



Supplement of

Atmospheric CO₂ and CH₄ measurements at Schauinsland station, Germany: a comparative study of diurnal and seasonal variations at 12 and 35 m intake height

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S1 Seasonal mean cycles under clean air selection criteria

Data that are strongly influenced by fluxes originating from the vicinity of the station need to be removed from the time series systematically, in order to guarantee the representativeness of the data on large scales. Selection criteria discussed in Schmidt et al. (2003), which are designed to filter for polluted air masses that are transported from the Rhine valley to the station, are

applied to the 12 m and 35 m time series. The selection criteria are:

- night-time values only (21:00–05:00 UTC)
- high wind speed ($> 2.5 \text{ m sec}^{-1}$ in summer and $> 3.5 \text{ m sec}^{-1}$ in winter)
- minimum 4 hourly values for a daily average
- small standard deviation of the daily averages ($< 1.5 \text{ ppm}$ in CO_2 and $< 7 \text{ ppb}$ in CH_4)

After applying this filter of high wind speeds and night-time data 19% of the hourly data remain. The results are analyzed regarding seasonal differences between the CO_2 and CH_4 measurement at an intake height of 12 m and 35 m a.g.l. in the following sections.

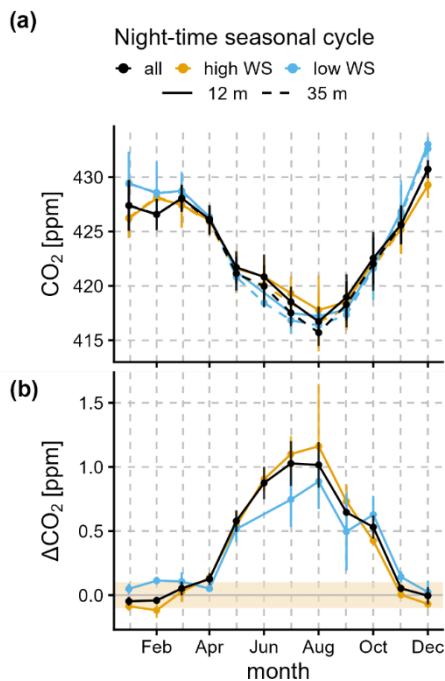


Figure S1. Mean seasonal cycle of CO_2 mole fractions measured during night-time at 12 m (solid line) and 35 m (dashed line) in panel (a). Data without an additional wind speed filter is depicted in black, filtered for high wind speeds ($> 2.5 \text{ m sec}^{-1}$ in summer and $> 3.5 \text{ m sec}^{-1}$ in winter) in orange and correspondingly for low wind speeds in blue. Panel (b) shows the respective mole fraction differences between the two intake lines (12–35 m), with the WMO/GAW compatibility goal in beige. The error bars represent the standard error of the seasonal mean.

The peak-to-peak amplitude of the mean CO₂ night-time seasonal cycle selected for high wind speeds is 10.3 ± 2.2 ppm at the 12 m intake height and 11.5 ± 2.3 ppm at the 35 m intake height (orange lines in Fig. S1a). Filtered for low wind speeds, the peak-to-peak amplitude is 2 to 3 ppm larger (blue line). The month of June is missing for the 12 m time series filtered for low wind speeds as too little data was available for a robust mean. Only using night-time data (black line) reduces the amplitude of the seasonal CO₂ cycle by approximately 2 ppm in contrast to full days, the high wind speed filter reduces the peak-to-peak amplitude of the mean seasonal CO₂ cycle additionally by about 0.3 ppm. This indicates that data filtered with the selection criteria by Schmidt et al. (2003) is generally less influenced by the regional biosphere. However, under these conditions, the difference between the lines are strongly pronounced in summer, reaching up to 1.2 ppm and are therefore 0.2 ppm higher than the differences calculated from data without wind speed filter (Fig. S1b). In contrast, no such pattern can be observed in winter, with mole fraction differences between the intake heights remaining smaller than ± 0.1 ppm from November until May.

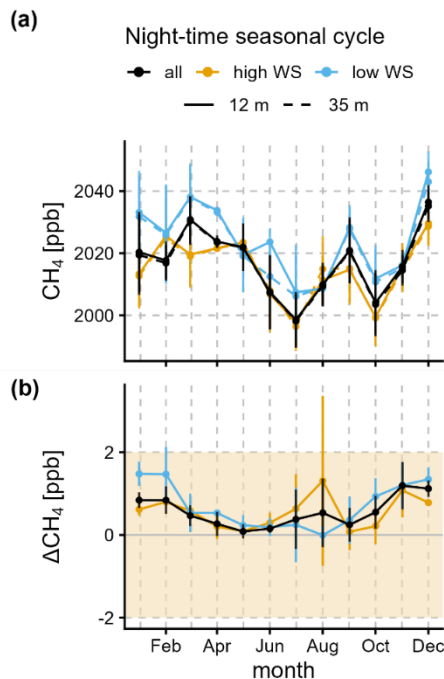


Figure S2. Mean seasonal cycle of CH₄ mole fractions measured during night-time (21:00-05:00 UTC) at 12 m intake height (solid line) and 35 m intake height (dashed line) in panel (a). Data without an additional wind speed filter is depicted in black, filtered for high wind speeds (> 2.5 m sec⁻¹ in summer and > 3.5 m sec⁻¹ in winter) in orange and for low wind speeds in blue. Panel (b) shows the corresponding mole fraction differences (12–35 m). The WMO/GAW compatibility goal is shown in beige. The error bars represent the standard error of the seasonal mean.

