Author comments on "On the diurnal, weekly, seasonal cycles and annual trends in atmospheric CO_2 at Mount Zugspitze, Germany during 1981–2016" *by* Ye Yuan et al.

Ye Yuan on behalf of all co-authors

Answers to **Anonymous Referee #1 (RC1)**

The referee comments are shown in black. The answers are shown in blue.

Authors: We would like to thank Anonymous Referee #1 for the efforts to review this manuscript and to provide very helpful comments and detailed remarks. All the referee's comments have been carefully examined and addressed in the revised manuscript as well as supplement.

Review of the manuscript: "On the diurnal, weekly, seasonal cycles and annual trends in atmospheric CO2 at Mount Zugspitze, Germany during 1981–2016" by Y.Yuan et al. (Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-850)

The paper is describing the long term CO_2 monitoring program at Zugspitze, Germany. Actually the time series is a composite from three periods during which the sampling location, the method and instrument were different: ZPT (1981-1997), ZUG (1995-2001), and ZSF (2001-ongoing). Consequently a major issue to be addressed in this study is the consistency of the three datasets, in order to determine if they can be grouped in a single series and with what limitations. I think this part is not detailed enough. The three datasets are merged for analysis of different time scale variabilities, although several indicators show that they differ significantly. A scientist using the Zugspitze long term time series without consideration of the change in the sampling location could misinterpret the signal. For this reason I would recommend the authors to clarify the uncertainties associated to such a merging of the different dataset.

Authors: Thank you very much for pointing this out. We have now included a detailed discussion about the offset adjustment between ZPT and ZUG in the manuscript and supplement. Later on we have always made the analyses for each measurement location (ZPT, ZUG, and ZSF) separately. Throughout the manuscript we have pointed out that the results of atmospheric CO_2 measurements at Mount Zugspitze are a composite of three data sets at different locations and for different time periods, which cover an overall time length of 36 years. When using these data sets, caution is needed and it is always

recommended to discuss questions regarding specific researches with the data provider. For more detailed changes please see the following answers.

2.1. Measurement sites: I would suggest not using the term 'sites' to distinguish between the three sampling locations (ZPT, SUG, ZSF) at Zugspitze. It is a source of confusion here and there in the manuscript.

Authors: Thank you very much for the suggestion. We changed all the expressions "sites" related to ZPT, ZUG, and ZSF into "locations" throughout the manuscript.

Schneefernerhaus (ZPT, 47°25′ N, 10°59′ E, slightly below the summit): please give the elevation asl

Authors: Done.

'Information for the first and second time periods were mainly collected based on personal communication with corresponding staff and logbooks': at least it would be good to get information on the general setup of the system (dryer, calibration, and data selection…).

Authors: A general instrumental setup of the measurement system at ZPT and ZUG has been implemented in the Section 2.2 (Instrumental setup and data processing).

"…The CO_2 measurement at ZPT was continuously performed with different, consecutively used instrument models (i.e., the URAS-2, 2T, and 3G) of nondispersive infrared (NDIR) technique. The measured values were corrected by simultaneously measured air pressure with a hermetically sealed nitrogen-filled gas cuvette due to no flowing reference gas used. Two commercially available working standards (310 and 380 ppm of CO_2 in N_2) were used for calibration every day at different hours. The CO_2 concentration in this gas bottle was compared in short intervals with a reference standard provided by UBA which was adjusted to the Keeling standard reference scale.

At ZUG the sampling line consisted of a stainless steel tube with an inner core of borosilicate glass and a cylindrical stainless steel top cup against intake of precipitation. The inlet with the structure of a small mast ended approximately 4 m on the top of the laboratory building, which is situated on the Zugspitze summit platform (see Fig. 1b). Inside the laboratory a turbine with a fast real-time fine control ensured a constant sample inflow of 500 l/min of in-situ air. The borosilicate glass tube (about 10 cm diameter) continued inside the laboratory, providing a number of outlets from where the instruments could get the sample air for their own analyses. The measurement and calibration were performed with a URAS-3G device and an Ansyco mixing box. The mixing controller allowed automatic switching for up to four calibration gases and sampling air by a self-written calibration routine using Testpoint software. The linear two-point calibration enveloping the actual ambient values with low and high CO_2 concentrations was taken at every 25^{th} hour. Every six months the working standards were checked and re-adjusted, when required, to the standard reference scale by inter-comparison measurements with the station standards…"

Do you use the data already selected (according to time of the day or other criteria) from previous site managers?

