Supplement of Atmos. Chem. Phys., 19, 999–1012, 2019
https://doi.org/10.5194/acp-19-999-2019-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

On the diurnal, weekly, and seasonal cycles and annual trends in atmospheric CO_2 at Mount Zugspitze, Germany, during 1981–2016

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1. Instrumental setup

Figure S1: Instrumental setups at ZSF, a) Modified HP 6890 with Gas Chromatography (GC); b) Picarro EnviroSense 3000i with Cavity Ring-down Spectroscopy (CRDS).

2. Offset adjustment

2.1. Offset adjustment background

From the observed data for the three-year parallel CO_2 measurements at ZPT and ZUG (1995–1997) we obtain an offset of –5.8 ± 0.4 ppm ($CO_{2,\ ZPT}$ minus $CO_{2,\ ZUG}$, $1 \cdot SD$). In the present situation, on-site corrections based on different calibration standards and different types of analysers are no longer possible. Therefore instead of a laboratory data based correction of this offset, we performed an offset adjustment, which was based on the historical time series. Above all, depending on the existing information, we have to make the assumption that none of the following effects have been corrected beforehand at ZPT but at ZUG.

As mentioned in the paper, it is assumed that such a large offset (several ppm) is mostly influenced by the so-called “carrier gas effect” on the infrared gas analysis investigated by Bischof (1975) and Pearman and Garratt (1975). There a considerable deviation was detected due to the pressure broadening effects on the different types of used gas analyser, and more importantly to the different carrier gases used in the standards (Table 1), i.e. CO_2/N_2 mixtures vs. CO_2/air mixtures. As shown in Table 1 of the original paper, it is shown that between ZPT and ZUG during 1995–1997, the same type of analysers (URAS 3G, Hartmann & Braun) were used, but however the calibration gases were different (CO_2/N_2 for ZPT and CO_2/natural air for ZUG). Experiments implied that the CO_2 concentration in air when using CO_2/N_2 mixtures as references is usually underestimated by several ppms for the URAS instruments. On the other hand, the measurement of CO_2 concentration in air is not affected if CO_2/air mixtures were used as references. From Pearman (1977), we learnt that the potential carrier gas error could range from –4.9 to +3.8 ppm (8.7 ppm in absolute difference) depending on different analysers (Bischof, 1975; Pearman, 1977). Griffith (1982) showed that this can vary even between analysers of the same type.

Pearman (1977) also mentioned that both the sign and magnitude of the carrier gas error depend on not only the configuration and model of analyser used, but also the ambient pressure at which measurements are made, i.e. the station altitude. With an altitude difference of around 1.6 km, a difference in carrier gas effect of ~0.6 ppm was found when measurements were made with a URAS 2 (Pearman and Garratt, 1975). At Mount Zugspitze, the altitude difference between ZPT and ZUG is approximately 250 m, and thus the carrier effect dependence on the ambient pressure is rather limited.

Another potential factor is the drying problem due to the varying water content as described in Reiter et al. (1986). By comparing an URAS 2T with a URAS 3G at another measurement station in Garmisch-Partenkirchen (GAP), the humidity-induced error ranged from the extreme conditions in summer (at most 6 ppm), to 2 ppm in winter. Pearman (1975) also addressed this problem as non-dispersive infrared gas analysers were influenced by water vapour in the air sample. The subsequent measurement must be corrected by multiplying the indicated concentration by $(1 + 1.61 * r)^{-1}$, where r is the water vapour mass mixing ratio of the undried air. However, such error indicated that the measured CO_2 concentration would be overestimated when not corrected. Moreover, this error also decreases with altitude and will be less than the resolution of the NDIR analysers (approximately ±0.2 ppm) above about 8 km a.s.l. Regarding that the absolute water content for mountain stations is, on average, very low (for example at ZSF, the relative humidity in sampling air ranges between 2–10% in winter and approximately 27–32% in summer at 20°C), such an effect of drying the air sample prior to analysis was assumed to be minor for Mount Zugspitze.

2.2. Offset adjustment at ZPT

In order to make the offset adjustment, we follow the approach from Griffith (1982) and Griffith et al. (1982), together with comparing similar carrier gas correction cases done by Manning and Pohl (1986b) and Cundari et al. (1990). The general assumption is that the carrier gas correction (CGC) term is proportional to CO_2 concentration (Griffith, 1982; Manning and Pohl, 1986a). Carrier gas effects were determined experimentally by comparing analyser values (apparent CO_2 concentration C_a) with true (mano-metrically determined) CO_2 concentration (true CO_2 concentration C_t). Two terms were used here as the carrier gas shift (Δ) and the correction factor (G).

$$\Delta = C_a - C_t \tag{1}$$

$$G = C_t / C_a \tag{2}$$

In our case, given that CO_2 measurements between ZUG and ZSF show a comparable result in 2001, and the altitude difference between ZSF and ZPT is only about 70 m a.s.l., we consider the CO_2 measurements at ZUG to be the true value ($C_{ZUG,t}$) and the CO_2 measurements at ZPT to be the apparent value ($C_{ZPT,a}$). Thus the offset can be expressed as (see Fig. S2a),

$$\Delta = C_{ZPT,a} - C_{ZUG,t} \tag{3}$$

and hence the correction factor can be expressed as (see Fig. S2b),

$$G = C_{ZUG,t} / C_{ZPT,a} . \quad (4)$$

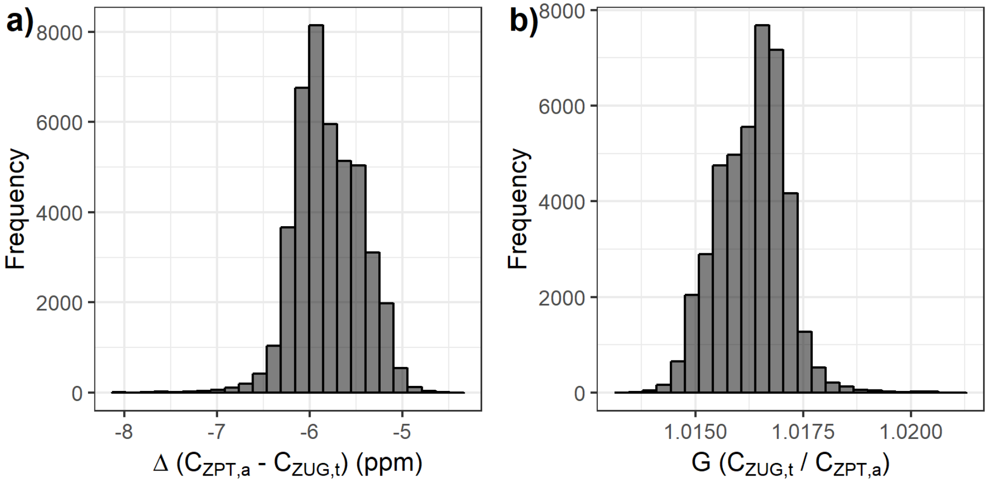

Figure S2: a) Histogram for the offsets (Δ) between CO_2 measurements at ZPT and ZUG for the period of 1995–1997. b) Histogram of the correction factor (G) between CO_2 measurements at ZPT and ZUG for the period of 1995–1997.