The seasonal mean CH₄ mole fraction under high or low wind speed selection and the corresponding differences are barely distinguishable within the error margins (Fig. S2). However, particularly high differences between the intake heights under high wind speed are observed in August, which is suspected to relate to the previously mentioned influence of local pollution. Furthermore, the wind speed sensor was out of order the entire August 2023, enhancing uncertainties on the mean mole fraction difference in August.

40 S2 Evaluation of two different spike detection algorithms and sensitivity tests

The Robust Extraction of the Baseline Signal (REBS) and the Standard Deviation of the Background Signal (SD) are two commonly used spike detection algorithms (El Yazidi et al., 2018; Cristofanelli et al., 2023), which are tested for the purpose of this study on an exemplary subset of the data. The REBS algorithm (Ruckstuhl et al., 2012) is summarized in section 2.6. The SD method (Drewnick et al., 2012) uses the standard deviation σ of the data between the first and the third quartile (σ_{25_75}) or below the median (σ_{50}), which is assumed to be unpolluted. A data point x_i is flagged if it exceeds a threshold defined by a random walk formula (Eq. 2), where x_{unf} is the last uncontaminated data point in the time series and n the number of time steps between x_i and x_{unf} . The factor α is set to 0.1, 0.5, 1 and 3 in this study.

$$x_i > x_{unf} + \alpha \times \sigma + \sqrt{n} \times \sigma \quad (2)$$

Figure S3 shows the results of the SD algorithm in various configurations applied to an exemplary 12 m time series from 19 to 29 June 2023, where periods with spikes attributed to local pollution are marked manually. Unfortunately, the algorithm is only able to identify the few highest spikes and does not detect the largest part of the pollution.

The results of the REBS algorithm applied to the CH₄ time series at 12 m is shown in Fig. S4. The baseline calculated by the algorithm matches the 35 m time series quite well and the CH₄ spikes are largely detected. To investigate the efficiency of the REBS algorithm more closely, one day with only few spikes (22 June 2023) and one day with a large number of spikes (26 June 2023) is analyzed in Fig. S5 and Fig. S6, respectively. During spike intensive periods, the baseline is overestimated, which leads an underestimation of the spike height. A qualitative sensitivity test of the bandwidth is shown in Fig. S7, suggesting the configuration of 60 minutes, which is consistent with El Yazidi et al. (2018) and Cristofanelli et al. (2023). The γ value is estimated as the standard deviation of all data below the fitted baseline curve. While in Cristofanelli et al (2023) this was done using a rolling window of the previous 24 h for each data point, in this study γ was estimated from the complete period to which the algorithm is applied to (May to November of the years 2022 to 2024). Figure S8 shows the application of the algorithm to an example time series using different approaches for estimating γ , including rolling windows ranging from 1 h to two weeks as well as γ estimates derived from the 10 day example period and the complete May to November time series. At the Schauinsland station the spikes occur very frequently during short periods, whereas other periods are largely unaffected. Therefore, estimating γ for shorter sections of the time series can lead to strongly enhanced γ values (e.g. grey line in Fig. S8a), reducing the performance of the spike detection algorithm. Hence, it was chosen to use a constant γ value of 1.65, calculated from the months May to November of the three years of data.

