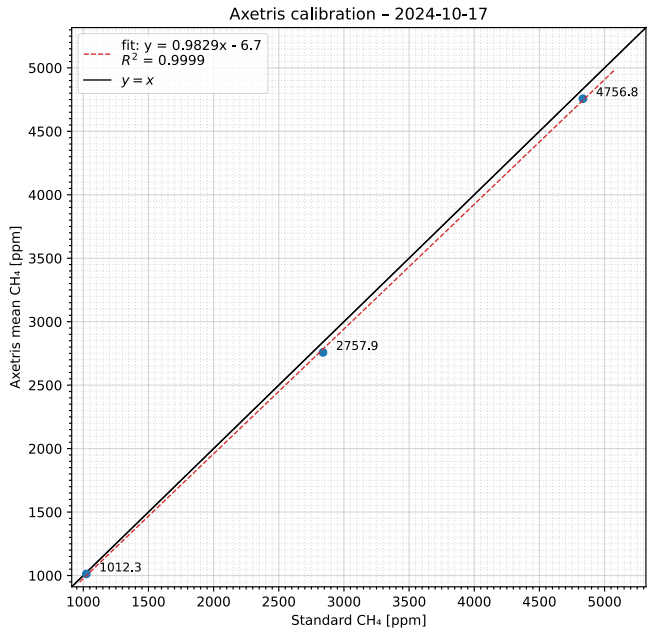
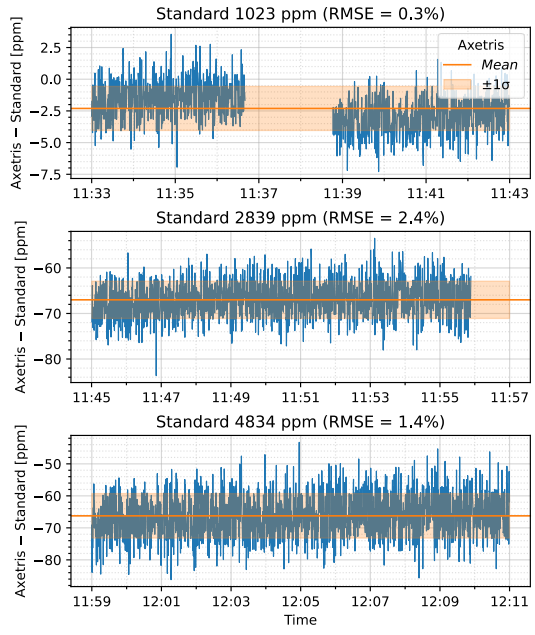
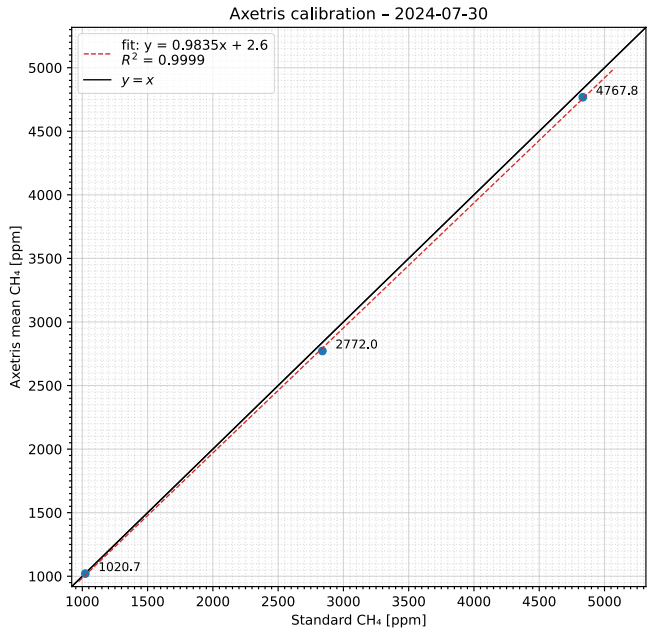
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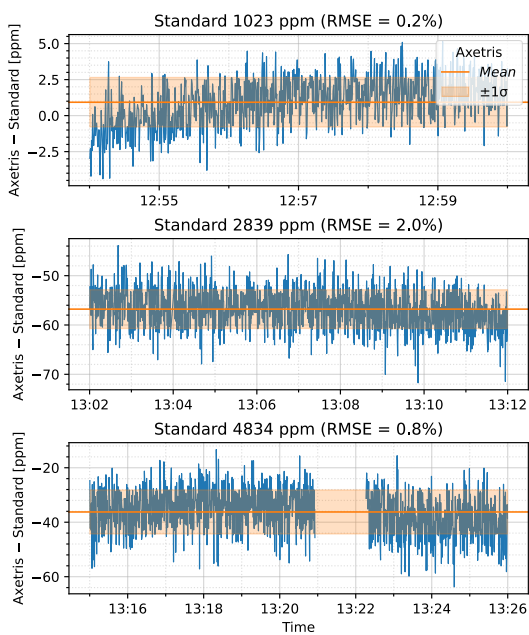
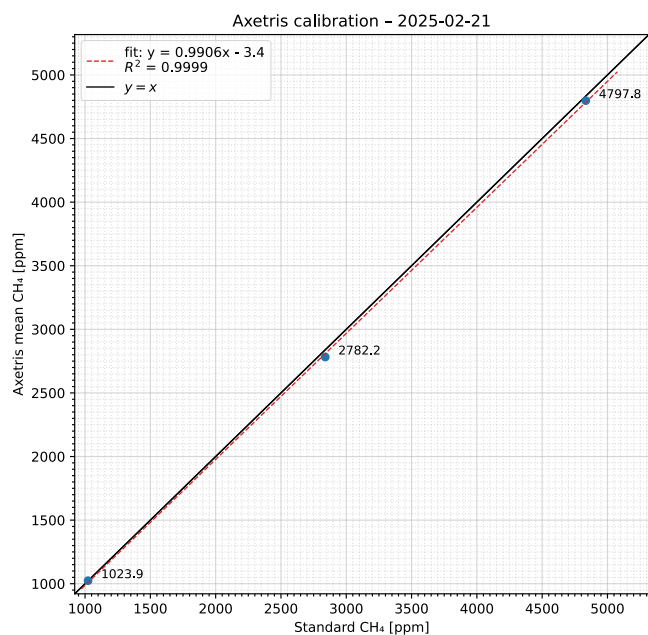
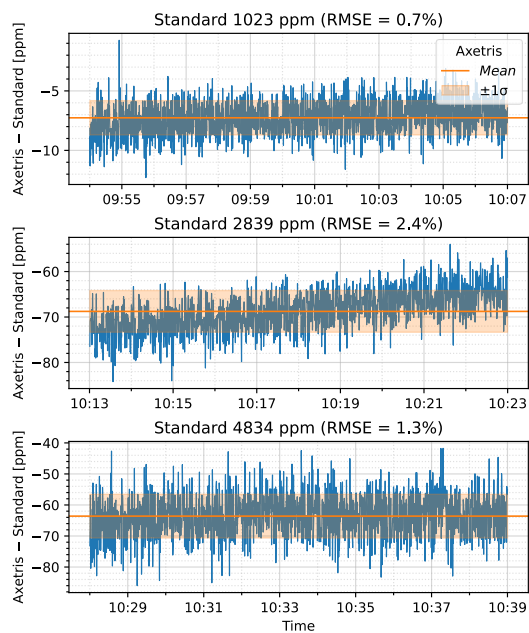
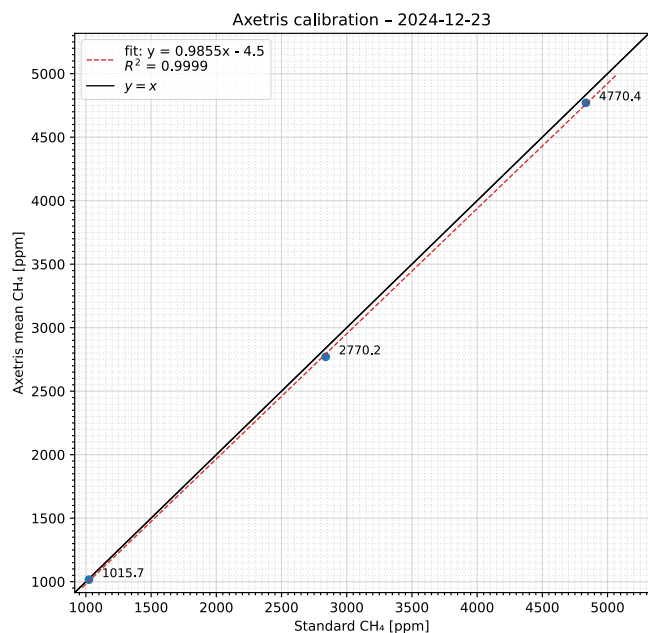
Text S1. Calibration procedure of the Axetris LGD System

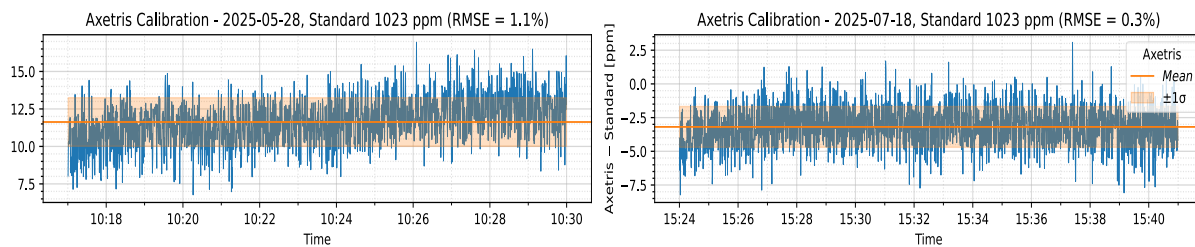
Linear regression was applied to verify instrument linearity across the low, medium, and high concentration ranges. The low-
10 concentration reference gas was primarily used for frequent verification of baseline accuracy, while the medium- and high-
concentration gases were used periodically to confirm linearity and full-scale response.

For each calibration level, the Axetris analyzer signal was recorded over a 10-min interval, and the mean and standard deviation (1σ) of the measured CH_4 concentrations were calculated from the time-series data, representing the span variability of the instrument response. The calibration charts illustrate both temporal concentration fluctuations around the mean value and the
15 relationship between measured and certified reference concentrations, expressed as the root mean square error (RMSE) (Fig. S1). The intercomparison between Axetris LGD and CRDS (Picarro G2201-i) measurements was evaluated based on bag sampling using scatter plots with 1:1 reference lines, time-series comparisons, and residual analyses (Fig. S.2).

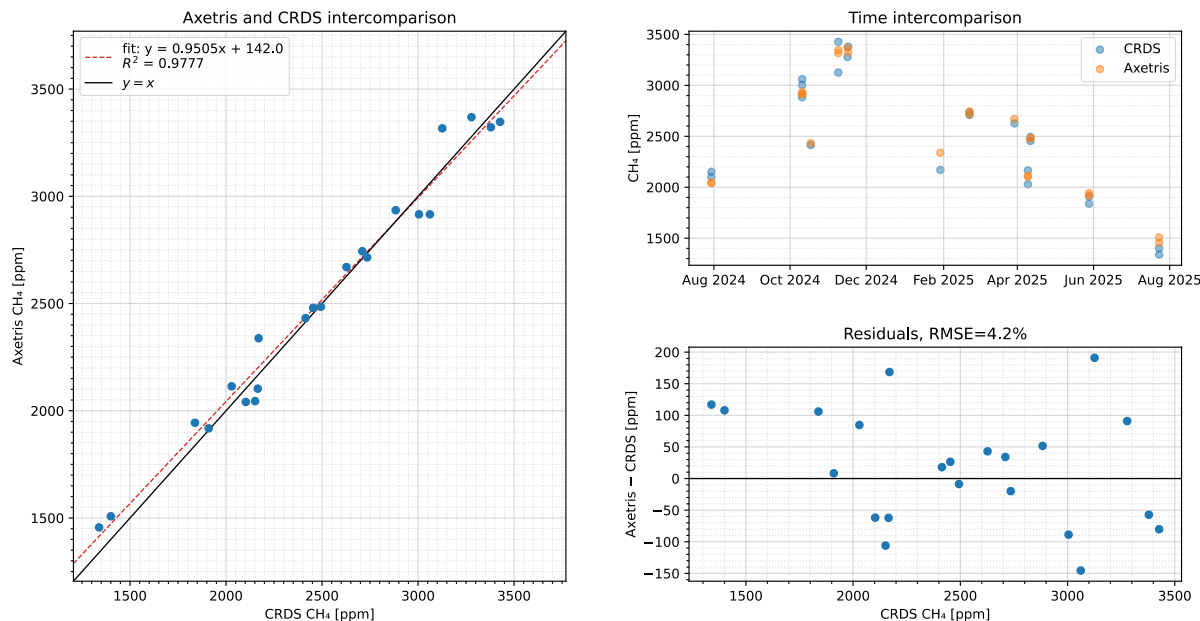








25 **Figure S1.** Time series of Axetris analyzer calibration performed using the three methane reference gas concentrations: low-concentration standard (1023 ppm CH₄), a medium-concentration standard (2839 ppm CH₄), and a high-concentration standard (4834 ppm CH₄).