We then plotted the computed correction factors G with the apparent concentration at ZPT ($C_{ZPT,a}$) throughout the three years (1995–1997) in Fig. S3. A linear relationship can be observed but for a certain interval of the data a clear shift is noticed. Then we tried to divide the time blocks and took a closer look at when or how this shift takes place. We found out that this shift happened from November to December 1995, possibly due to instrumental setup changes. Figure S4 showed the time blocks before, during, and after. Nevertheless, by fitting linear regression nearly identical regression lines were produced for all three time blocks. At the CO_2 concentration of 360 ppm, the correction factors for the three time blocks were computed as 1.01728, 1.01684, and 1.0172 respectively, in terms of the adjusted values of 366.2208, 366.0624, 366.192 ppm with a span of ±0.08 ppm. Within the interval from 340 ppm to 370 ppm of atmospheric CO_2 concentrations, the same calculation applied shows an error range in the adjusted values from ±0.06 to ±0.09 ppm.

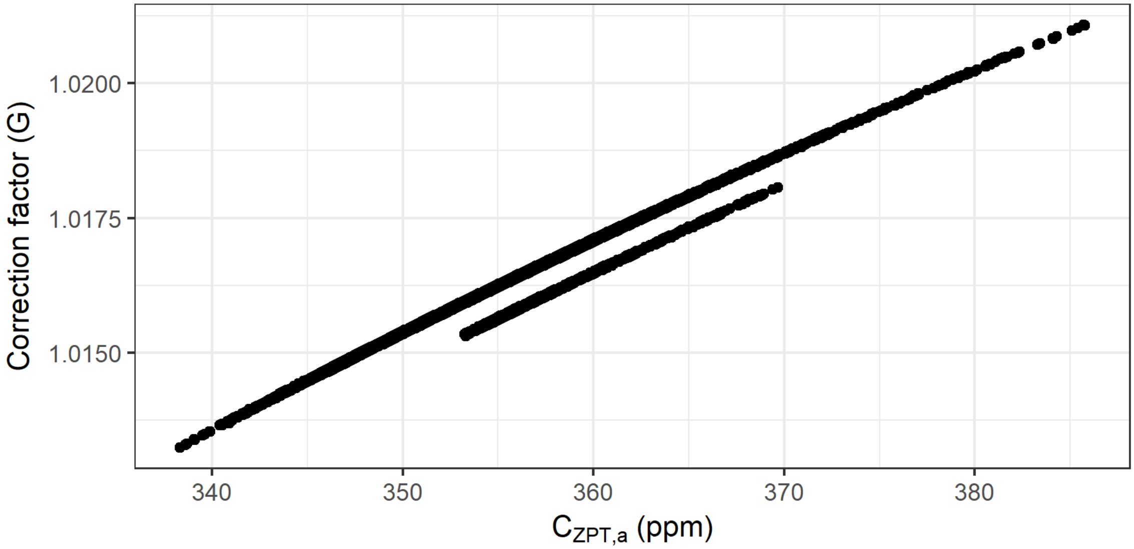

Figure S3: Computed correction factor *G* against CO$_2$ concentrations at ZPT from 1995 to 1997.

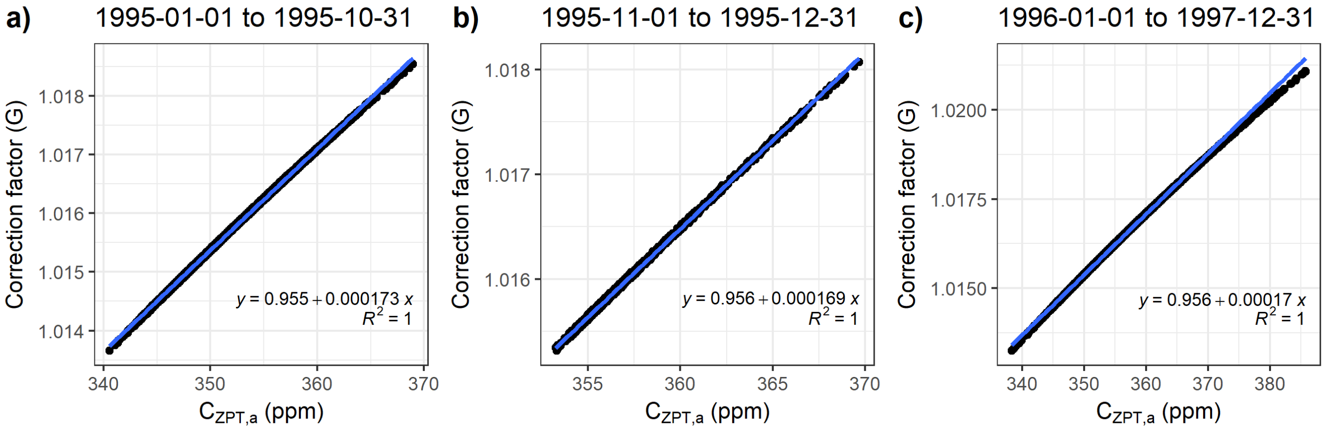

Figure S4: Computed correction factor *G* against CO$_2$ concentrations at ZPT from 1995 to 1997 with three separate time blocks.