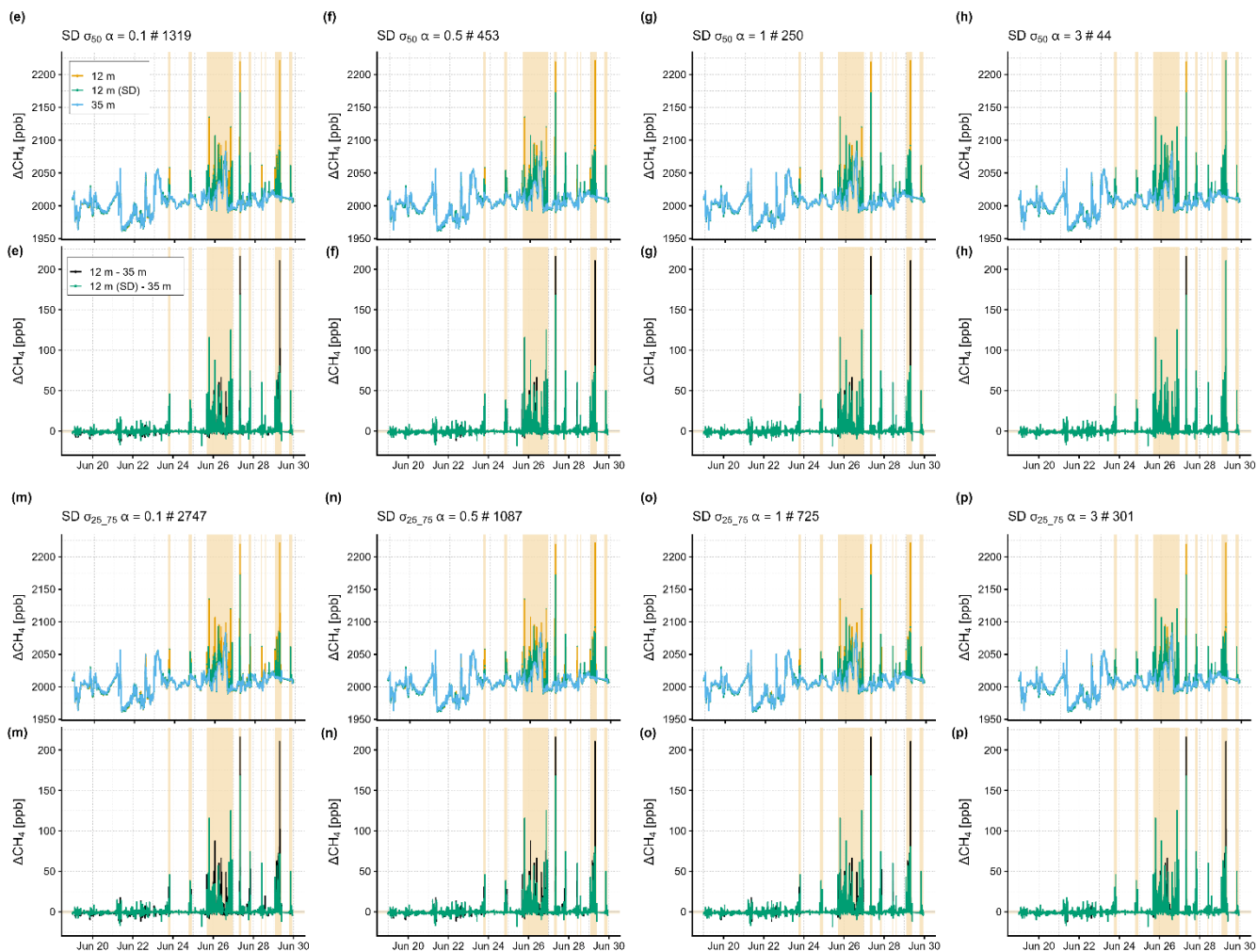
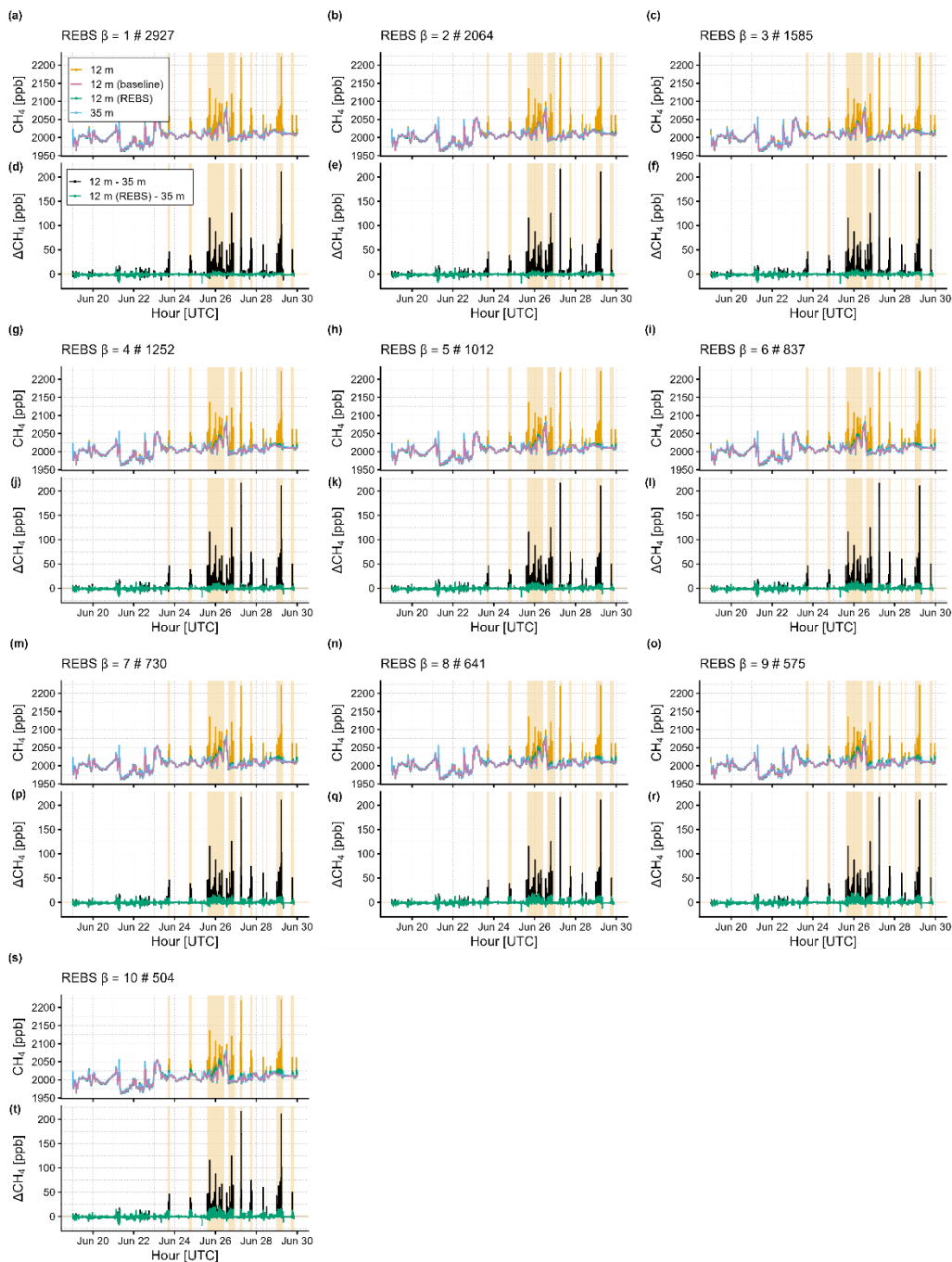