30 **Figure S2.** Time-series comparison of Axetris LGD and CRDS (Picarro G2201-i) methane concentrations obtained for each paired bag sampling point.

Text S2. Instrument intercomparison: Axetris LGD vs Pellistor sensor

The two methane detection systems used in this study are based on different measurement principles and temporal resolutions. The Axetris LGD analyzer operates on laser absorption spectroscopy, while the mine's permanent pellistor sensor relies on a catalytic combustion method. Additionally, both instruments were operated and calibrated independently, with the Axetris system managed by the research team and the pellistor sensor maintained by mine personnel following routine safety protocols. Given the combined use of datasets from both instruments, a detailed intercomparison and harmonization approach was necessary to ensure consistency.

The sampling inlet of the Axetris system was installed at the same point in the main ventilation airflow channel as the pellistor sensor, enabling direct comparison of CH₄ concentrations in the shaft. The relationship between the two instruments was assessed during simultaneous measurement periods. A linear scaling method (1), incorporating both offset and proportional adjustments, was applied to correct the pellistor data using the Axetris measurements as the reference. Statistical indicators such as the coefficient of determination (R²), mean relative error (RE) and root mean square error (RMSE) were used to evaluate agreement, systematic bias, and overall performance between the two measurement methods. Uncertainty associated with corrected pellistor data was estimated by propagating uncertainties from the Axetris measurements and the regression-derived correction coefficients.

$$C_{corr} = a \times C_{pel} + b \quad (1)$$

where

C_{corr} – the corrected pellistor CH₄ concentration;

C_{pel} – the raw pellistor measurement;

a – the proportional (span) correction factor;

b – the offset correction.

Both instruments captured methane concentration variations over time consistently, reflecting similar short-term fluctuations and long-term trends. However, differences in amplitude measurements were often observed, with the pellistor sensor showing response levels that were sometimes lower or higher depending on operational conditions. To correct this, the pellistor data were categorized into seven correction groups based on data availability and signal behavior. The most common correction groups were Categories 1, 2, and 3 (Table S1). After recalibration, the agreement between the two instruments improved significantly, with R² rising from 0.18 for the uncorrected data to 0.93 after correction. This highlights the success of the scaling and correction methods in aligning long-term methane records.

Table S1. Performance comparison between the Axetris LGD analyzer and the Pellistor sensor the applied recalibration methods.

Cate gory	Procedure	*Proportion of raw dataset [%]	**rRMSE before correction [%]	rRMSE after correction [%]
0	No correction needed.	7.0	4.9	–
1	Multiplicative correction using the mean ratio between Axetris and pellistor values within the same period (span correction).	41.3	31.0	4.4
2	Multiplicative correction using the mean ratio, excluding the 1 and 99% quantiles, to reduce outlier effects.	2.1	61.0	5.7
3	Multiplicative correction using the mean ratio from the selected reference period.	18.5	37.0	11.0
4	Additive correction assuring continuity with the previous period. Used in cases without Axetris data for reference.	19.8	–	–
5	Additive correction ensuring continuity with the subsequent period.	1.2	–	–
6	Data excluded from further analysis due to poor quality or inconsistency.	0.9	–	–

*The percentages refer only to the portion of data that met the criteria of evaluation, rather than to the entire 100 % dataset.

**Values were not calculated for options 4–6 due to poor quality or inconsistency of the reference dataset.

Uncertainty of the individual categories has been calculated as root mean square error of relative residuals (2):

70
$$rRMSE = \frac{1}{N} \sqrt{\sum_i^N \left(\frac{P_i - A_i}{A_i} \right)^2}$$
(2)

where

N – number of minutes in the given category;

A_i and P_i – Axetris and Pelistor data points respectively.

75 The uncertainty could not be established in case of categories 4 to 6 because of the inherent absence of referential Axetris data points.

Text S3. Quantifying methane emissions released from the mine ventilation shaft into the atmosphere and determining coal production-based emission factor

- 80 Methane emissions from the mine ventilation shaft were quantified using CH₄ concentration measurements from the Axetris LGD analyzer and corresponding ventilation airflow rates provided by the mine's real-time airflow monitoring system. Emission rates were calculated according to (1):

$$Q = \frac{C \times F_{air} \times \rho}{100} \quad (1)$$

where

- 85 Q – CH₄ emission rate [kg·min⁻¹];
C – CH₄ concentration in the exhaust ventilation air stream [% vol.];
F_{air} – airflow rate at the main ventilation channel [m³·min⁻¹];
ρ – CH₄ density at standard conditions [0.665 kg·m⁻³].

- 90 The airflow rate through a ventilation channel was determined from (2):

$$F_{air} = A_{ch} \times v_{ch} \quad (2)$$

where

- F_{air} – airflow rate at the main ventilation channel [m³·min⁻¹];
A_{ch} – cross-section of ventilation channel [m²];
95 v_{ch} – air velocity in ventilation channel [m·s⁻¹].

The site-specific methane emission factor (EF) for the coal mine was expressed as methane mass emitted per unit of coal produced over the selected period (3):

$$EF = \frac{Q_{tot}}{P} \quad (3)$$

- 100 where

EF – emission factor for methane release from the coal mine [kg CH₄·t⁻¹];
Q_{tot} – CH₄ emission rate [kt CH₄·yr⁻¹];
P – coal production obtained from mine operational records [kt·yr⁻¹].

- 105 To evaluate the influence of mining geometry on methane release, a regression analysis was performed between cumulative CH₄ emissions for each 10-day period and the corresponding longwall cross-sectional advance. The slope of the resulting relationship was converted from methane mass to volume using a CH₄ density of 0.665 kg·m⁻³, yielding a geometrical emission factor of 13.4 ± 2.4 m³ CH₄·m⁻² of longwall progression. The cross-sectional advance was calculated as the product of longwall face length and panel advance for each reporting period. The derived factor characterizes CH₄ emissions associated with the

110 progressive development of 2–4 simultaneously active longwall panels operated during the study period, with average face
lengths ranging from 160 to 190 m (Section 2.1).

Reported methane emission factors for underground coal mines vary substantially across regions and mining conditions,
reflecting differences in geological setting, coal rank, mining depth, production intensity, and estimation methodology. The
summary of published emission factors from Poland and selected international coal-producing regions, together with the
115 corresponding mining conditions and calculation approaches is reparented in Table S2.

Table S2. Comparison of methane emission factors (CH₄ EF) from this study with selected regional and global datasets.

Coal Basin	Depth [m]	Coal rank	Mining method	EF [m ³ CH ₄ ·t ⁻¹]	Time scale	Calculation type	Study
USCB Poland	600–700	Bituminous	Longwall	5.1 ± 1.0	Annual	Measurements	This study
USCB Poland	650–1290*	Bituminous	Longwall	10.0	Annual	Measurements + Inventory	WUG Poland (2026)
USCB Poland	400–1030**	Bituminous	Longwall	7.5	Annual	Measurements + Inventory	WUG Poland (2026)
USCB Poland	600–1000	Bituminous	Longwall	5.7–15.2	Annual	Inventory	Dreger and Kędzior (2019)
European Union (average)	–	Lignite / Bituminous	–	8.5–13.2	Annual	Inventory (UNFCCC)	Zięba and Smoliński (2025)
Global	>400	All ranks	–	10–25	Annual	Inventory (Tier 1)	IPCC (2006)
China	–	All ranks	–	6.9–11.0	Annual	Bottom-up inventory	Gao et al. (2020)
India	–	All ranks	–	2.9–23.7	Annual	Measurements + Inventory	Singh and Mallick (2015)
Turkey	350–630	Bituminous	–	7.2–21.7	Annual	Measurements + Inventory	Rend et al. (2023)
Canada	800–1500	Bituminous	Longwall	9.4–15.6	Annual	Inventory	CMM Country Profiles (2015)
Australia	200–400	All ranks	–	14.9–17.2	Annual	Measurements + Inventory	Sadavarte et al. (2021)

*Knurów-Szczygłowice, Ruch Szczygłowice – Budryk (JSW).

**Bolesław Śmiały – Ruda Halemba (PGG).

Text S4. Uncertainty estimates for CH₄ emission rates from coal mine exhaust ventilation shaft

Uncertainty associated with methane emission rates ($\frac{u(Q)}{Q}$) from the ventilation shaft was quantified by propagating uncertainties from all contributing measurement components (1), including CH₄ concentration measurements by Axetris analyzer, reflecting calibration-derived instrumental uncertainty ($\frac{u(C)}{C}$) from repeated readings, uncertainty of ventilation
125 airflow rates ($\frac{u(F)}{F}$), and methane density uncertainty ($\frac{u(\rho)}{\rho}$) estimated based on variability in temperature and pressure measurements recorded at the shaft.

$$\frac{u(Q)}{Q} = \sqrt{\left(\frac{u(C)}{C}\right)^2 + \left(\frac{u(F)}{F}\right)^2 + \left(\frac{u(\rho)}{\rho}\right)^2} \tag{1}$$

where

- Q – calculated CH₄ emission rates [kt·yr⁻¹];
130 C – repeated multi-point calibration Axetris LGD measurement precision [ppm];
F – airflow rate through a ventilation channel [m³·min⁻¹];
ρ – the molar density of methane [kg·m⁻³].

Uncertainty of ventilation airflow rate was obtained from specifications and operational variability of the mine’s ventilation
135 monitoring system, including air velocity measurement from sensor accuracy and placement, temporal resolution, and fan operating conditions (e.g., slowing down of fans or power failures). To assess temporal variability in uncertainty, emission uncertainties were calculated for individual time steps and subsequently aggregated over monthly and annual periods (Table S3).

Uncertainty associated with emission factor estimates was determined by propagating uncertainties from cumulative methane
140 emission rates and coal production data.

Table S3. Uncertainty components calculated for methane emission rates from the mine ventilation shaft over monthly and annual time series.

Measurement period	Q [t CH ₄]	u(Q) [t CH ₄]	C [ppm]	u(C) [ppm]	F [m ³ ·min ⁻¹]	u(F) [m ³ ·min ⁻¹]	ρ [kg·m ⁻³]	u(ρ) [kg·m ⁻³]
Aug 2024	836.0	72.4	2278.0	31.9	12343	987	0.660	0.020
Sep 2024	908.2	78.6	2532.8	35.5	12477	998	0.660	0.020
Oct 2024	932.3	80.7	2521.7	35.3	12430	994	0.663	0.020
Nov 2024	1088.3	94.2	3137.9	43.9	12081	966	0.665	0.020
Dec 2024	1194.3	103.4	3296.6	46.2	12133	971	0.669	0.020
Jan 2025	1051.6	91.0	2774.1	38.8	12717	1017	0.669	0.020
Feb 2025	867.9	75.1	2629.1	36.8	12270	982	0.669	0.020
Mar 2025	952.5	82.5	2515.0	35.2	12568	1005	0.667	0.020

Apr 2025	707.3	61.2	2029.4	28.4	12115	969	0.665	0.020
May 2025	702.9	60.9	1913.7	26.8	12355	988	0.663	0.020
Jun 2025	662.9	57.4	1864.9	26.1	12306	984	0.663	0.020
Jul 2025	621.6	53.8	1680.5	23.5	12487	999	0.660	0.020
*Annual	10703.0	926.7	2469.7	34.6	12358	989	0.665	0.020

*Estimation captures the complete yearly dataset, not the monthly averages.

Text S5. Histograms of methane concentration measured with Axetris and Pellistor sensors and ventilation airflow rates in the mine shaft

The normality of the CH₄ concentration dataset and the ventilation airflow rates in the mine exhaust shaft was assessed using the Kolmogorov-Smirnov (KS) test. Additionally, the skewness and excess kurtosis of each distribution were calculated, and
150 quantile-quantile (Q–Q) plots were constructed to visually evaluate deviations from normality (Fig. S3 – Fig. S5). The analysis was performed for the entire annual dataset and three distinct measurement periods (I–III).

To remove long-term trends and seasonal variability, an additional moving-window analysis was conducted using a 13-day window (2-week centered dataset). For each analyzed day, statistical parameters (skewness, kurtosis, and the p-value for the KS) were calculated based on hourly measurements within a range of ± 6 -days. In the KS test, the null hypothesis assumes that
155 the data follow a normal distribution. Therefore, distributions with p-values > 0.05 (were considered not significantly different from normality).

The distribution of the Axetris CH₄ measurement dataset exhibits a positive (right) skewness and moderate deviations from a normal distribution. For the yearly data and Periods II–III, the distributions are close to normal with a slight right skew and moderate excess kurtosis. More noticeable deviations from normality were observed in Period I, with increased skewness and
160 kurtosis, likely due to the wider concentration range and more frequent high-concentration events during this interval. The Q–Q plots confirmed deviations from the theoretical normal distribution, especially in the upper quantiles.