Authors: No, the data we used in this study were quality validated without application of any pre-selection procedures. Only obvious outliers, due to such as malfunction or power failure, were left out as mentioned in Section 2.2. Therefore we added in the manuscript,

"…The CO_2 data from these measurement sites and from Mount Zugspitze locations were considered as validated data set (Level 2: calibrated, screened, artefacts and outliers removed), without any further data processing prior to the selection of representative data…"

2.3. Offset adjustment: The offset between the two sites (ZPT and ZUG) is huge with a large dispersion (5 to 6 ppm). A more detailed analysis of this offset, looking at its variation in time (and instrumental change), as a function of the atmospheric pressure, or CO2 concentration must be provided.

I support the hypothesis that the carrier gas effect can explain most of the differences between ZPT and ZUG, since it is well known that the CO2 concentration in air when using N2 mixtures as references, is under-estimated by few ppm. However, a discussion on this issue must be provided by the authors, with references to previous studies based on similar NDIR instruments (e.g. Pearman et al., Tellus, 1975; Griffith et al., Tellus, 1982). Is the observed differences compatible with what we can expect considering the literature, and the atmospheric pressure at this altitude site?

Authors: Thank you very much for the helpful literature. We have made a more detailed description and analysis for the offset adjustment now in both the manuscript and supplement. Please check the following text.

In manuscript:

"…However, for the three-year parallel CO_2 measurements at ZPT and ZUG (1995–1997), clear offsets of –5.8 ± 0.4 ppm ($CO_{2,\ ZPT}$ minus $CO_{2,\ ZUG}$, $1 \cdot SD$) were observed. The major reason for this bias is assumed to be the pressure-broadening effect in the used gas analyzers and the different gas mixtures used in the standards, CO_2/N_2 vs. CO_2/air, the so called "carrier gas correction (CGC)" (Bischof, 1975; Pearman and Garratt, 1975). It is known from previous studies that the measured CO_2 concentration, when using CO_2/N_2 mixtures as reference, is usually underestimated by several ppms for the URAS instruments, and such offsets vary from different types of analyzers (Pearman, 1977; Manning and Pohl; 1986). The carrier gas effect varies even between the same type of analyzer as well as with replacement of parts of the analyzer (Griffith et al., 1982; Kirk Thoning, personal communication, August 1, 2018). Due to lack of information and impossible on-site experiments with previous calibration standards, an offset adjustment to the CO_2 data set at ZPT was made for further analyses based on the offsets in data computed in the overlapping years instead of a physically derived correction. A single correction factor

$$G = 0.956 + 0.00017 \cdot C_{ZPT} \qquad (1)$$

was applied to the ZPT data while C_{ZPT} denotes the CO_2 concentrations at ZPT. Because of the same calibration mixtures, an additional adjustment was applied to the CO_2 concentrations at WNK by calculating the CO_2 differences between ZPT and

WNK. A detailed description on the offset adjustment of CGC with potential errors is given in the supplement. Two similar CGCs by Manning and Pohl (1986) at Baring Head, New Zealand and Cundari et al. (1990) at Mt. Cimone, Italy, were comparable in magnitude to our offset adjustment…"

In supplement:

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, i.e. CO_2/N_2 mixtures vs. CO_2/air mixtures. In Table S2, 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.

Table S1: Detailed description of atmospheric CO_2 measurement techniques (NDIR = Nondispersive infrared, GC = Gas chromatography, and CRDS = Cavity ring-down spectroscopy).

ID	Time period	Instrument (Analytical method)	Scale	Calibration gas
ZPT	1981–1997	1981–1984: Hartmann & Braun URAS 2 (NDIR) 1985–1988: Hartmann & Braun URAS 2T (NDIR) 1989–1997: Hartmann & Braun URAS 3G (NDIR)	WMO X74 scale	CO_2 in N_2
ZUG	1995–2001	Hartmann & Braun URAS 3G (NDIR)	WMO X85 scale	CO_2 in natural air
ZSF	2001–2016	2001–2016: Hewlett Packard Modified HP 6890 Chem. station (GC) 2012–2013: Picarro EnviroSense 3000i (CRDS)	WMO X2007 scale	CO_2 in natural air
WNK	1981–1996	Hartmann & Braun URAS 2T (NDIR)	WMO X74 scale	CO_2 in N_2

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).