Figure S3. Minutely CH_4 mole fractions measured at 12 m and 35 m intake height and the respective differences (12–35 m) from 19 to 29 June 2023. The SD spike detection algorithm is applied to the minutely CH_4 mole fraction at 12 m. Data after filtering is shown in green, the original data in orange and the 35 m intake height in blue. The plots show the results for $\alpha = 0.1$ (left) to $\alpha = 3$ (right) and using the standard deviation of data below the median (panel (a) to (h)) and between the first and third quantile (panel (i) to (p)), as indicated in the plot title together with the respective number of minutely values marked as polluted. The areas marked in light beige indicate periods of increased mole fractions at 12 m, which are attributed to local pollution manually.



75 **Figure S4. Minutely CH_4 mole fractions measured at 12 m and 35 m intake height and the respective differences (12–35 m) from 19 to 29 June 2023. The REBS spike detection algorithm is applied to the minutely CH_4 mole fraction at 12 m. Data after filtering is shown in green, the original data in orange, the 35 m intake height in blue and the baseline calculated by the algorithm in purple. The plots show the results for $\beta = 1$ to $\beta = 10$, as indicated in the plot title together with the respective number of minutely values marked as spike. The areas marked in beige indicate increased concentrations at 12 m which are attributed to local pollution manually.**