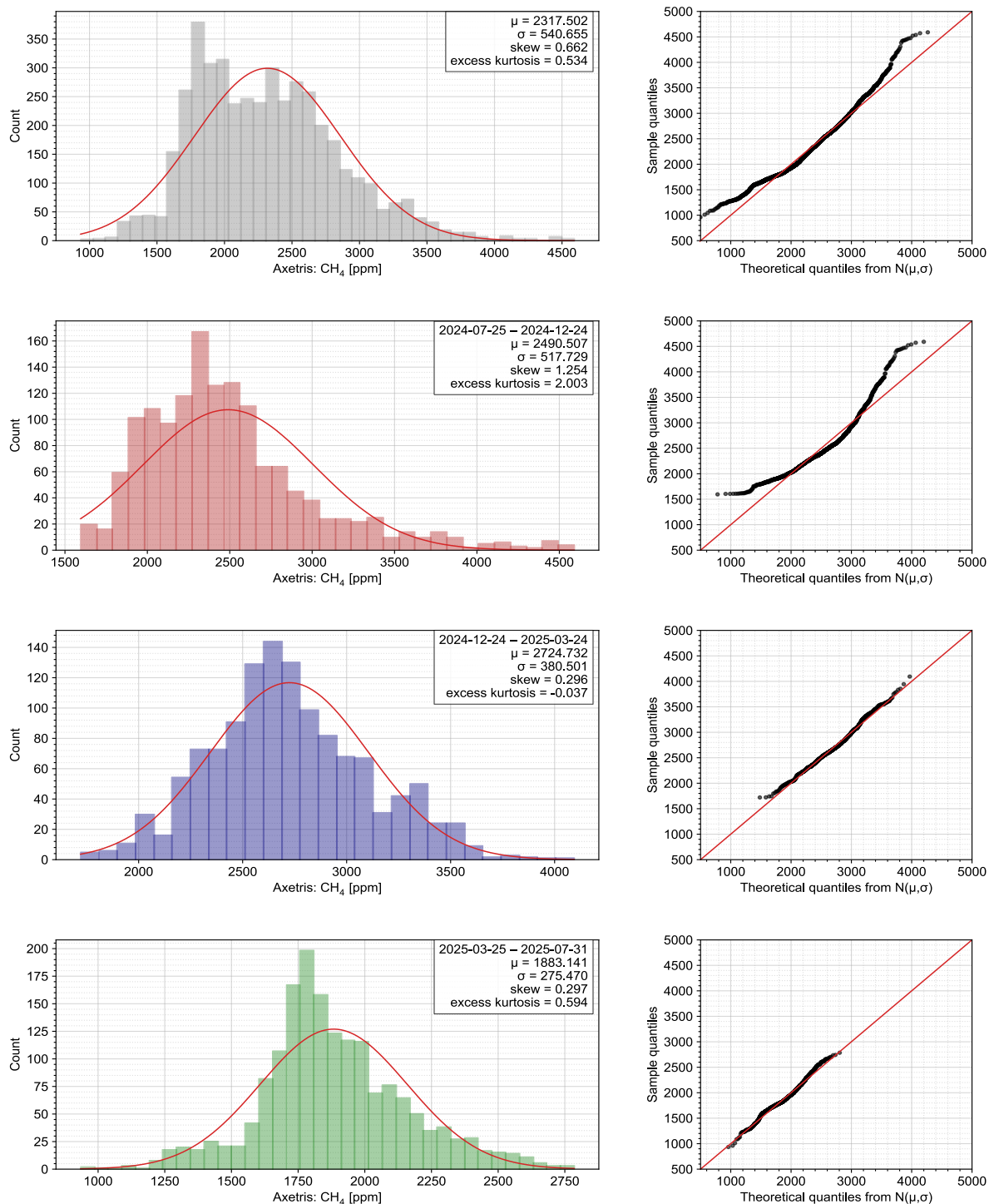


Figure S3. Time-series of CH₄ concentrations measured by the Axetris LGD analyzer in the exhaust shaft, with corresponding frequency distribution curves and a QQ plots shown for the annual timescale (top panel) and three distinctive (I–III) periods.

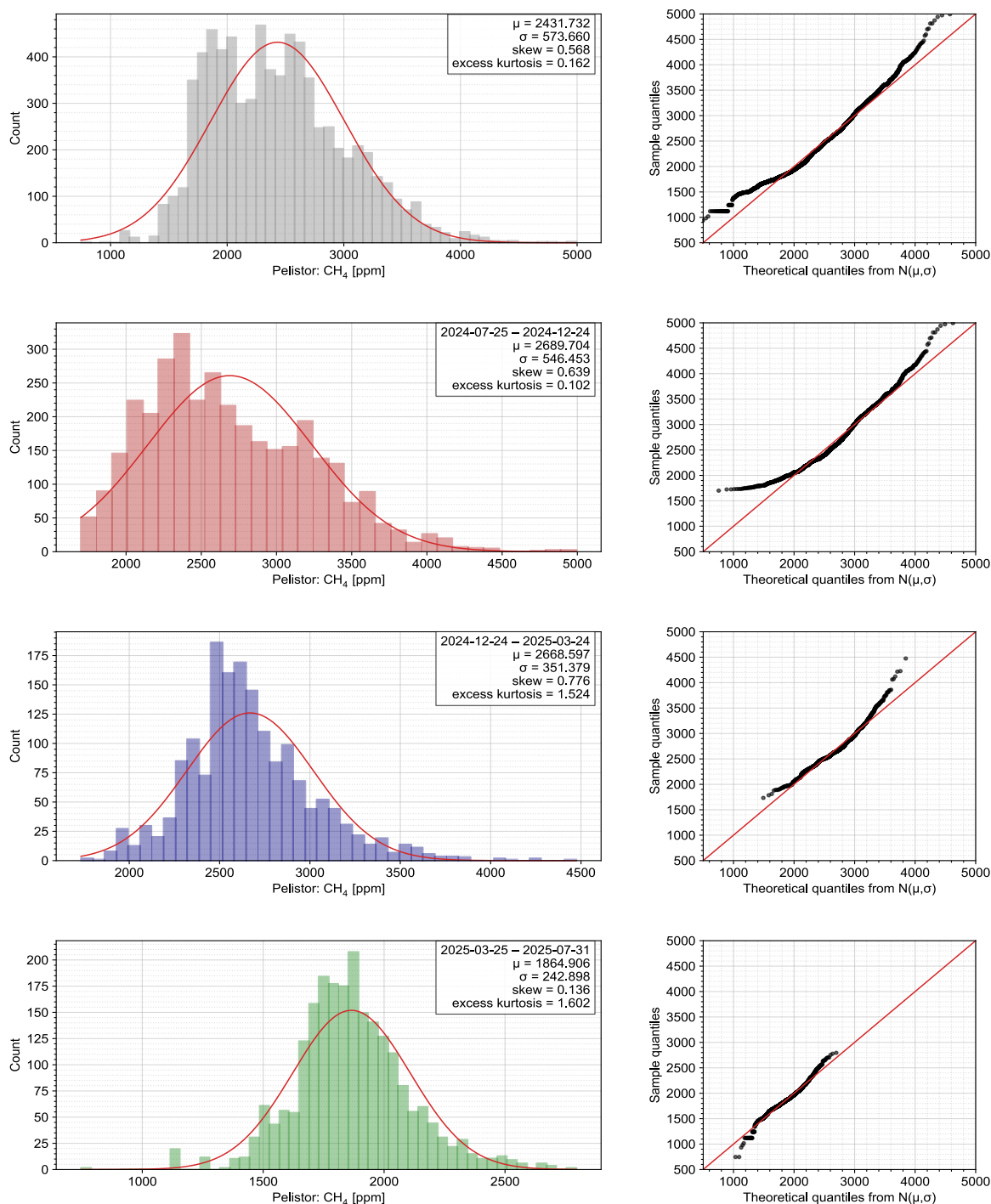


Figure S4. Time-series of mine's Pellistor measured CH_4 concentrations in the exhaust shaft and their frequency distribution curves and a QQ plots selected for the annual timescale and three distinctive (I–III) periods.