Therefore, for the shifted time block (1995-11-01 to 1995-12-31), we used the correction factors by the linear regression function in Fig. S4b. Since the rest of the time blocks showed nearly identical results, we combined the data together and made a new linear regression. Based on this regression function, we made the following offset adjustment for all the remaining CO$_2$ data sets at ZPT (1981–1997) except for the two months in 1995, as shown below

$$G = 0.956 + 0.00017 \cdot C_{ZPT,a}. \tag{5}$$

And the adjusted CO$_2$ concentrations at ZPT can be expressed as

$$C_{ZPT,t} = C_{ZPT,a} \cdot G = C_{ZPT,a} \cdot \left(0.956 + 0.00017 \cdot C_{ZPT,a}\right). \tag{6}$$

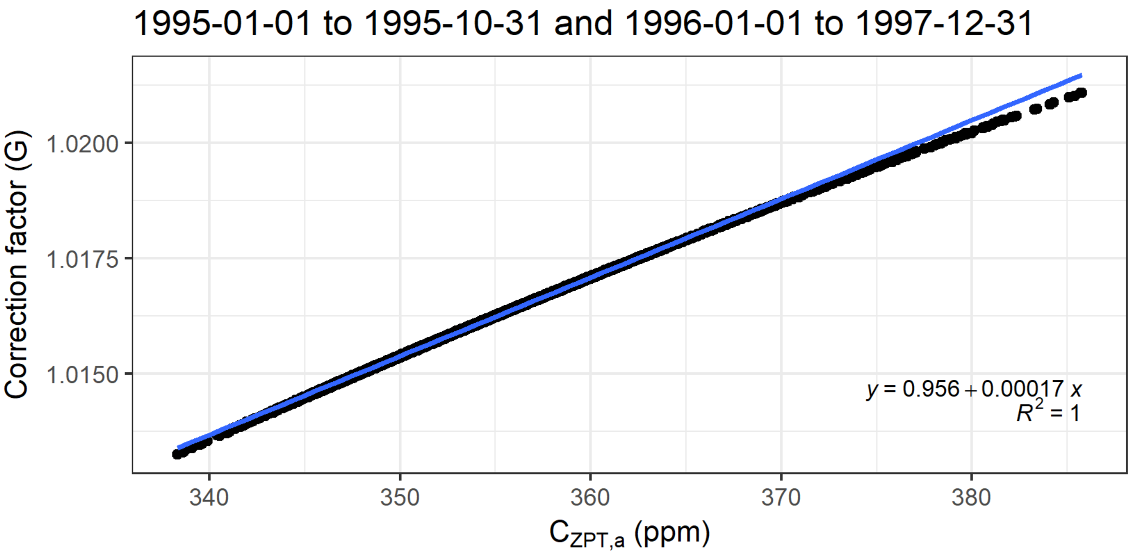

Figure S5: Computed correction factor G against CO_2 concentrations at ZPT from two separate time blocks, used for offset adjustment on the CO_2 data set at ZPT.

The reason we chose a single correction factor for most of the years is that, from the given comparison of the three separate time blocks, the error is small (less than 0.1 ppm). Therefore it is assumed that with different instruments used throughout the measurement periods the offsets remain small and hence relatively stable. Figure S5 also showed that the points were slightly off the regression line at both the head and tail even with $R^2 = 1$. This leads to errors of up to 0.2 ppm for a range of 338.32 to 385.69 ppm (CO_2 minimum and maximum at ZPT for this period), which agrees well with Griffith et al. (1982) as same errors of up to 0.2 ppm were detected for a range of 200 to 450 ppm. As a result, the offset adjustment of single correction factor is considered to be adequate.

In two similar cases, Manning and Pohl (1986b) showed the CGC at a concentration of 340 ppm for the URAS-2T analyser varied from 5.5 ppm to 3.2 ppm. With our correction factor function at the concentration of 340 ppm, the CGC turns out to be 4.7 ppm, which is in a good agreement. From another study by Cundari et al. (1990), by a least-square linear interpolation the experimentally determined means of the ratios were expressed by the following equation

$$\bar{G} = 1.0008 + 2.51 \cdot 10^{-5} \cdot C_a. \qquad (7)$$

Given the described range of C_a approximately from 320 to 360 ppm, the ratio varied from 1.008832 to 1.009836 which in terms of CGC the values changed 2.8 to 3.5 ppm. With the same described range, the CGC based on our regression function results in the values between 3.3 and 6.2 ppm.

2.3. Offset adjustment at WNK

Due to lack of information and no available comparable additional measurements at nearby locations, we decided to make a more general offset adjustment on CO_2 data at WNK based on the adjusted CO_2 data at ZPT because the same CO_2/N_2 mixtures were used for calibration (see Table 1). The time period of CO_2 measurements at WNK used in this study is 1981–1996, which is completely covered by CO_2 measurements at ZPT. We assume that the differences in CO_2 concentrations remain similarly before and after the offset adjustment, which means

$$C_{WNK,a} - C_{ZPT,a} \approx C_{WNK,t} - C_{ZPT,t}. \tag{8}$$

Therefore, the adjusted CO_2 concentrations at WNK can be expressed as

$$C_{WNK,t} = C_{ZPT,t} + \left(C_{WNK,a} - C_{ZPT,a}\right). \tag{9}$$

Finally the offset adjustment at WNK was done by calculating the differences in CO_2 concentrations between WNK and ZPT raw data and then adding it to the adjusted CO_2 concentrations at ZPT to compute the adjusted CO_2 concentrations at WNK.

2.4. Offset adjustment error estimation (ZPT to ZUG)

At the end, the maximum possible error should be estimated. Based on literature review, several additional factors which may contribute to it apart from carrier gas effect, pressure effect, and drying problem (varying water content) were listed as mentioned above.

- Absolute limit error on every single G ratio: 0.4 ppm (Cundari et al., 1990)
    - Station relative accuracy: ± 0.2 ppm (Pearman, 1975)
- Temperature effects: URAS analyzers are thermostated and small temperature variations, as are likely to occur, should not cause noticeable errors and thus can be neglected (Griffith et al., 1982).
- Leaking detectors: 0.4 ppm (+ 0.4 ppm) for URAS analyzers with different leaking scenarios (Griffith et al., 1982)
    - We assume that according to the applied quality standard from the former IFU (Fraunhofer Institute for Atmospheric Environmental Research, today KIT/IFU) the analyzers did not have a systematic leaking.
    - Further it is assumed, that the measurements did not have a drift in the data, because of continuous quality assurance for the former IFU.

Based on the given information about the measurements, we did a practically best possible description of obviously existing errors in the values. Please always keep in mind that this is an attempt and approach to make proper use of these historical data with given errors. Different time period, different types of analysers (also the same type), different used reference gases, or any potential replacement on the instruments and artefacts would introduce more errors to the offset adjustment. Caution should always be taken when using this combined data set. We would recommend contacting the data provider for more detailed discussion, whenever a detailed analysis requires reliable information.