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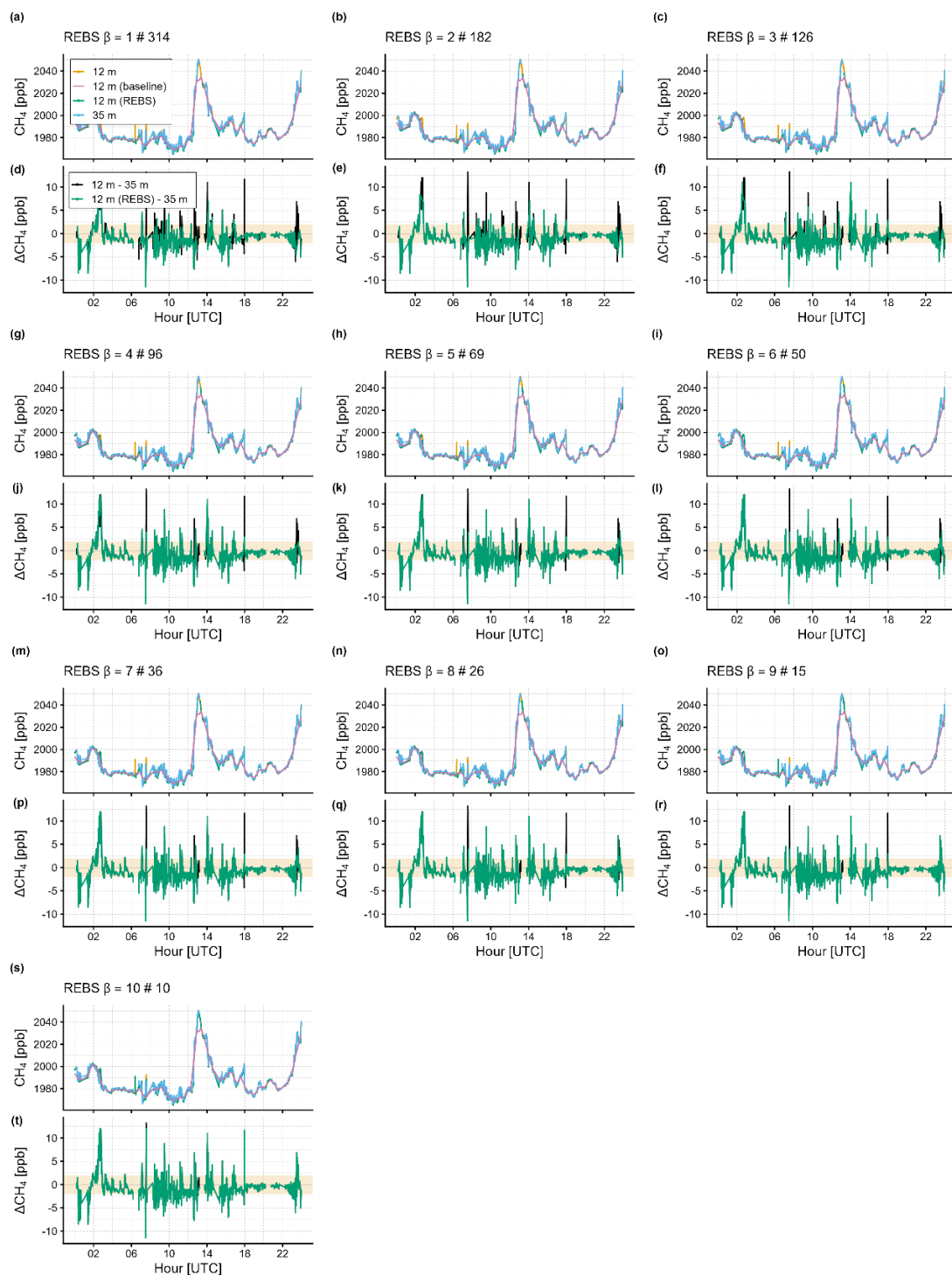
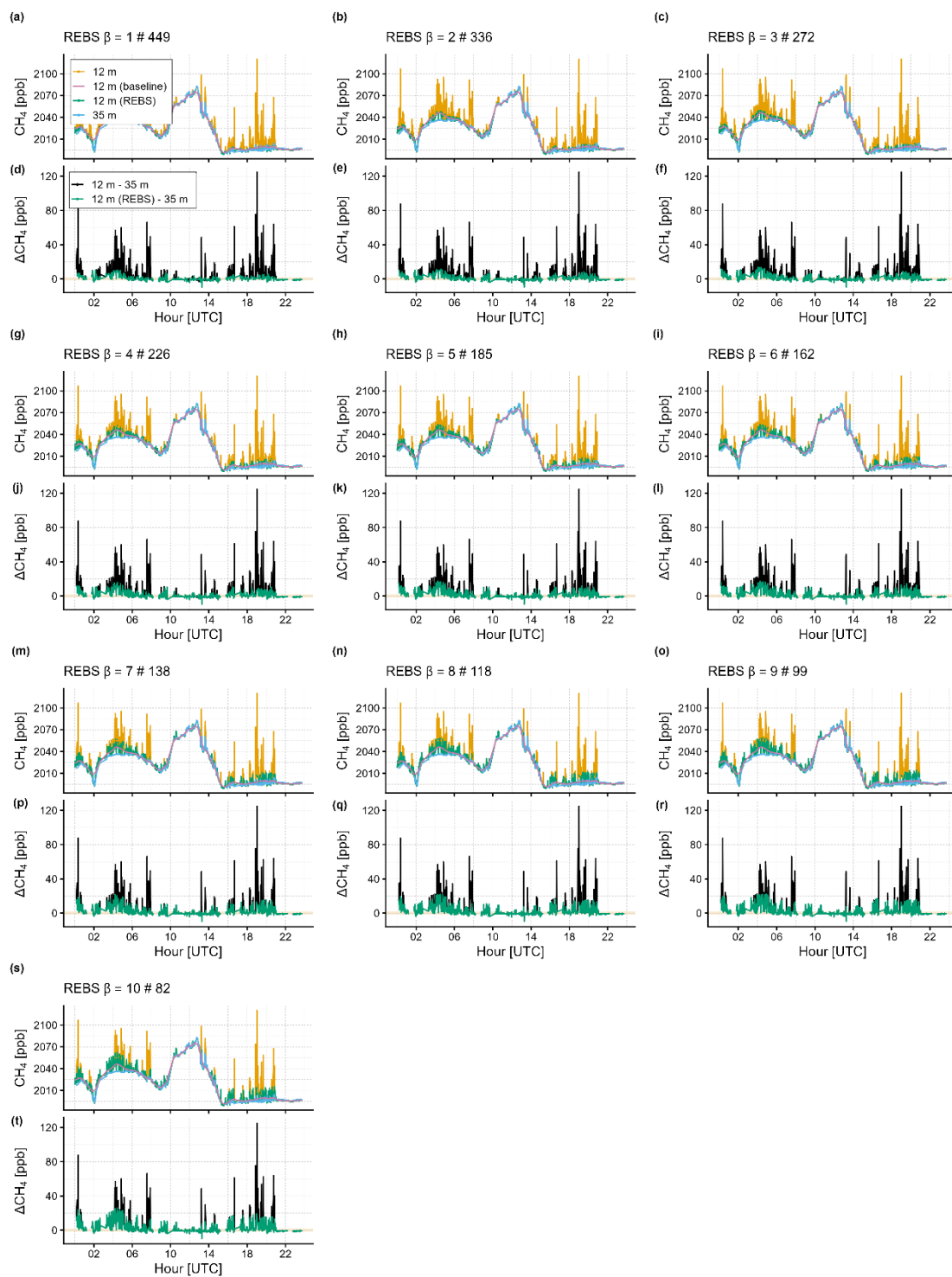


Figure S5. Same as for Fig. S4 but for 22 June 2023 with almost no spikes attributed to local pollution. The beige area marks the WMO/GAW compatibility goal.



85 **Figure S6.** Same as for Fig. S4 but for 26 June 2023 with very frequent spikes. The beige area marks the WMO/GAW compatibility goal.