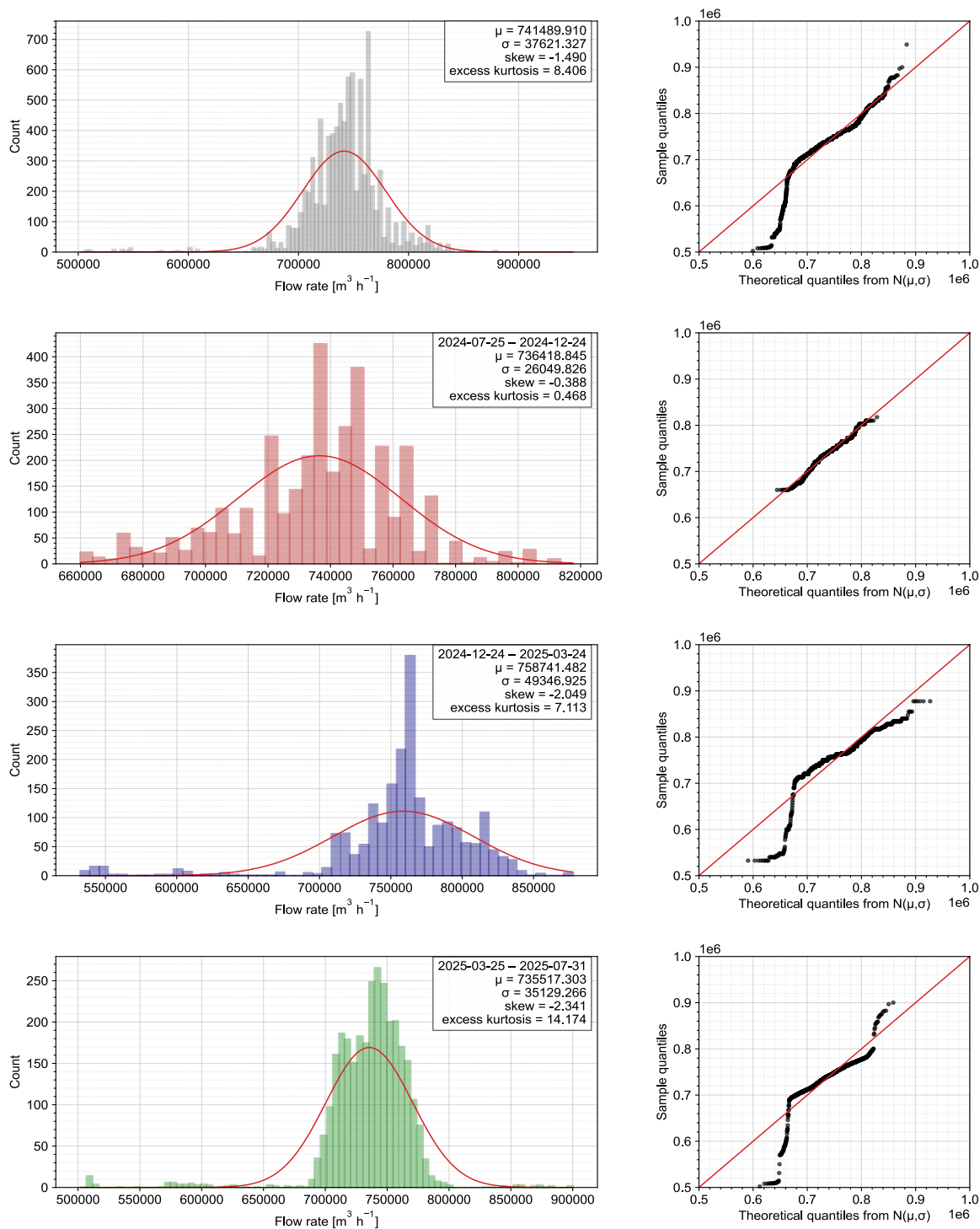
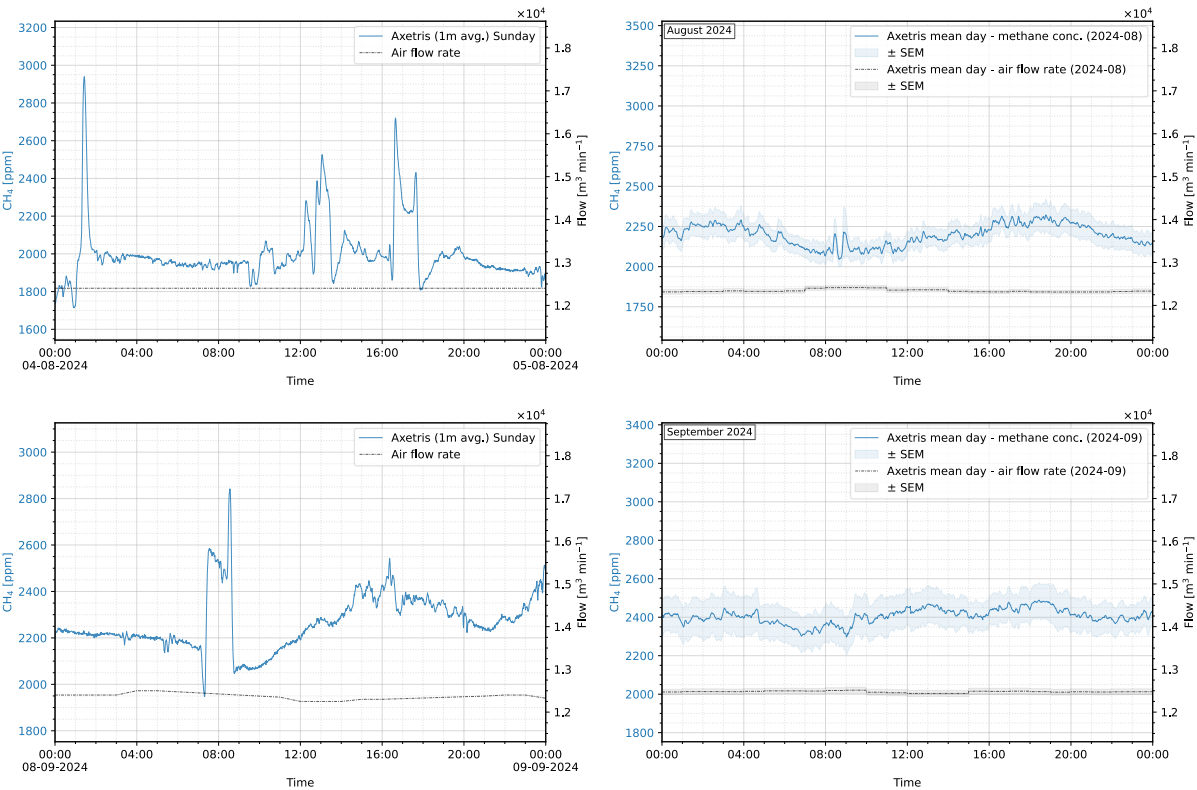
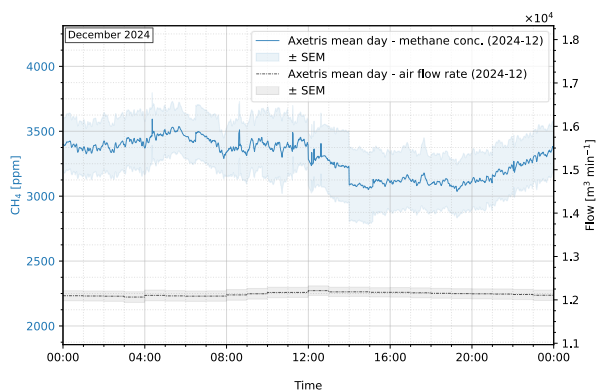
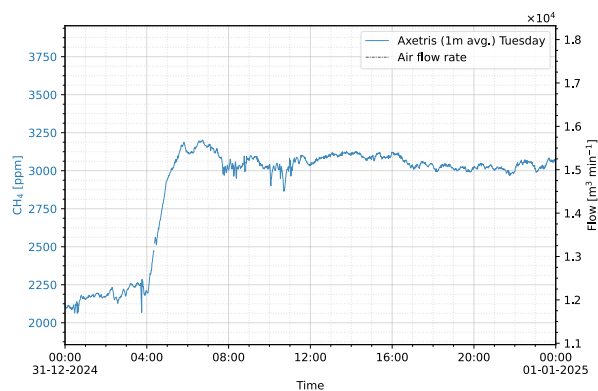
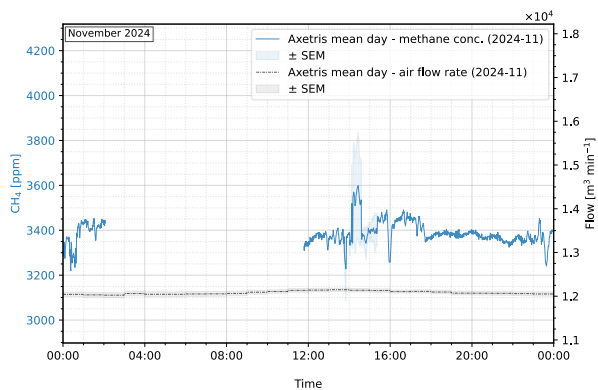
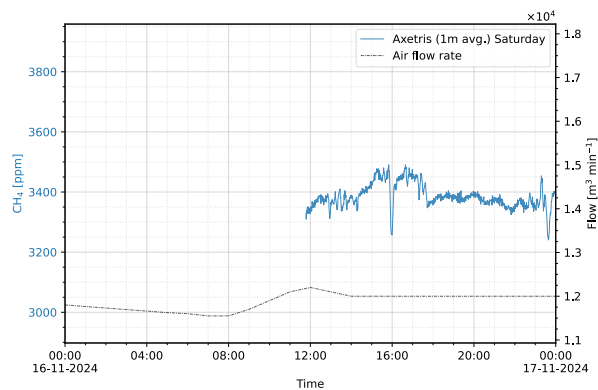
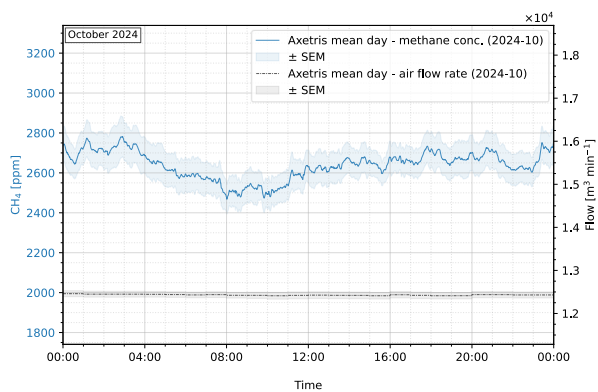
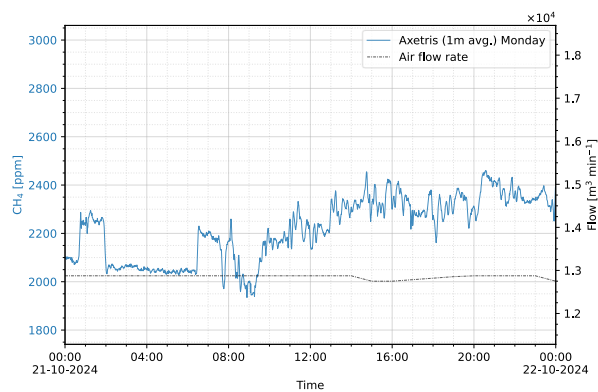


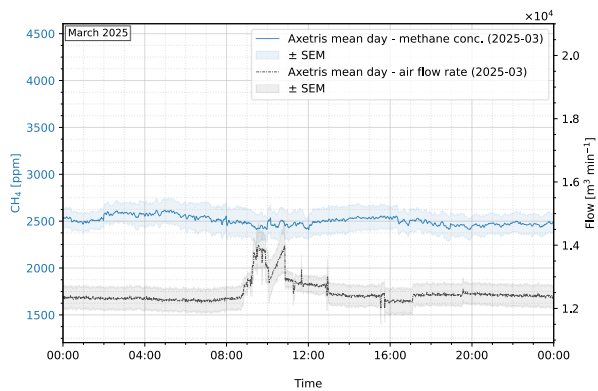
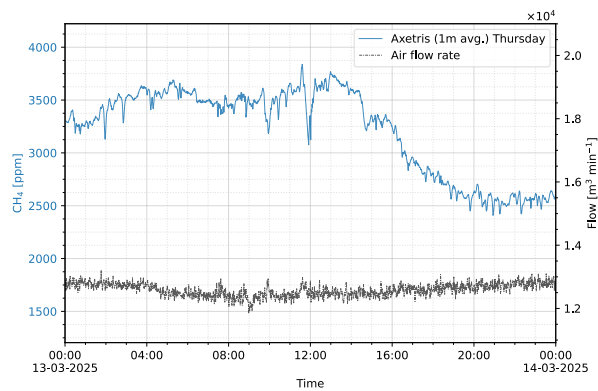
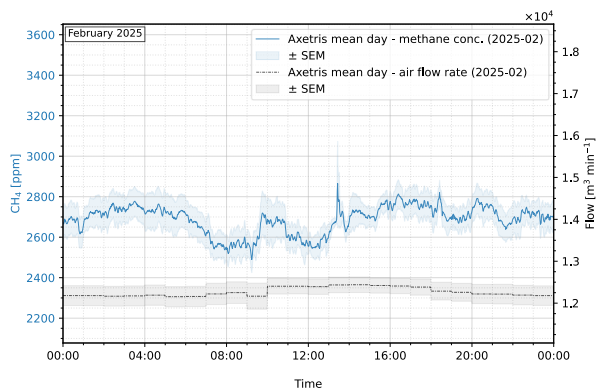
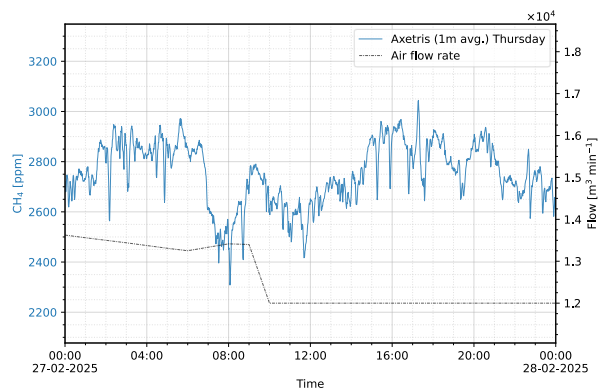
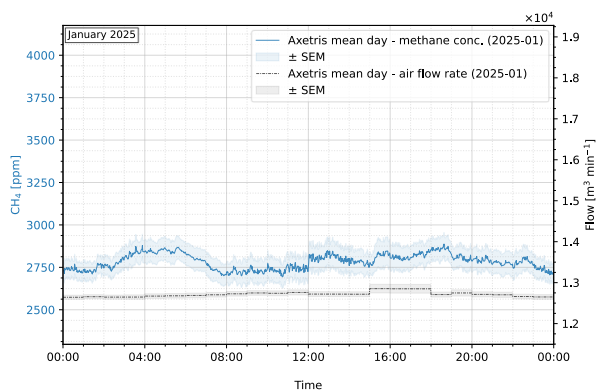
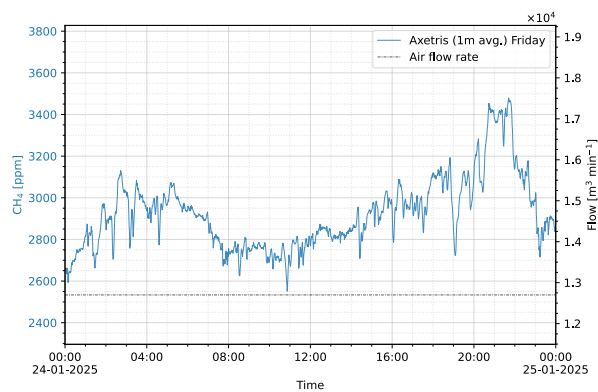
Figure S5. Time-series of ventilation airflow rates in the exhaust shaft and their frequency distribution curves and a QQ plots selected for the annual timescale and three distinctive (I–III) periods.

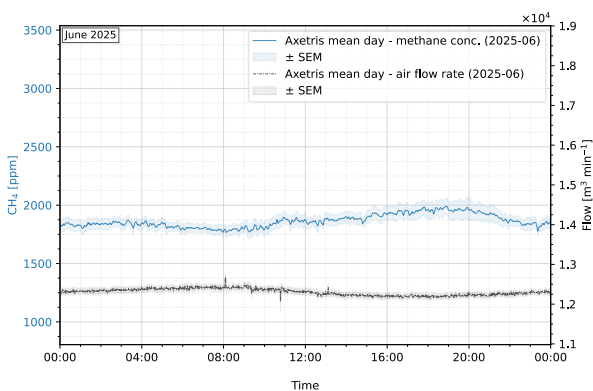
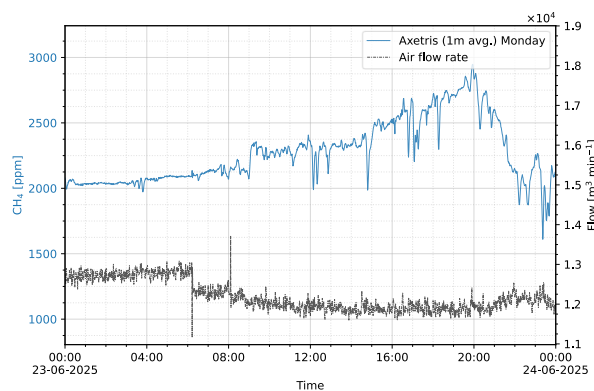
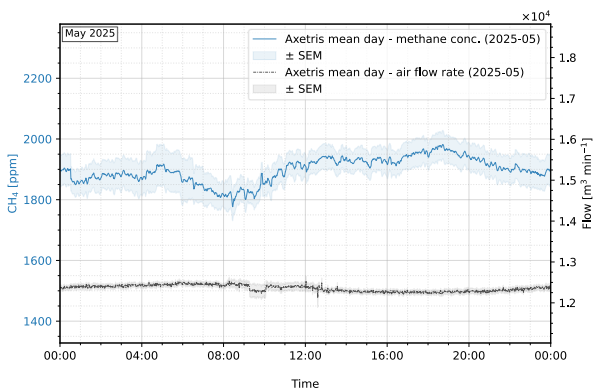
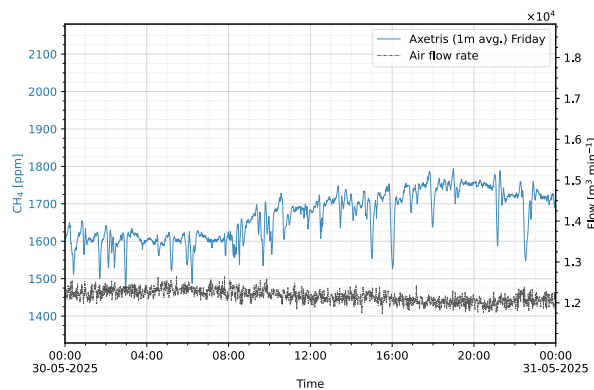
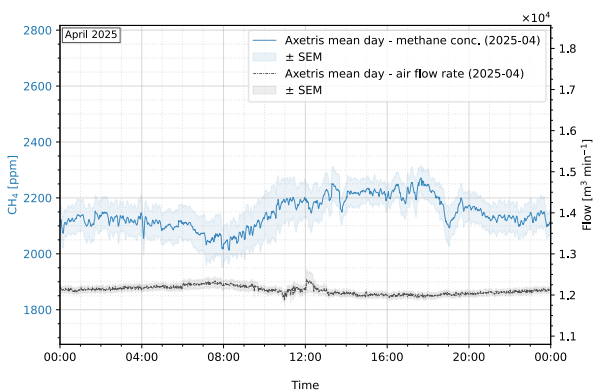
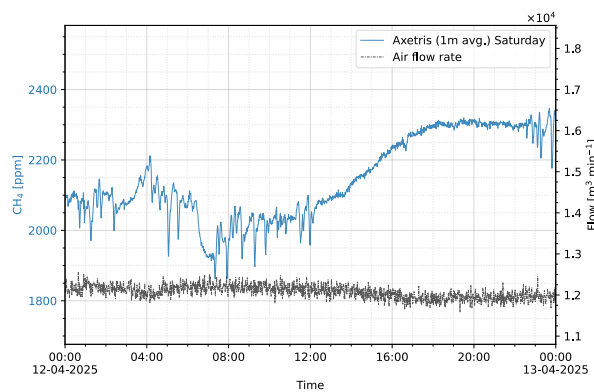
Text S6. Temporal variations in methane levels measured with the Axetris LGD analyzer and ventilation airflow rates