$$\Delta = C_a - C_t \quad (1)$$

$$G = C_t / C_a \quad (2)$$

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),

$$\Delta = C_{ZPT,a} - C_{ZUG,t} \quad (3)$$

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

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

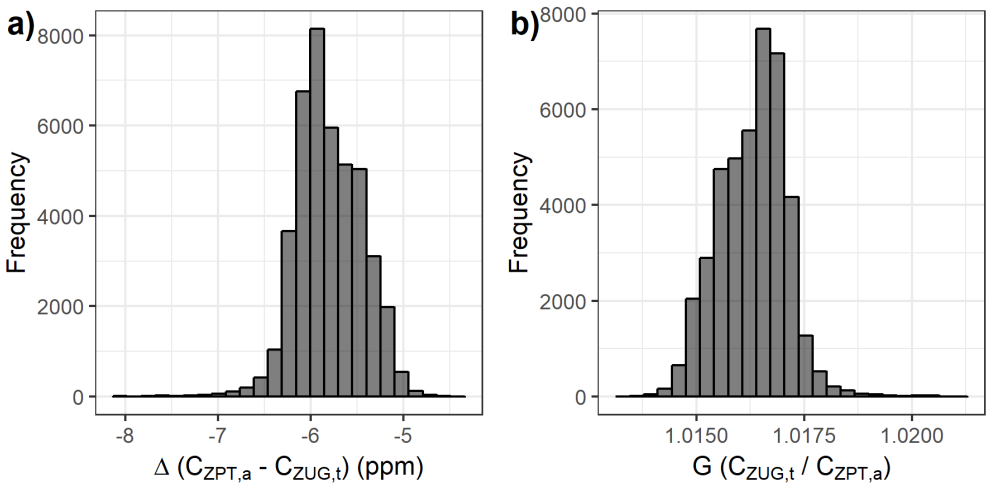

Figure S2: a) Histogram for the offsets (Δ) between CO_2 measurements at ZPT and ZUG for the period of 1995–1997. b) Histogram of the correction factor (G) between CO_2 measurements at ZPT and ZUG for the period of 1995–1997.

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.

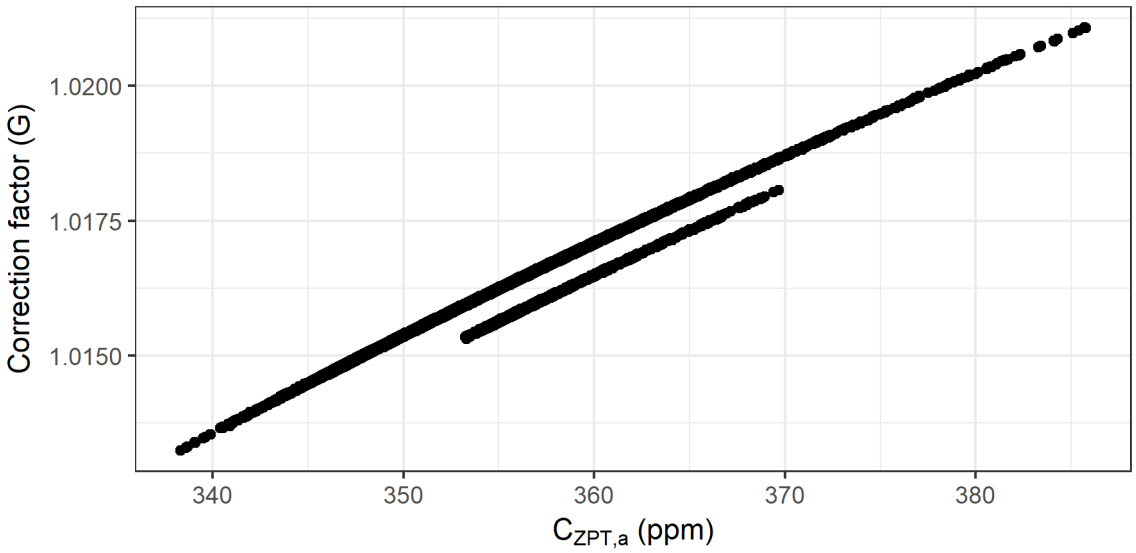

Figure S3: Computed correction factor G against CO_2 concentrations at ZPT from 1995 to 1997.