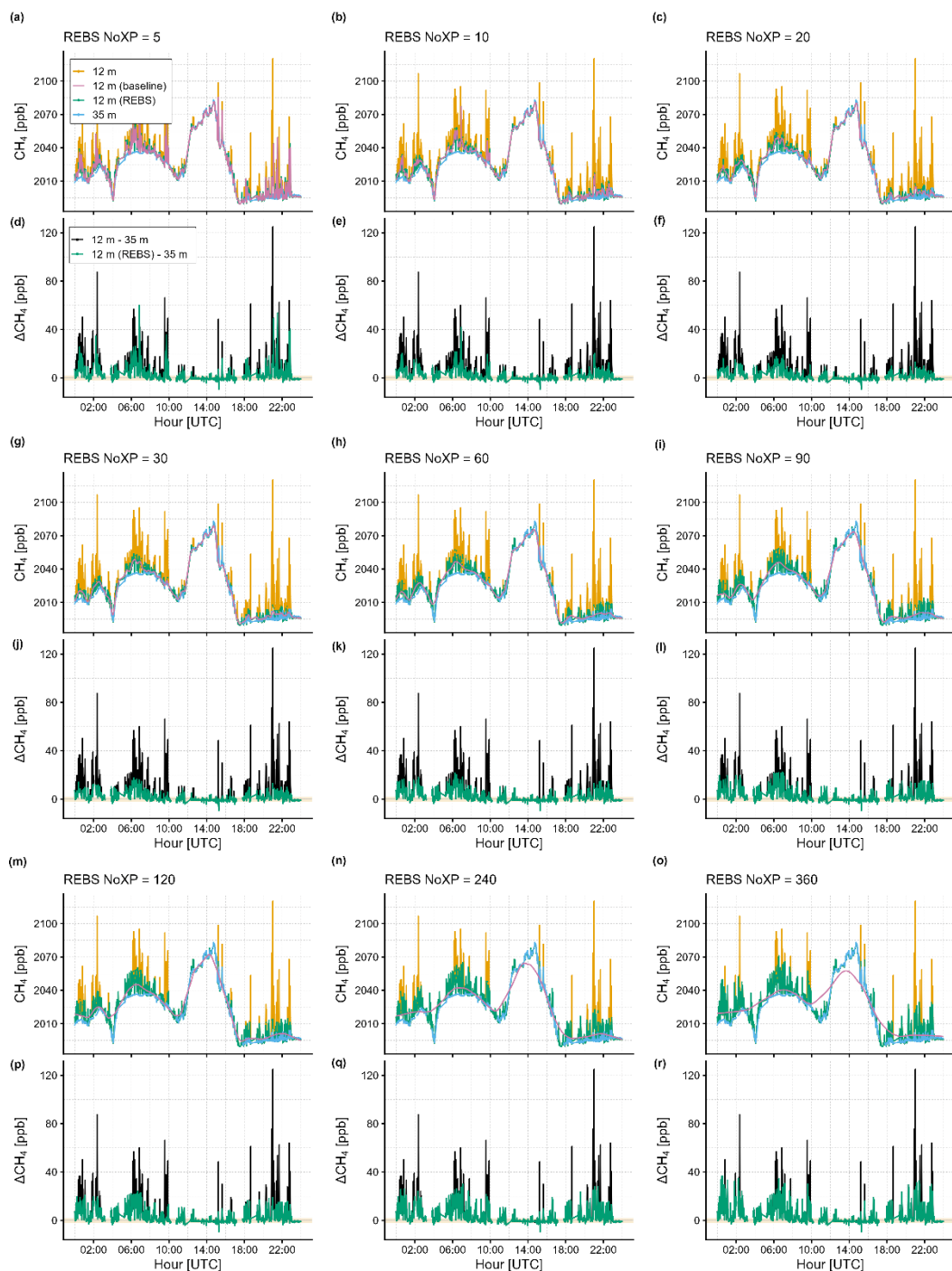


Figure S7. Minutely CH₄ mole fractions measured at 12 m and 35 m intake height and the respective differences (12–35 m) on 26 June 2023. The REBS spike detection algorithm ($\beta = 3$) is applied to the minutely CH₄ mole fraction at 12 m using different values for the bandwidth ($NoXP$) indicated in the plot title. Data after filtering is shown in green, the original data in orange, the 35 m intake height in blue and the baseline calculated by the algorithm in purple.