Methane concentrations and ventilation airflow rates were recorded in the exhaust ventilation shaft at 1-minute resolution from August 2024 to July 2025. At 1-minute resolution, CH₄ concentrations exhibit short-term variability characterized by rapid fluctuations and episodic peaks. For analytical purposes, the data were additionally aggregated to 1-hour averages in order to reduce high-frequency noise and highlight broader temporal trends of relationship between airflow rate and CH₄ concentration. The plots illustrate both a short-term daily (minute average) and mean monthly (hourly average) fluctuations of CH₄ concentrations and variations in ventilation airflow rates for the study period (Fig. S6).









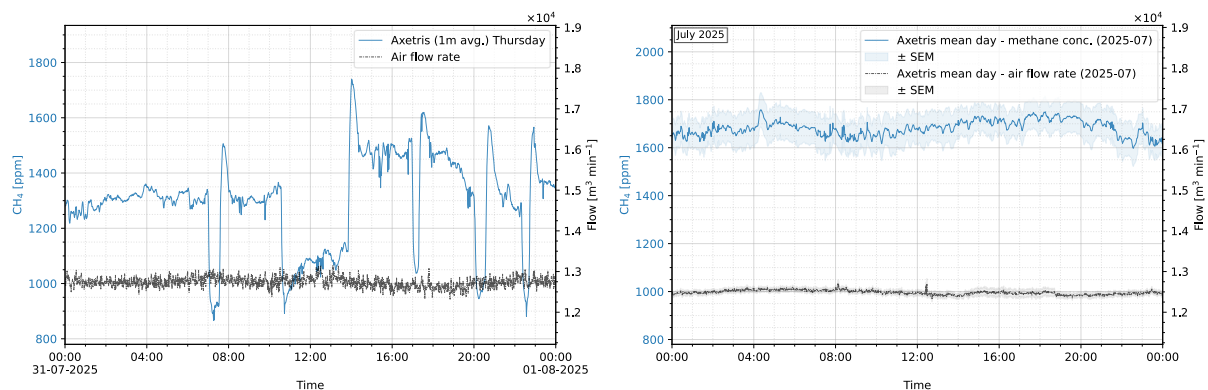
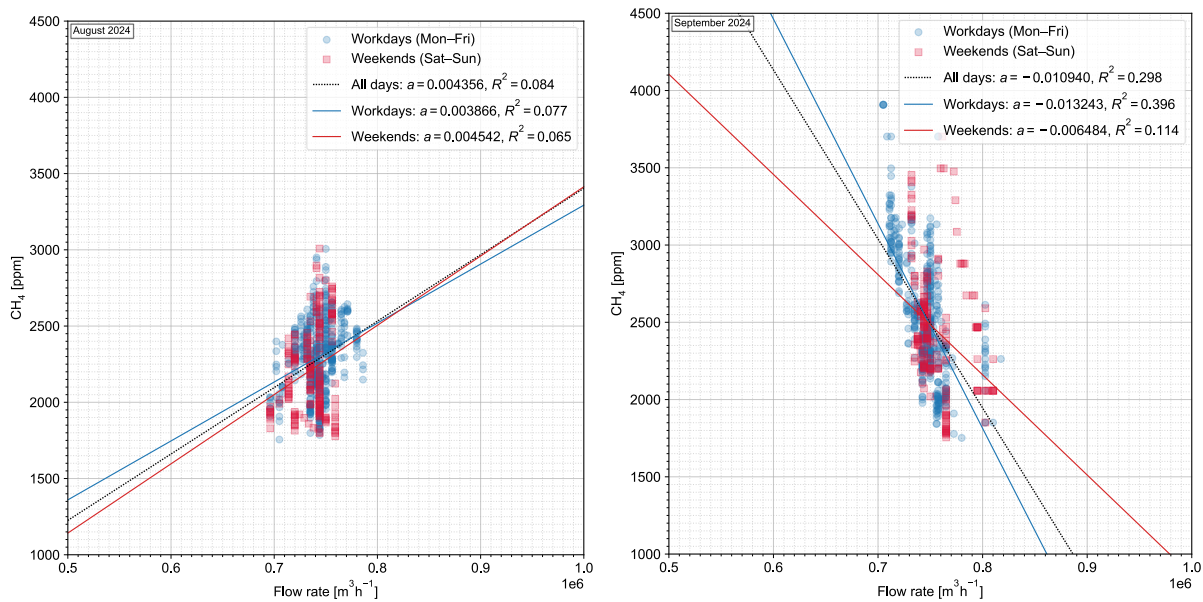


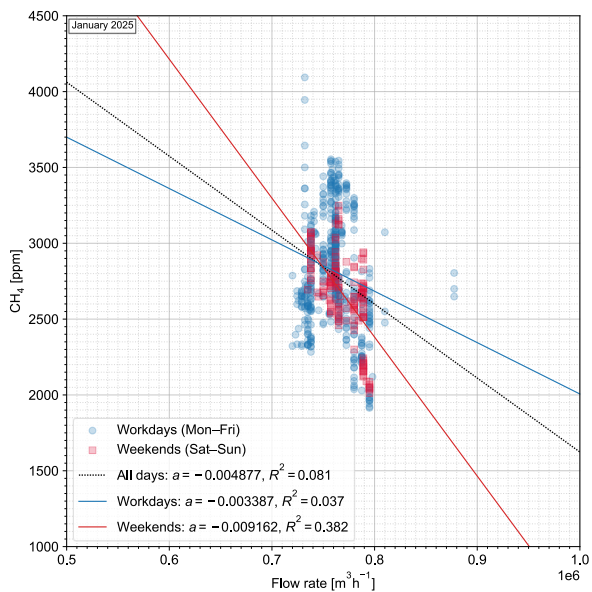
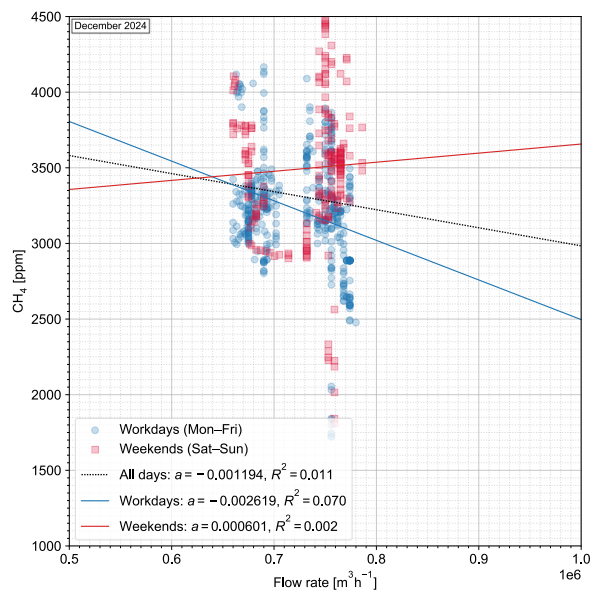
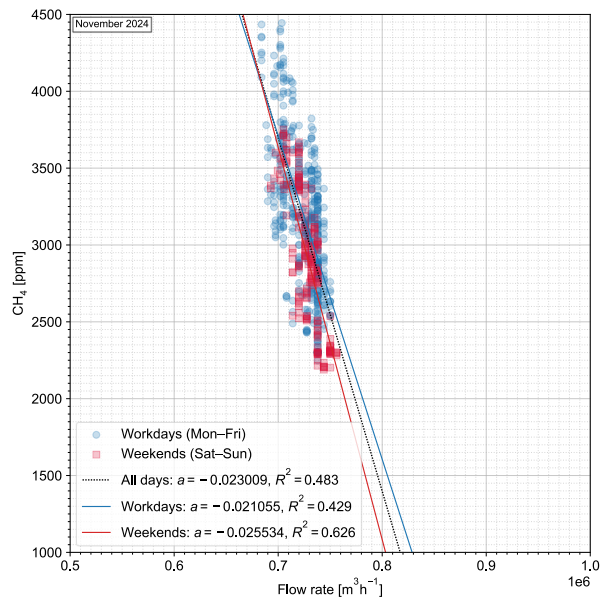
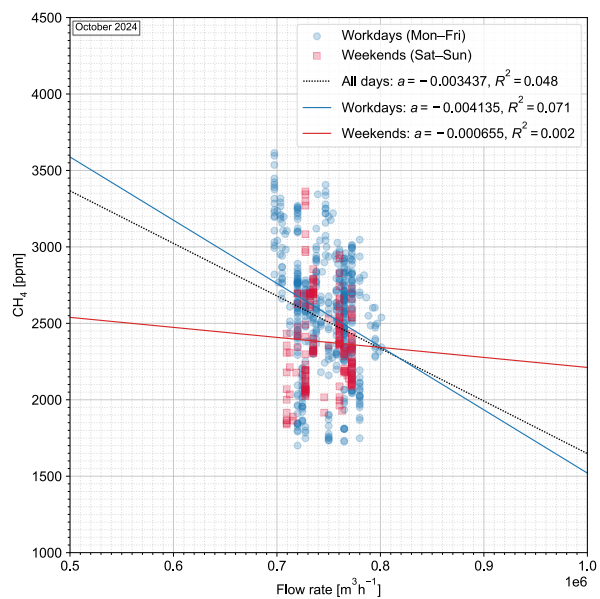
Figure S6. Time-series of CH₄ concentrations measured by the Axetris LGD analyzer and corresponding ventilation airflow rates in the exhaust shaft. Data are presented at daily 1-minute resolution as raw data – left panel and as daily averages – right panel for successive months over the monitoring period (August 2024 – July 2025). The airflow monitoring system was upgraded in March 2025, resulting in an increase in the real-time airflow measurement frequency to 1-minute resolution.