3. STL decomposition results

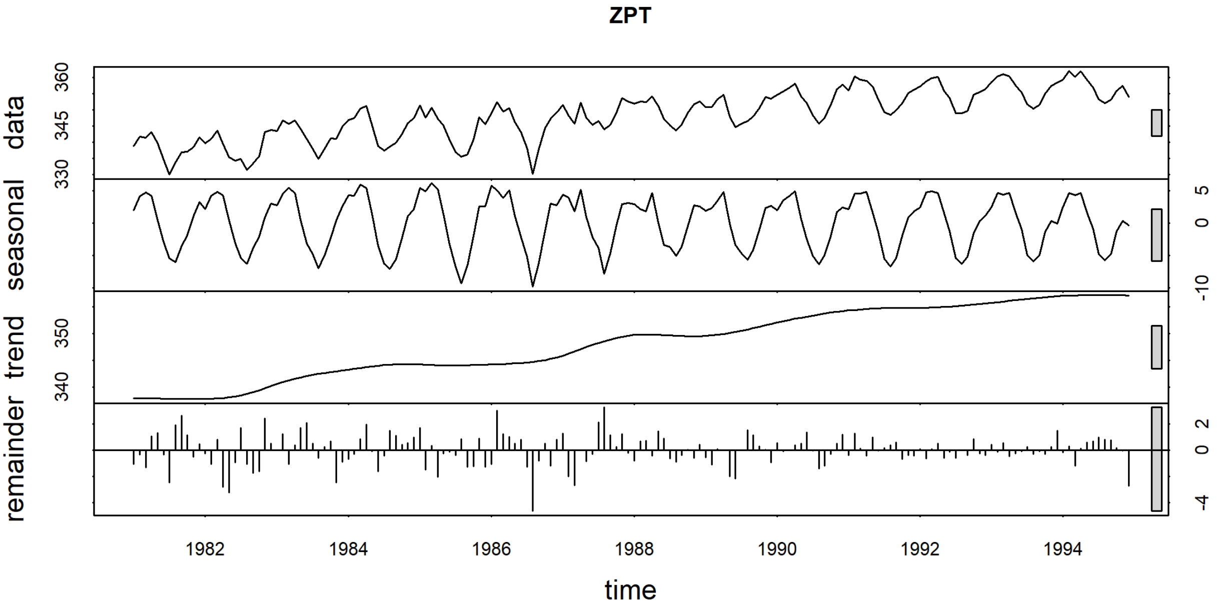

Figure S6: STL-decomposed results of CO$_2$ measurements at ZPT.

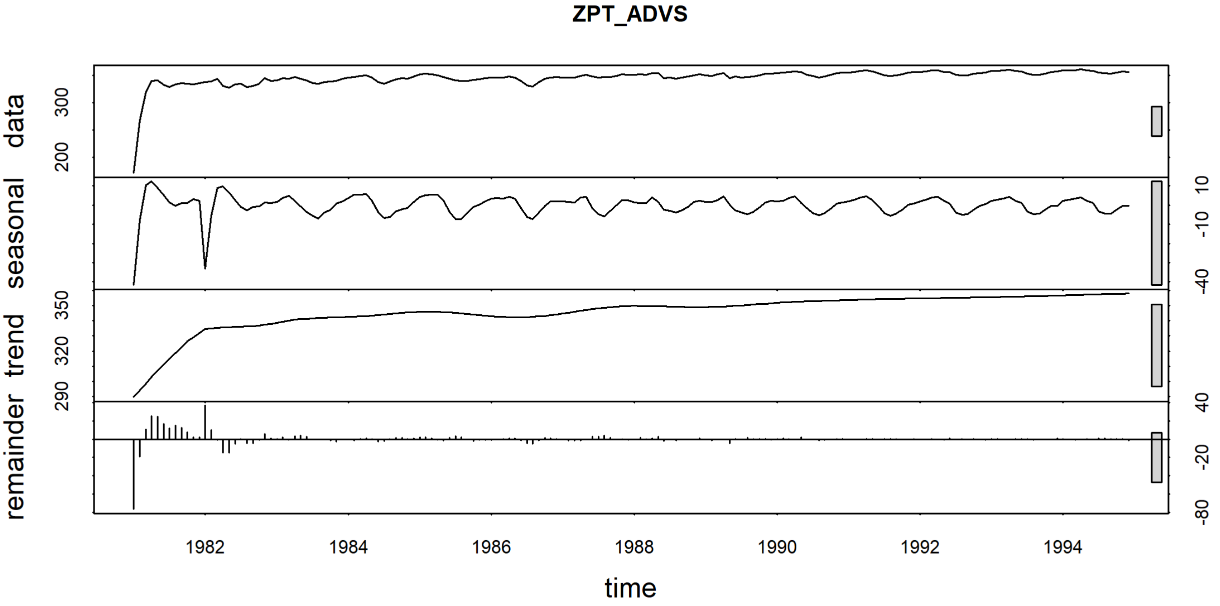

Figure S7: STL-decomposed results of ADVS-selected CO$_2$ measurements at ZPT.

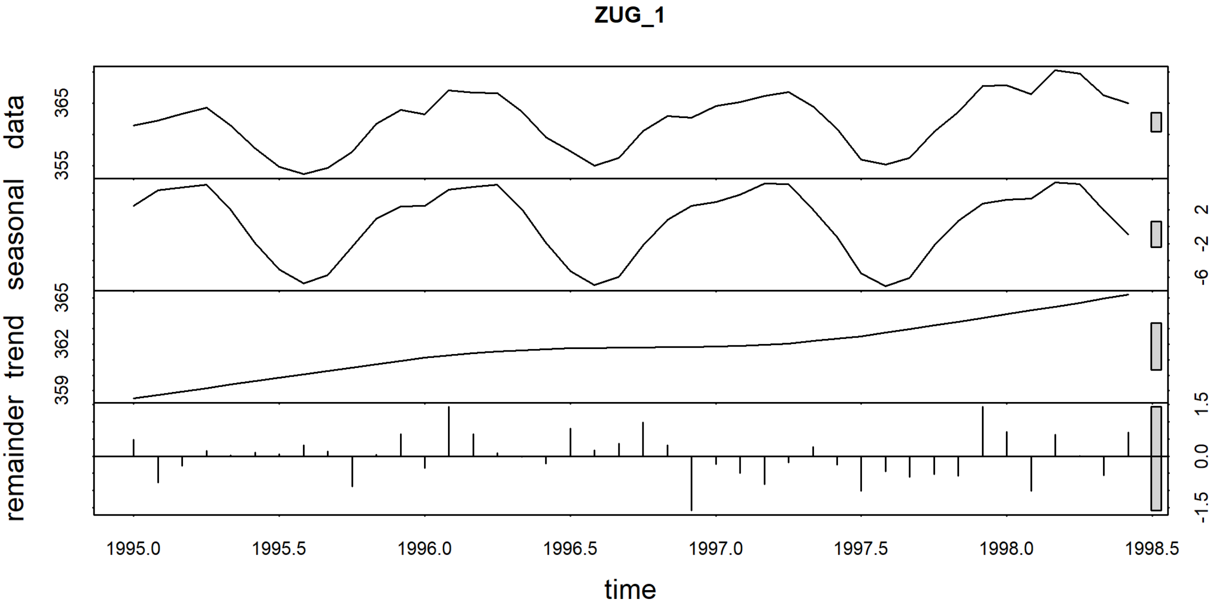

Figure S8: STL-decomposed results of CO_2 measurements at ZUG (1st part).