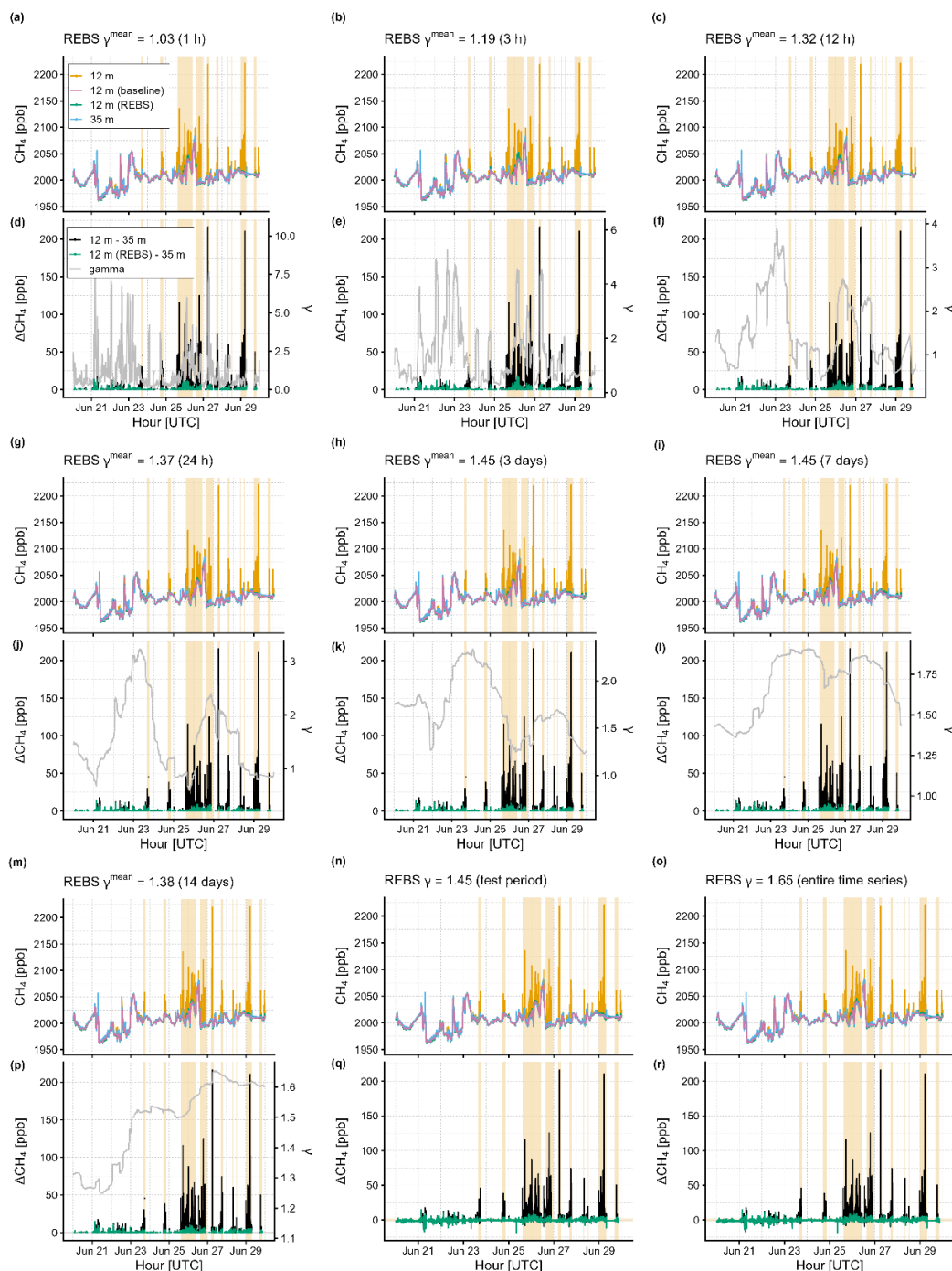
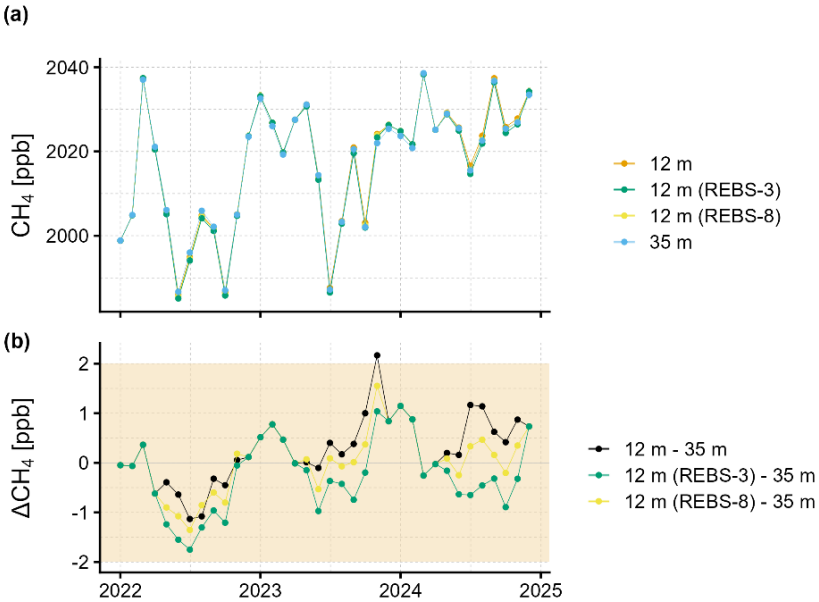


Figure S8. Minutely CH_4 mole fractions measured at 12 m and 35 m intake height and the respective differences (12–35 m) from 20 to 30 June 2023. The REBS spike detection algorithm ($\beta = 3$) is applied to the minutely CH_4 mole fraction at 12 m using different γ estimates indicated in the plot title. The γ value is shown in grey referring to the right y axis. Data after filtering is shown in green, the original data in orange, the 35 m intake height in blue and the baseline calculated by the algorithm in purple. The areas marked in beige indicate increased concentrations at 12 m which are attributed to local pollution manually.