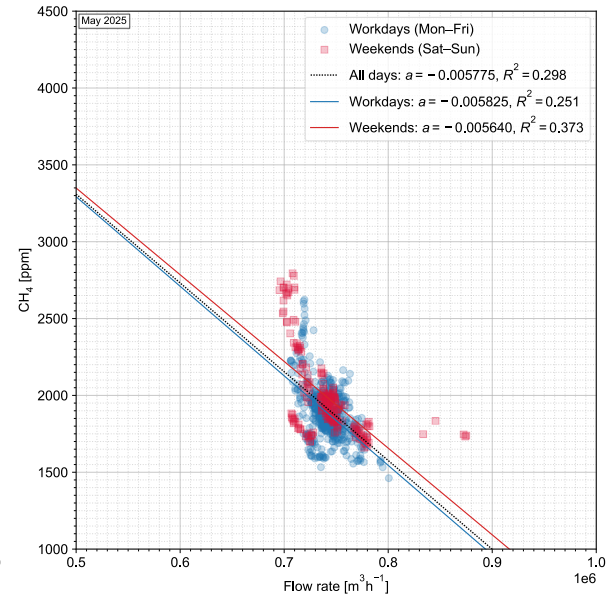
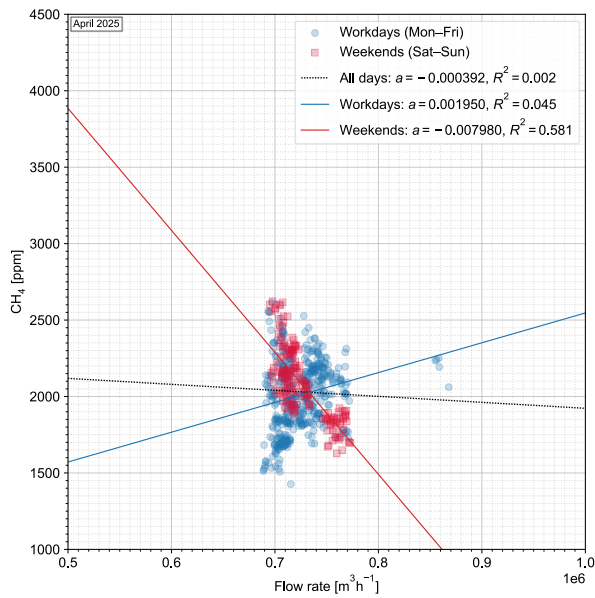
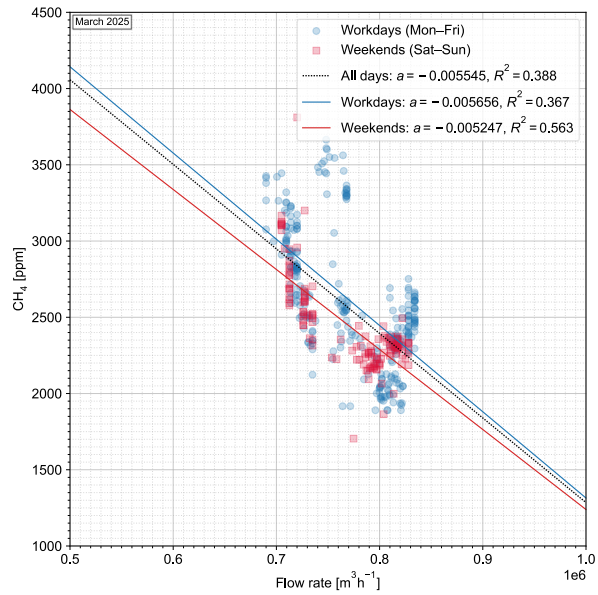
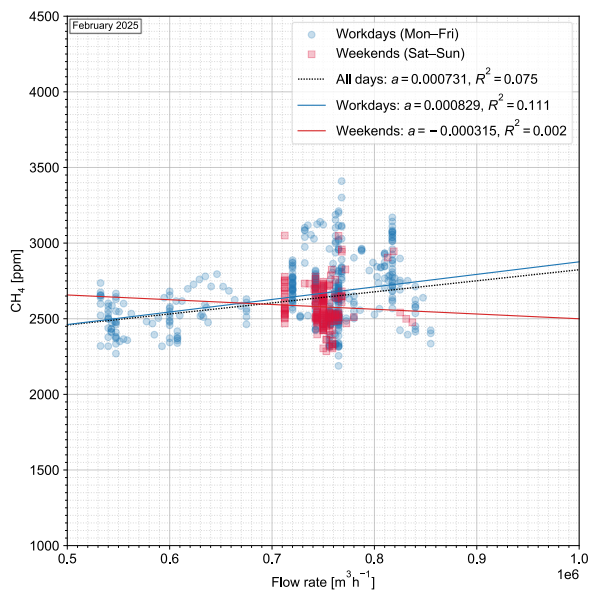
Text S7. Airflow rates and methane concentration in the ventilation shaft

200 Corresponding CH₄ concentration measurements obtained using the Axetris LGD analyzer were analysed together with ventilation shaft airflow rates to examine the influence of ventilation intensity on methane variability. The dataset was grouped by individual months and further separated into weekday (Monday–Friday) and weekend (Saturday–Sunday) operating conditions to reflect potential differences in mining activity. Linear regression analysis was performed for each monthly dataset, with regression lines calculated separately for weekdays, weekends, and complete monthly observations in order to

205 evaluate the direction and strength of methane–airflow dependence under varying mine operational conditions (Fig. S7).







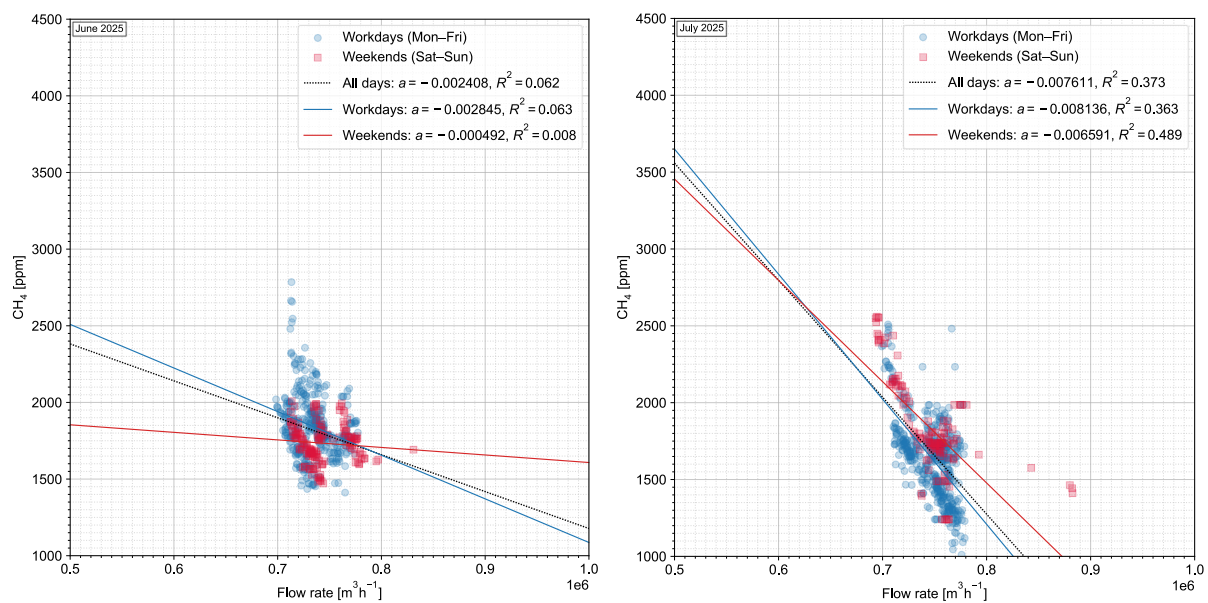


Figure S7. Relationship between methane concentration and airflow rate in the ventilation shaft at monthly time scale during the measurement period (August 2024–July 2025), with separate regression lines for weekday and weekend operating conditions.

Text S8. Evaluation of the Pellistor sensor records against the Axetris LGD data series

The comparative analysis of short-term methane records (1-min averages) measured by the Axetris laser gas detection analyzer and the pellistor sensor reveals systematic differences in both absolute concentration levels and temporal response characteristics (Fig. S8). The pellistor CH₄ readings remain systematically lower and exhibit reduced variability relative to the Axetris measurements, indicating limited sensitivity, mostly at elevated gas concentrations. In addition, the pellistor signal shows a later response to rapid concentration changes, leading to partial smoothing of short-term fluctuations (Fig. S9). These discrepancies emphasize the importance of proper calibration when pellistor sensors are used for quantitative CH₄ assessment in the mine ventilation system.