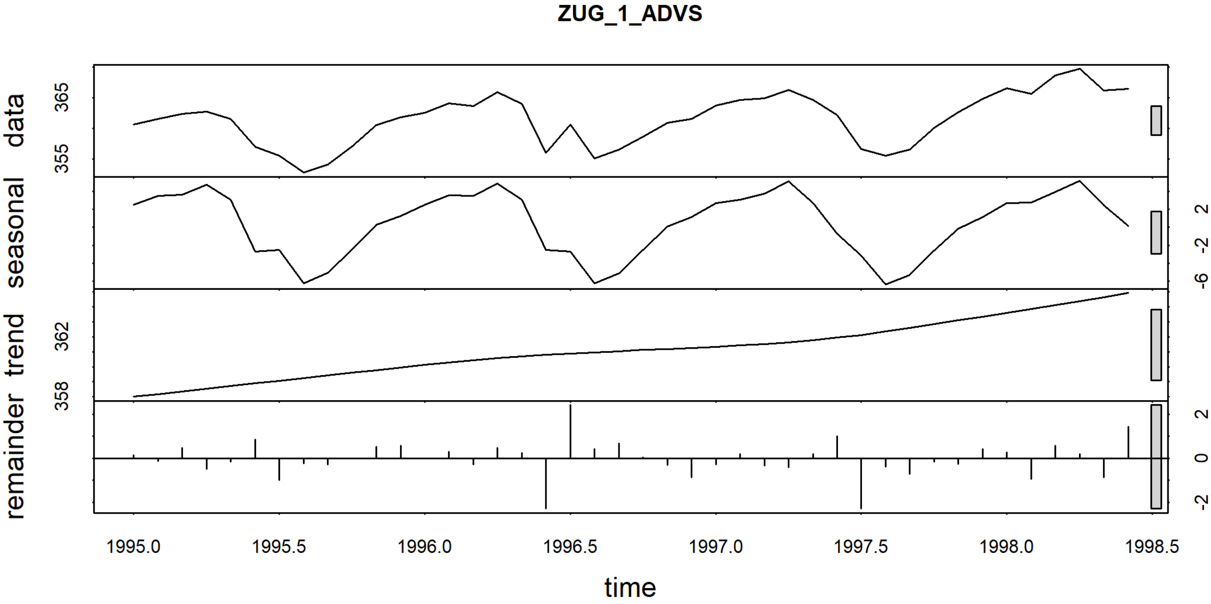

Figure S9: STL-decomposed results of ADVS-selected CO_2 measurements at ZUG (1st part).

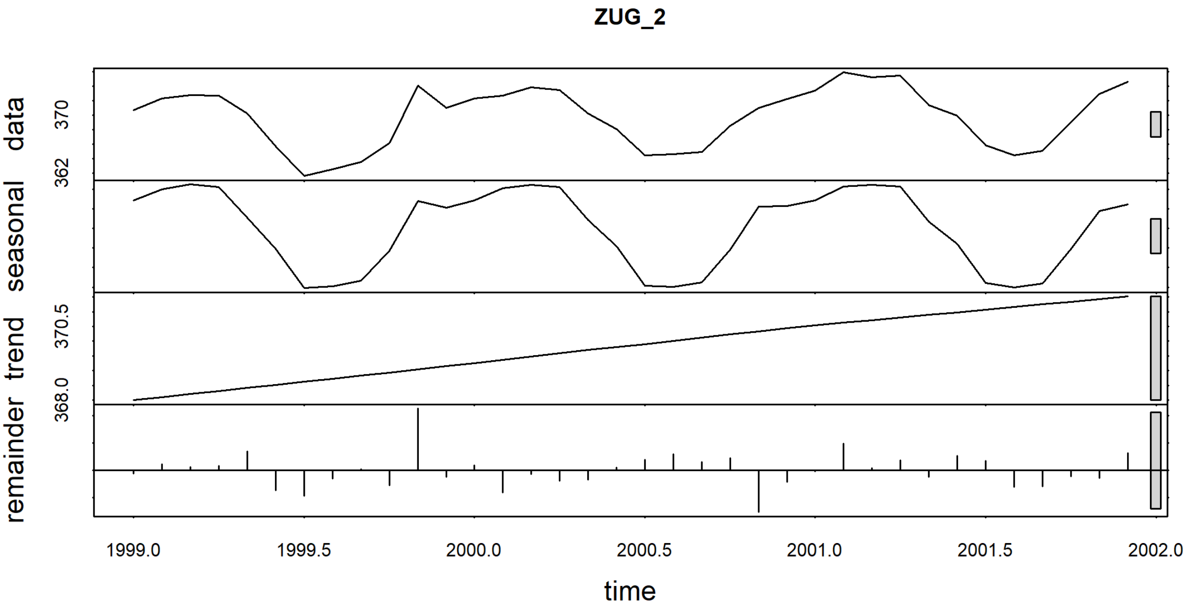

Figure S10: STL-decomposed results of CO_2 measurements at ZUG (2^{nd} part).