S3 Diurnal and seasonal distribution of hourly values affected by the REBS algorithm

100 The REBS spike detection algorithm is applied to minutely mean CH₄ mole fractions from 2022 to 2024 and the data averaged over hours, days and months. At least 8 hourly values had to be available for the daily mean to be accepted. The monthly mean CH₄ mole fractions for both intake heights and after filtering with the REBS algorithm as well as the differences between the intake heights are shown in Fig. S9.



105 **Figure S9. Monthly mean CH₄ mole fraction at Schauinsland station measured at 12 m (orange) and 35 m (blue) in panel (a) and the corresponding difference (12–35 m) in black in panel (b). The time series after application of the REBS algorithm with $\beta = 3$ and $\beta = 8$ is shown green and yellow, respectively. The WMO/GAW compatibility goal of 2 ppb is indicated in beige.**

The diurnal and seasonal distribution of hourly mean CH₄ mole fractions that are affected by the filtering with the REBS algorithm is shown in Fig. S10. A larger number of such hourly means are observed during daytime (05:00–19:00 UTC) and in the month of July.

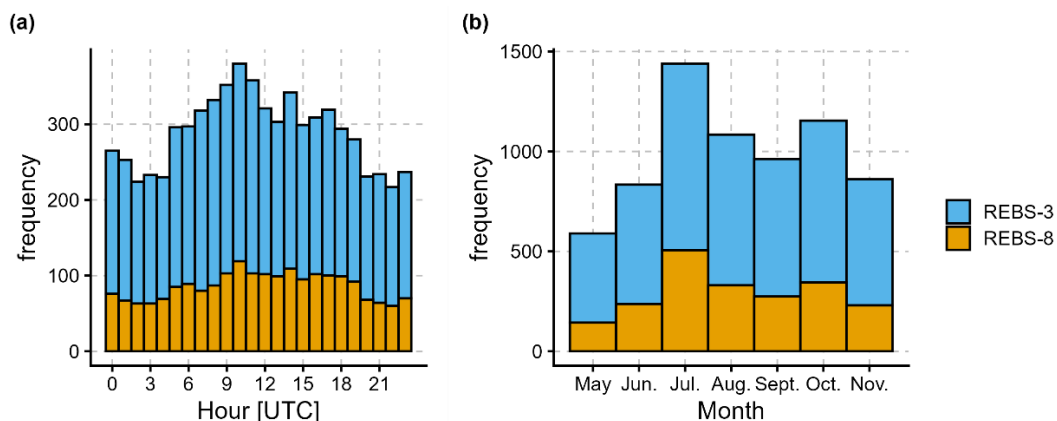


Figure S10. Histogram of hourly values affected by the spike detection algorithm per hour of the day (a) and month (b) for $\beta = 3$ (blue) and $\beta = 8$ (orange).

Figure S11 shows the distribution of hourly values that are affected by the filtering with the REBS algorithm per wind direction and per difference to the original data set, which are mainly within the west to southwest sector. A large part of the meadows is located in this sector and it corresponds to the main wind direction at the station.

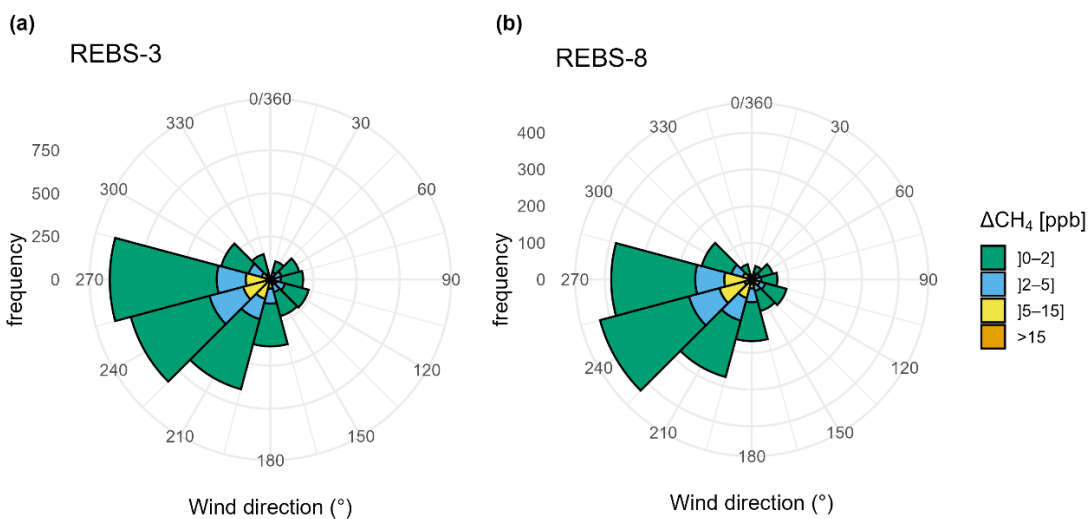


Figure S11. The histogram shows the number of hourly values affected by the spike detection algorithm per wind direction and within a certain interval of difference to the original data set for $\beta = 3$ (a) and $\beta = 8$ (b).

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