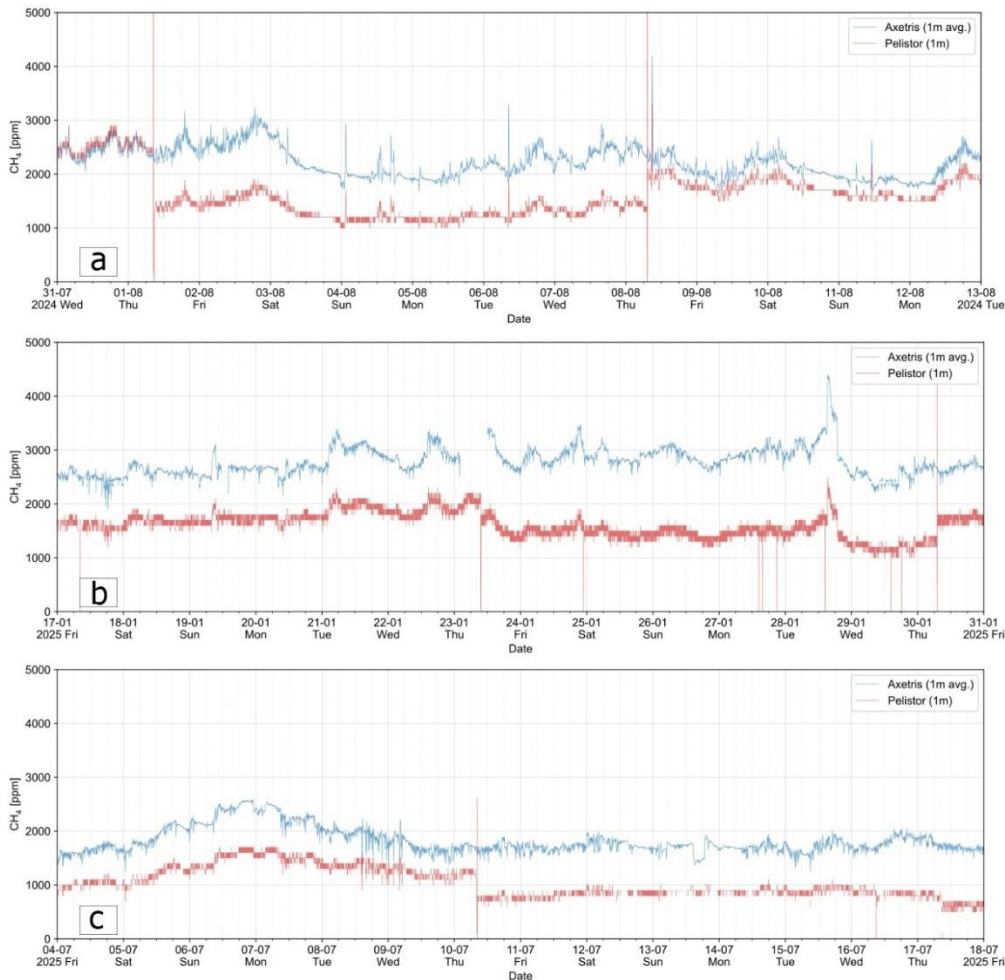
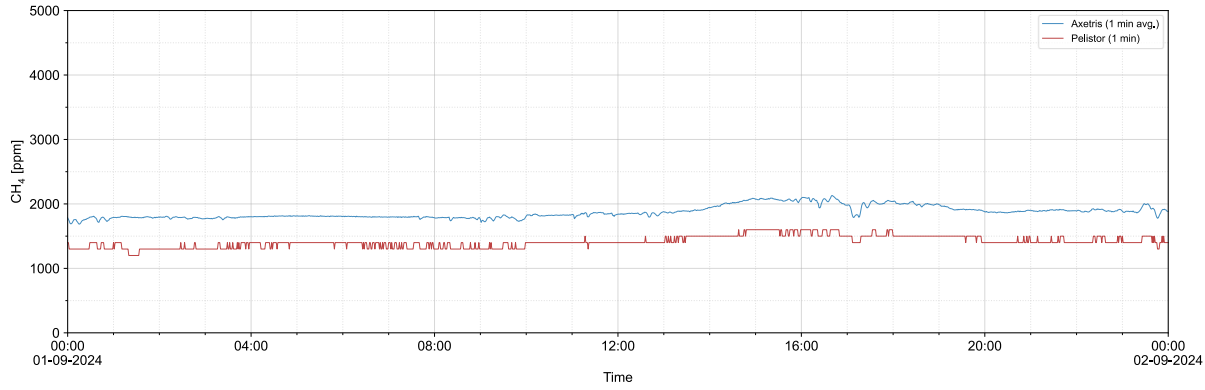
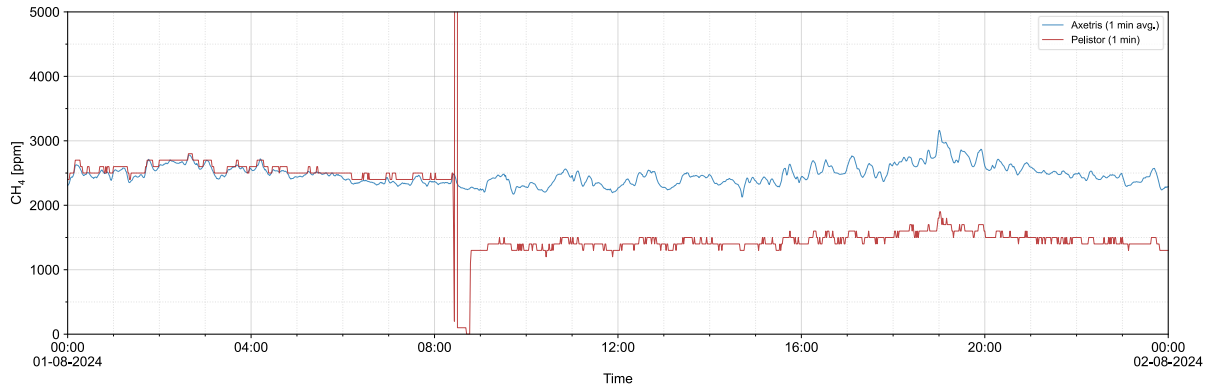
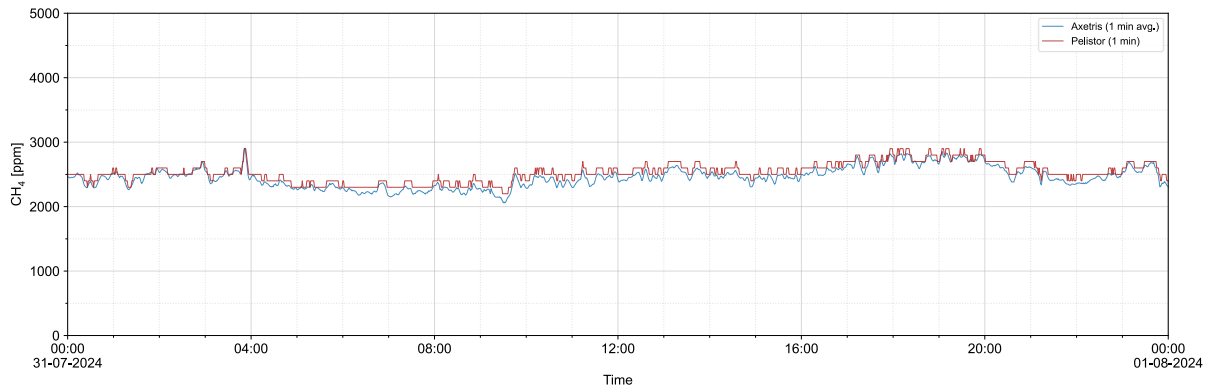
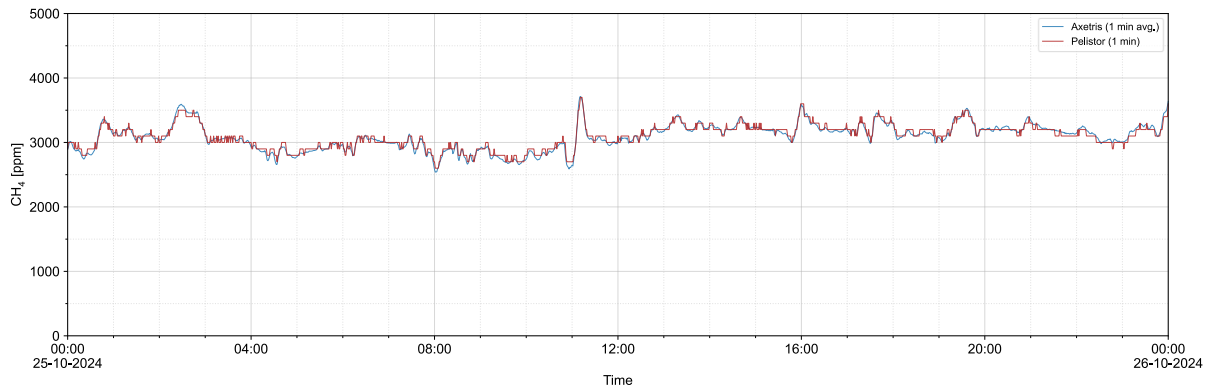
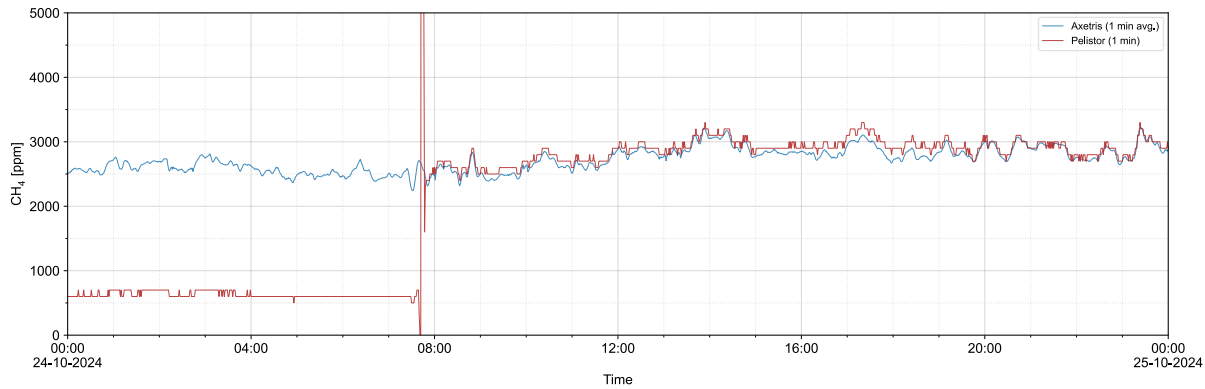
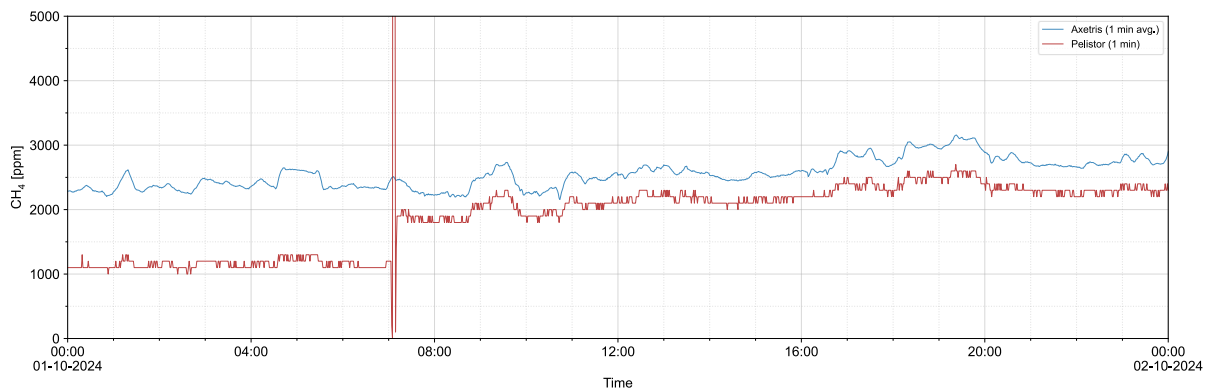
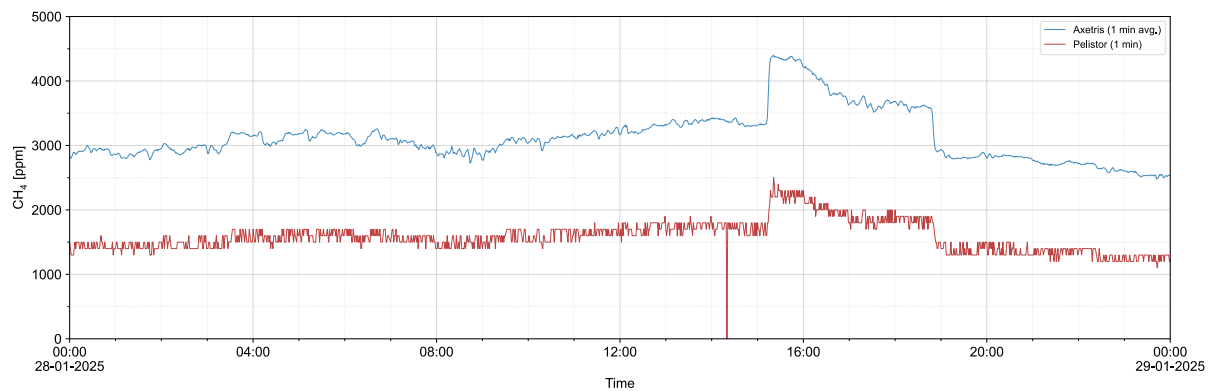
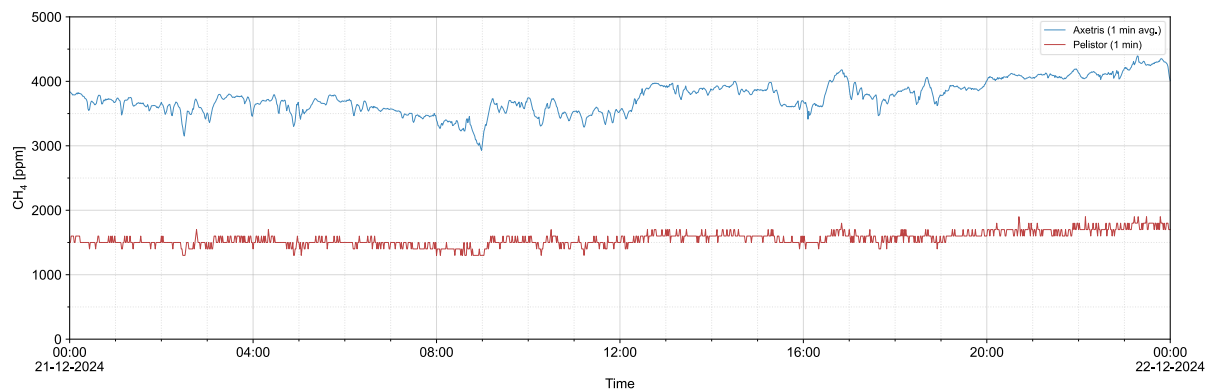
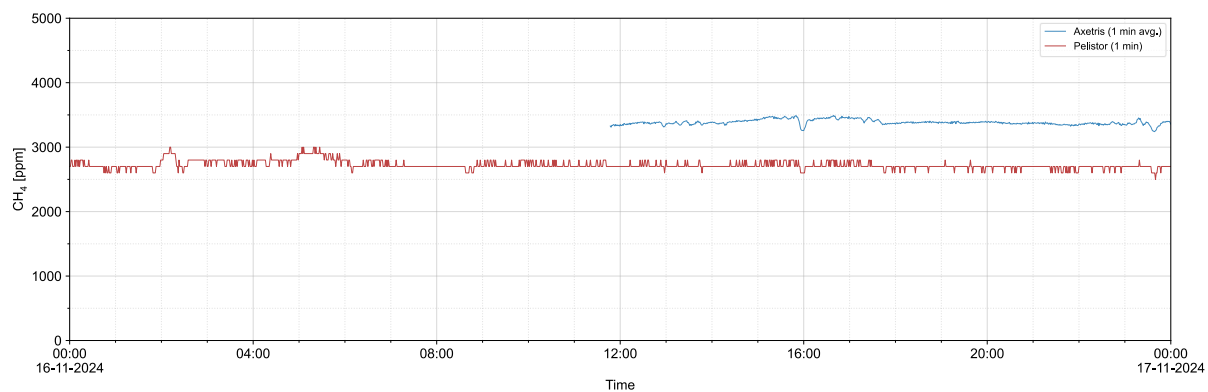


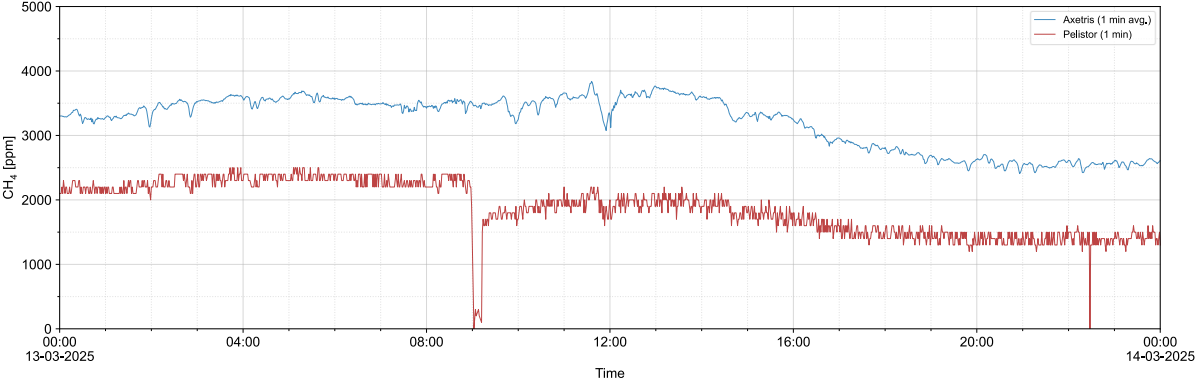
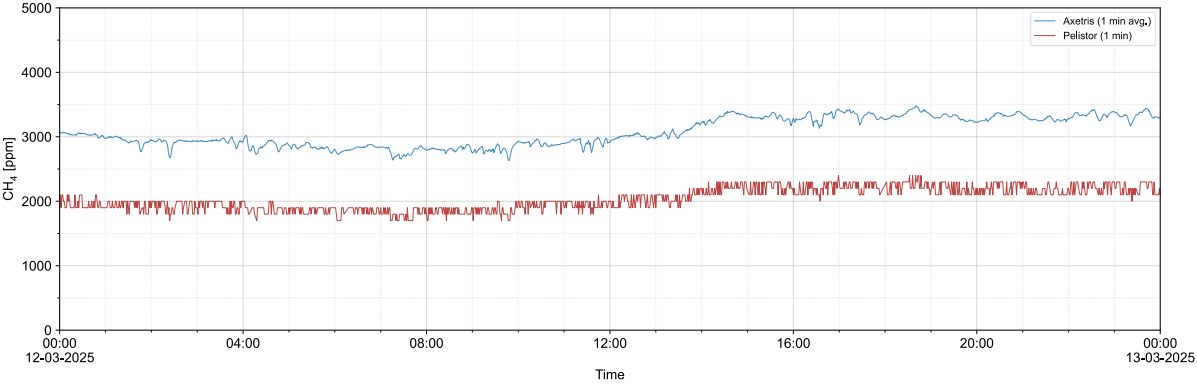
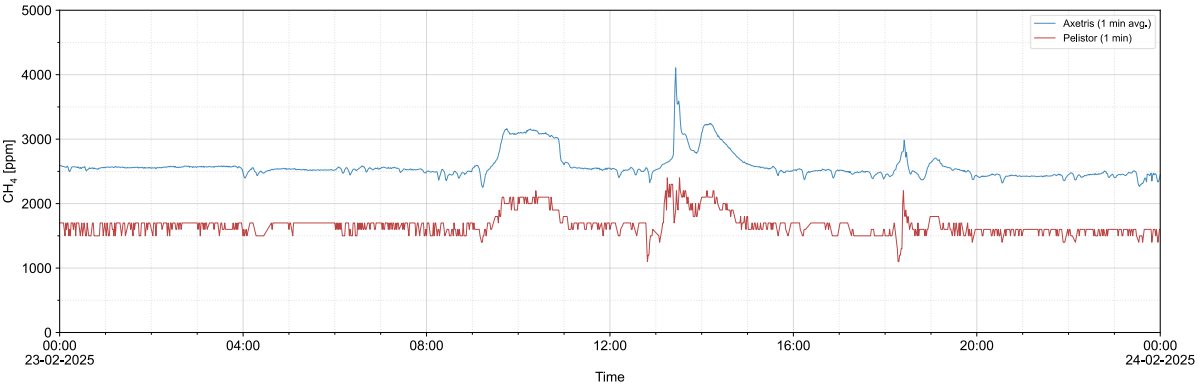
Figure S8. Comparison of methane concentrations measured by the Axetris LGD analyzer (1-min averages) and the pellistor sensor (1-min data) in the mine ventilation shaft for three representative periods: (a) August 2024 (Period I), (b) January 2025 (Period II), and (c) July 2025 (Period III). Signal dropouts and abrupt decreases to near-zero values correspond to calibration events of the pellistor sensor conducted by the mine ventilation team.