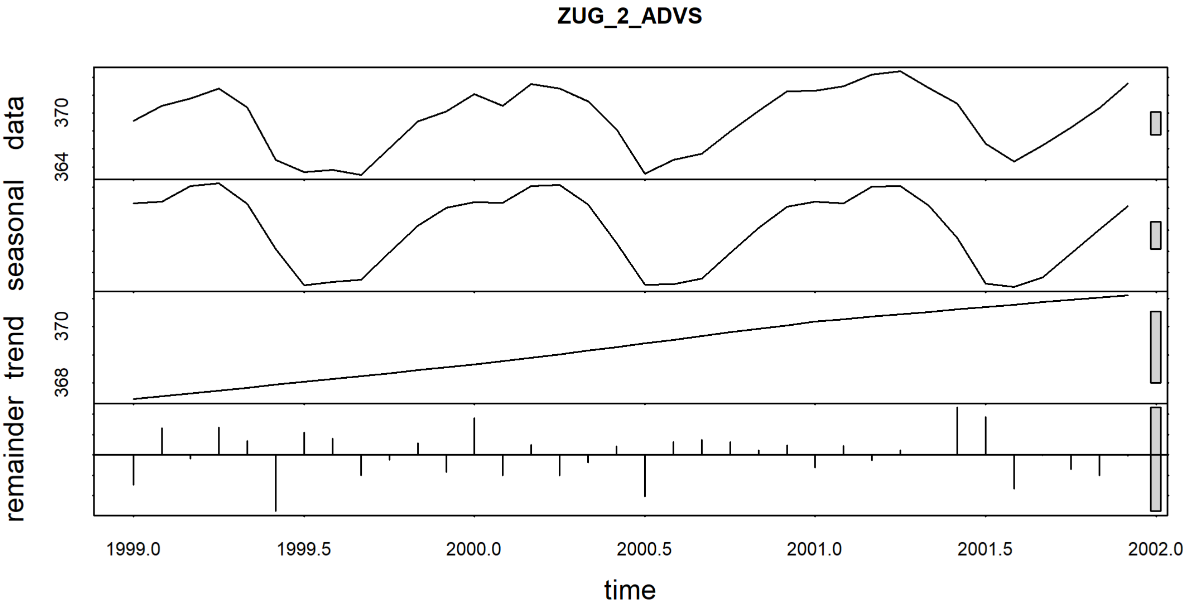

Figure S11: STL-decomposed results of ADVS-selected CO_2 measurements at ZUG (2^{nd} part).

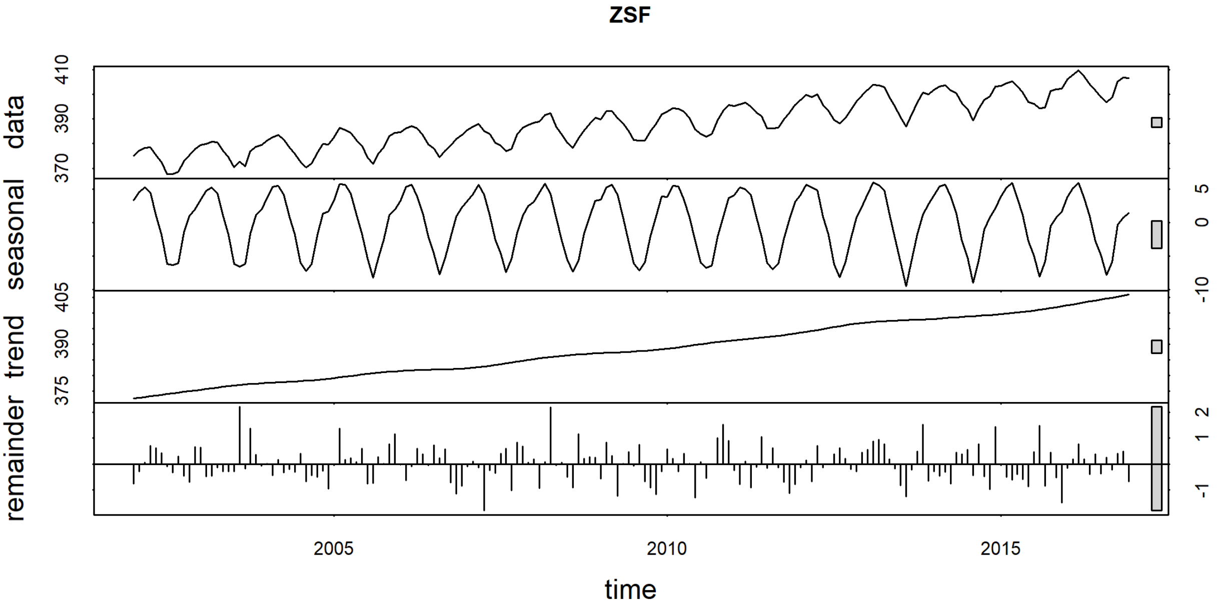

Figure S12: STL-decomposed results of CO_2 measurements at ZSF.

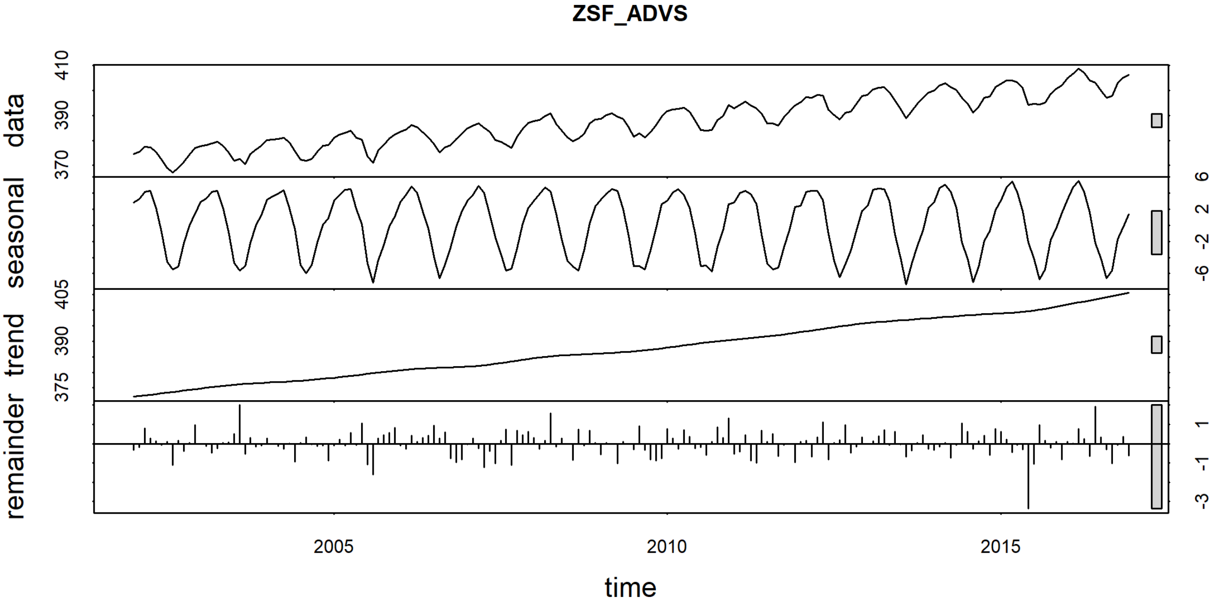

Figure S13: STL-decomposed results of ADVS-selected CO_2 measurements at ZSF.