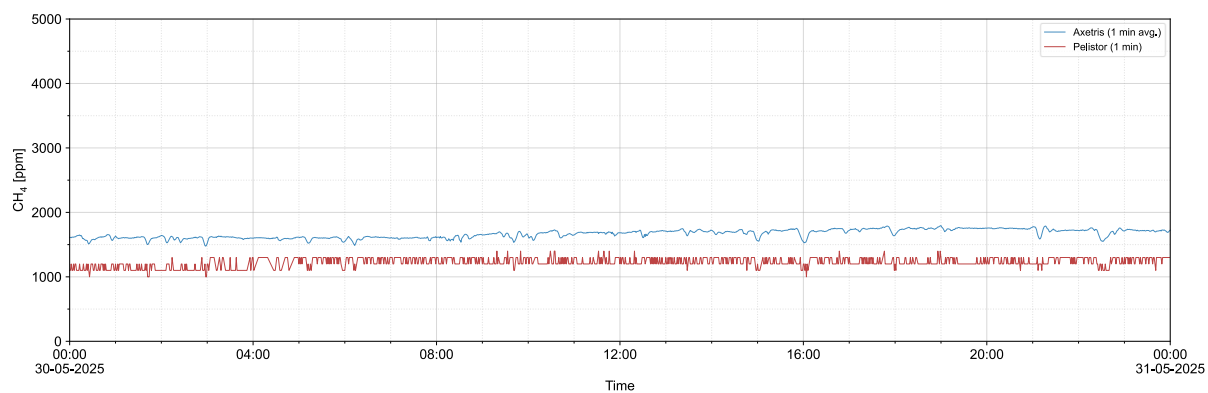
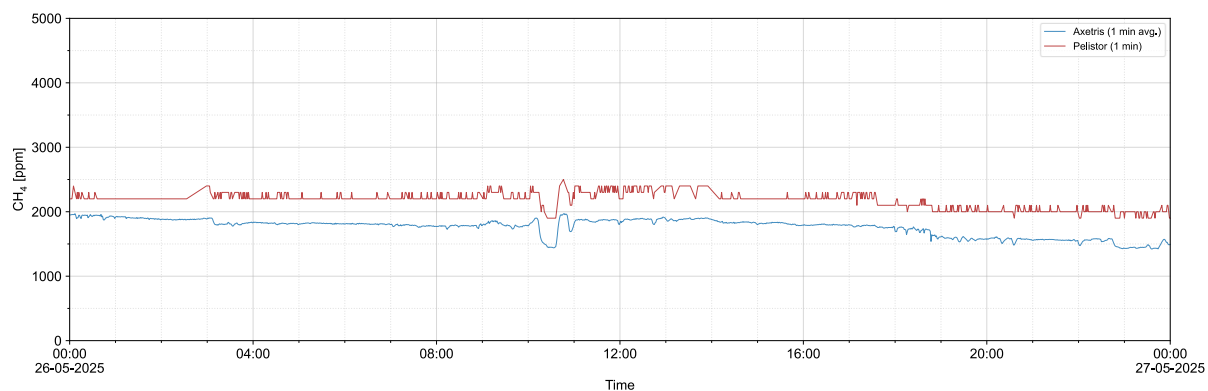
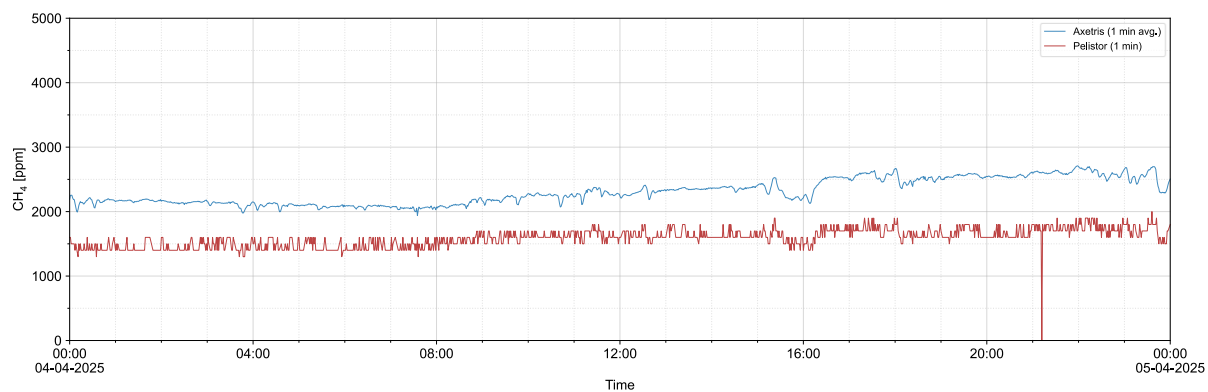


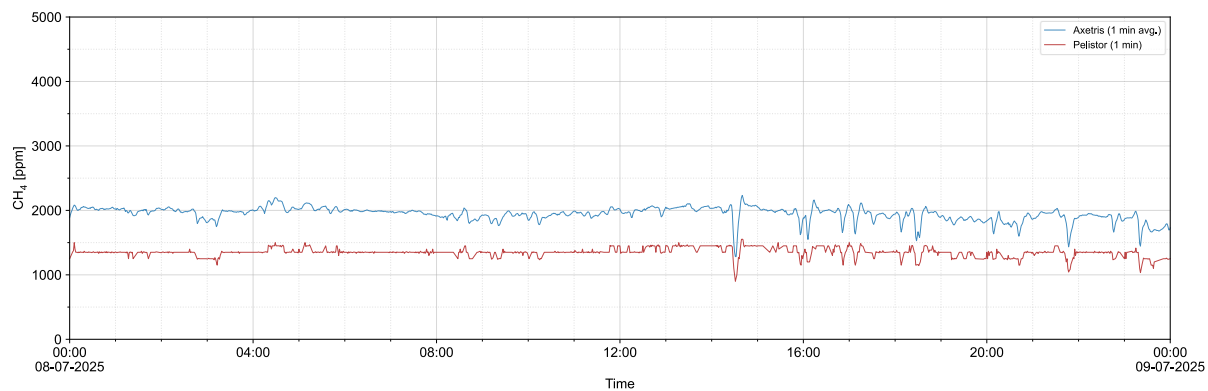
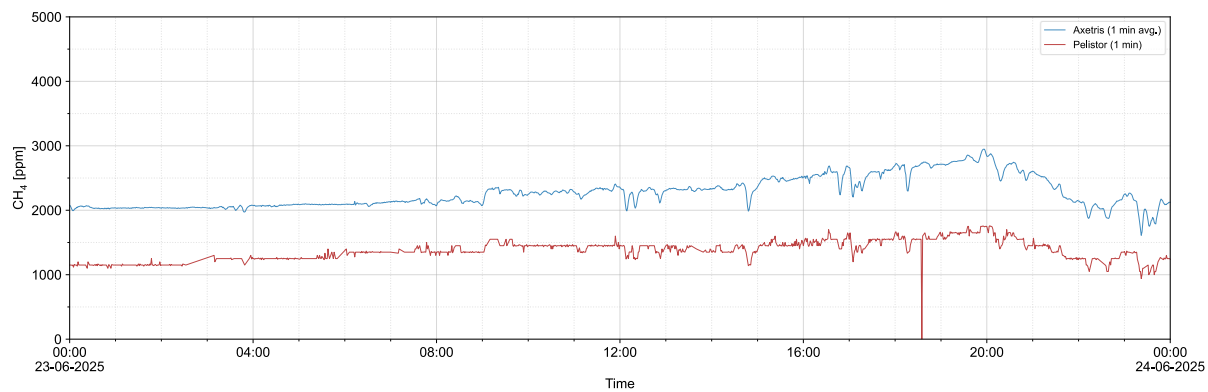
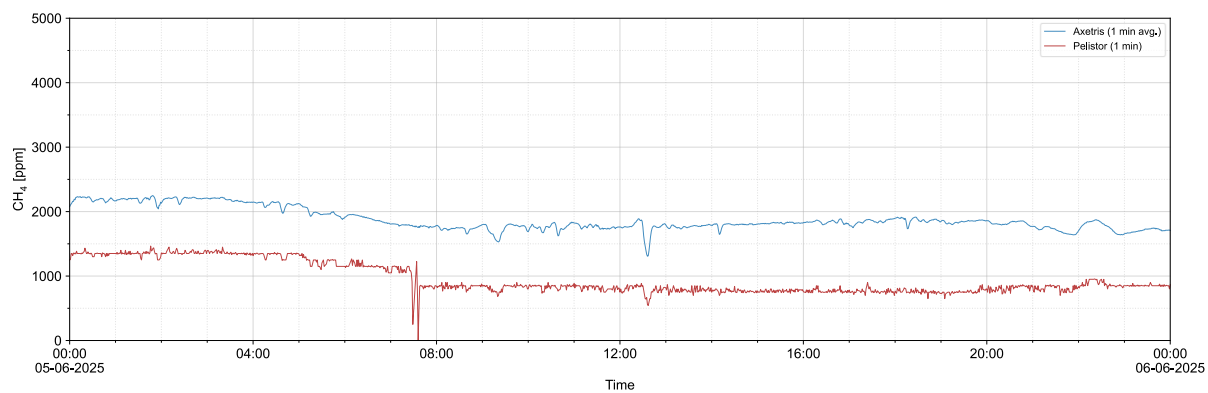
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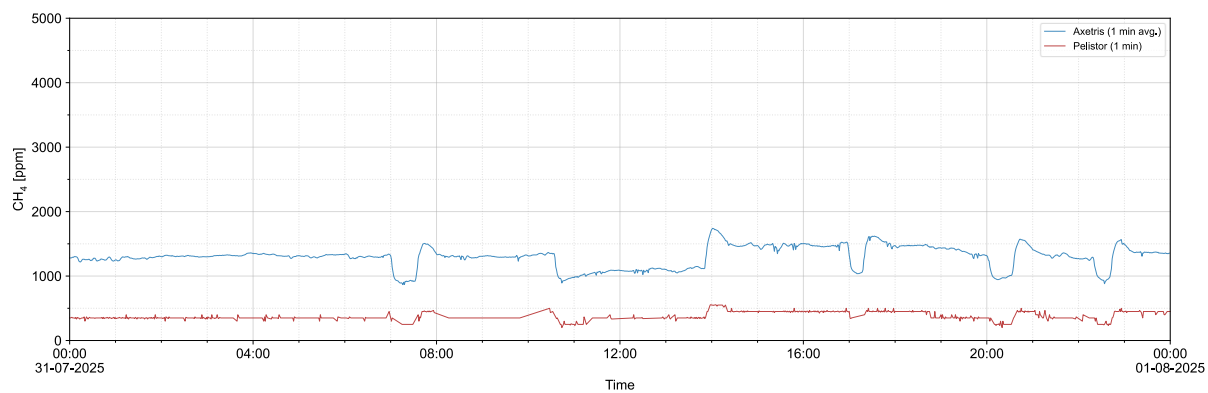












250 **Figure S9.** Time series of CH₄ concentrations (1-min averages) measured by the Axetris LGD analyzer and the pellistor sensor in the mine ventilation shaft for selected months during the monitoring period (August 2024–July 2025).

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