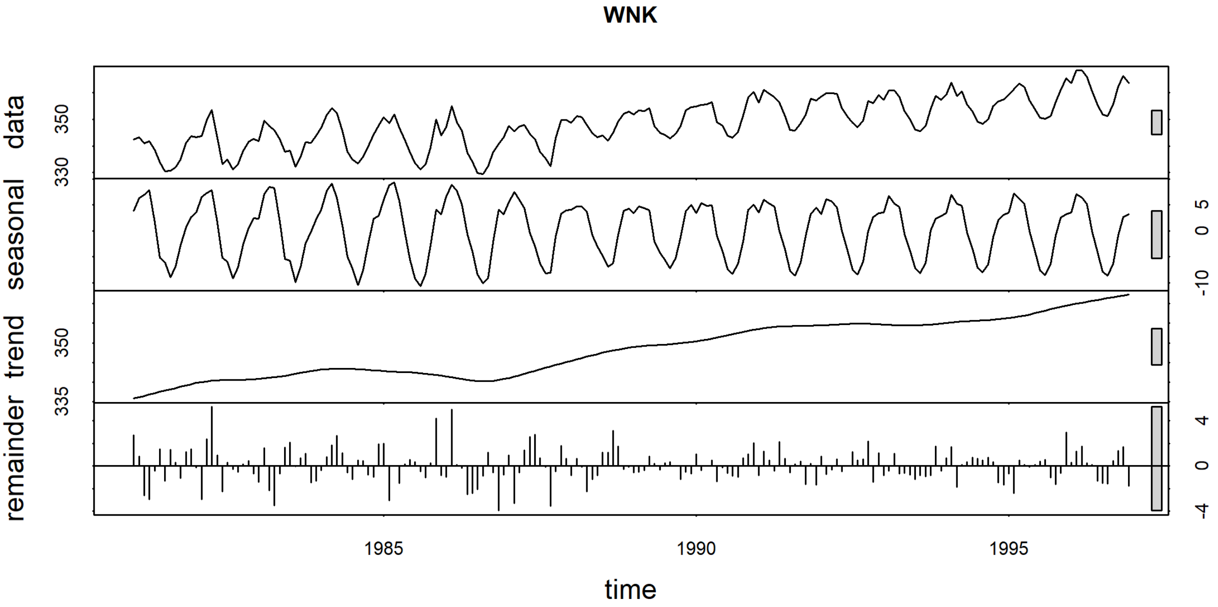

Figure S14: STL-decomposed results of CO_2 measurements at WNK.

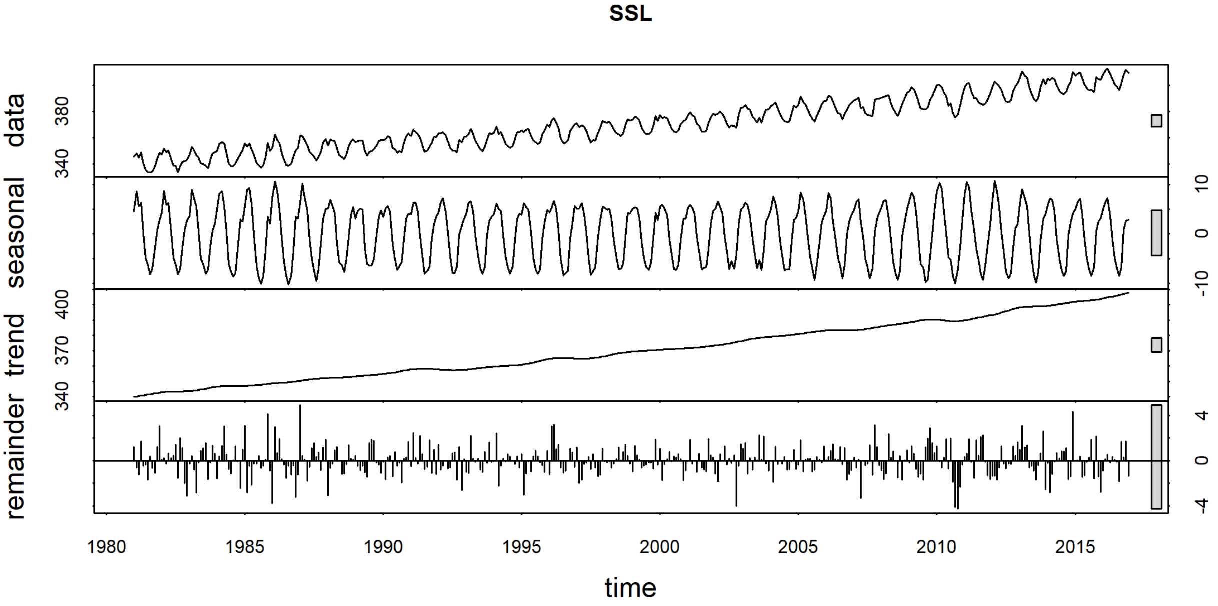

Figure S15: STL-decomposed results of CO_2 measurements at SSL

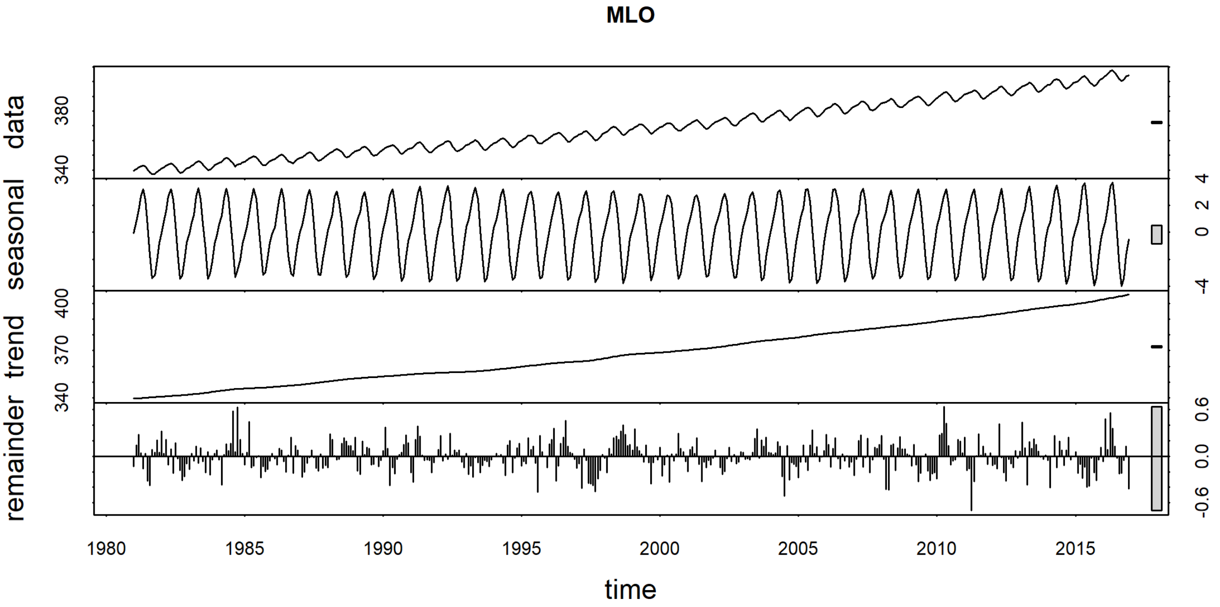

Figure S16: STL-decomposed results of CO_2 measurements at MLO.

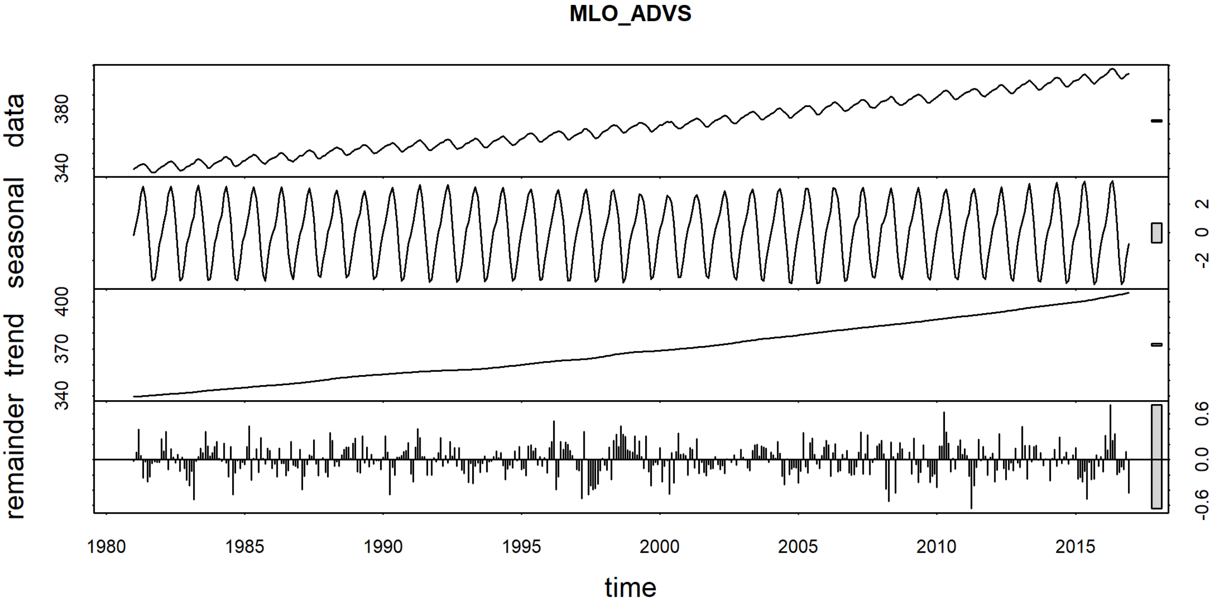

Figure S17: STL-decomposed results of ADVS-selected CO_2 measurements at MLO.

4. Diurnal cycles

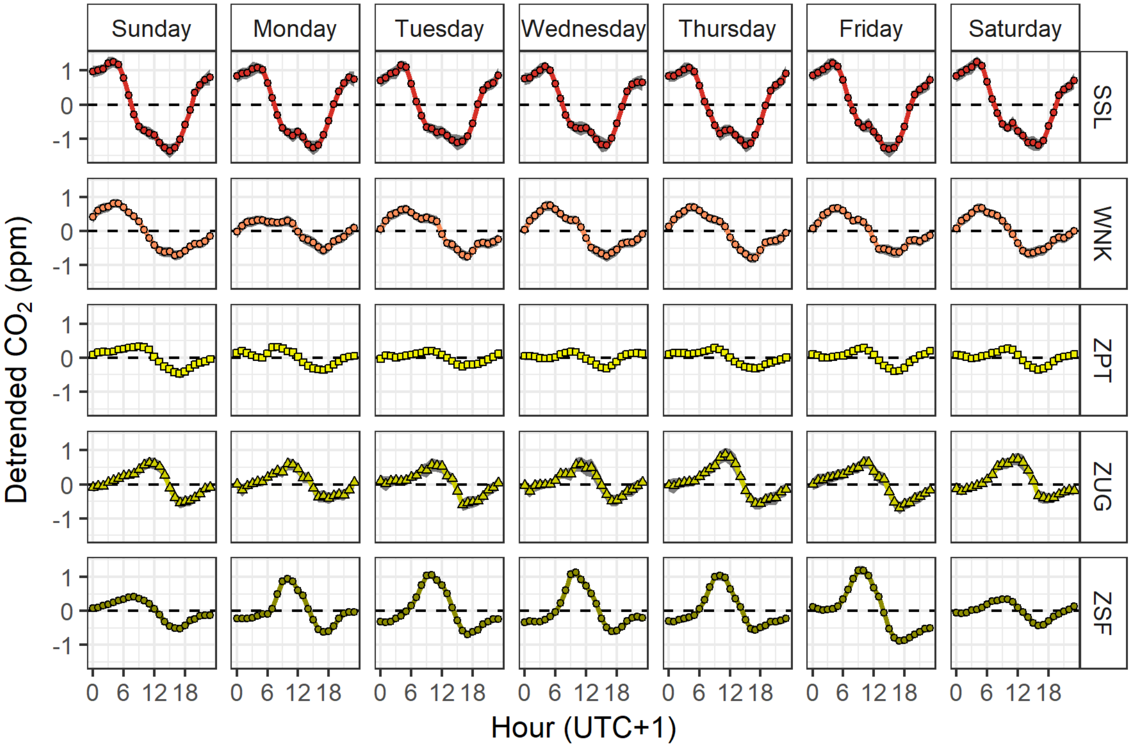

Figure S18: Detrended mean CO_2 diurnal cycles by days of the week. Uncertainties of 95% confidence intervals are shown by the shaded areas.

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