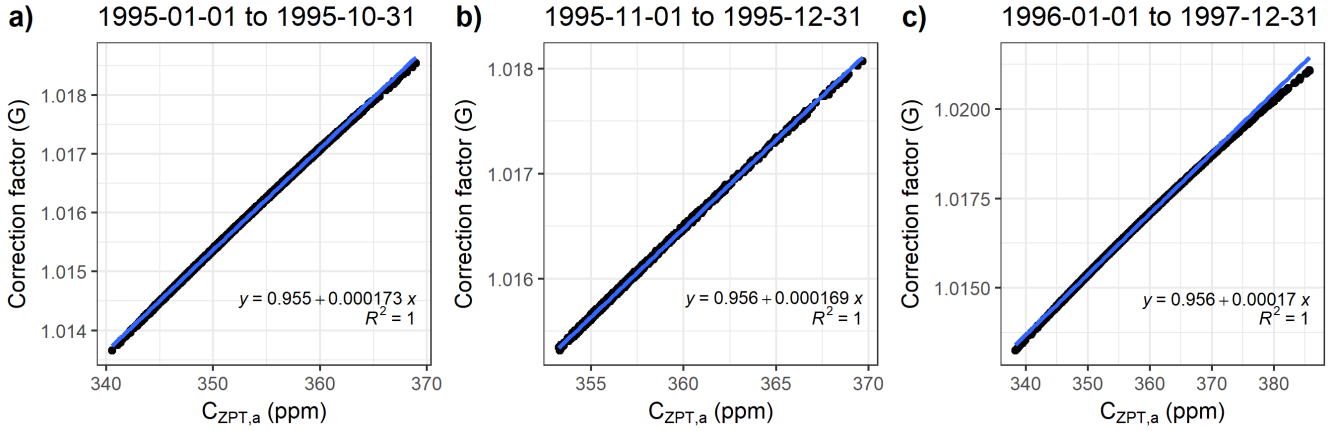

Figure S4: Computed correction factor G against CO_2 concentrations at ZPT from 1995 to 1997 with three separate time blocks.

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

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

And the adjusted CO_2 concentrations at ZPT can be expressed as

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

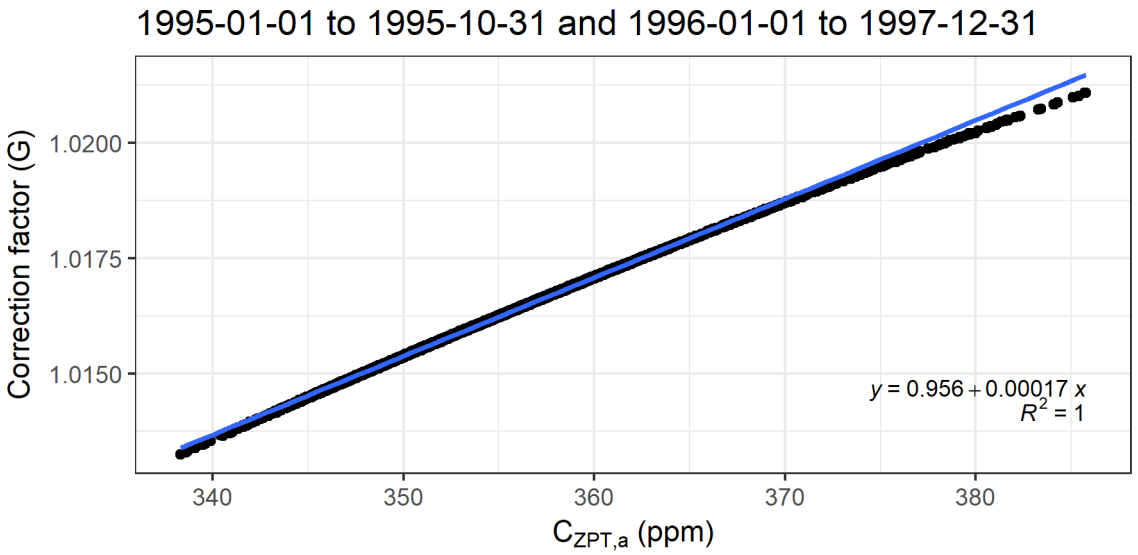

Figure S5: Computed correction factor *G* against CO_2 concentrations at ZPT from two separate time blocks, used for offset adjustment on the CO_2 data set at ZPT.

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 S1). 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

$$C_{WNK,a} - C_{ZPT,a} \approx C_{WNK,t} - C_{ZPT,t}. \quad (8)$$

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

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

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.

I understand that you have not applied the offset correction (-0.11ppm) between ZUG and ZSF. Please make it clear.

Authors: Done. We added, "…Therefore, no adjustments regarding this offset were applied to the data sets…"

2.4. ADVS data selection: "The percentages of ADVS-selected data are … 13.5% for Zugspitze": have you merged all three Zugspitze stations together in this analysis? Does it mean there is none significant differences between them?

Authors: For the ADVS data selection, the three measurement locations at Mount Zugspitze were processed separately. Previously the results of selected percentage were computed after combining the three data sets together. Now we calculated the selected percentages separately as well as shown in the plot (see Fig. 2a). There are significant differences in the selected percentages at a 95% confidence interval among the three measurement locations. From the selected results, we can see different percentages of selected data at the three measurement locations, i.e. ZPT (9.9%) > ZSF (13.6%) > ZUG (19.5%). In that way we can detect the highest data variability at the pedestrian tunnel (ZPT) and the lowest variability at Zugspitze Summit (ZUG).

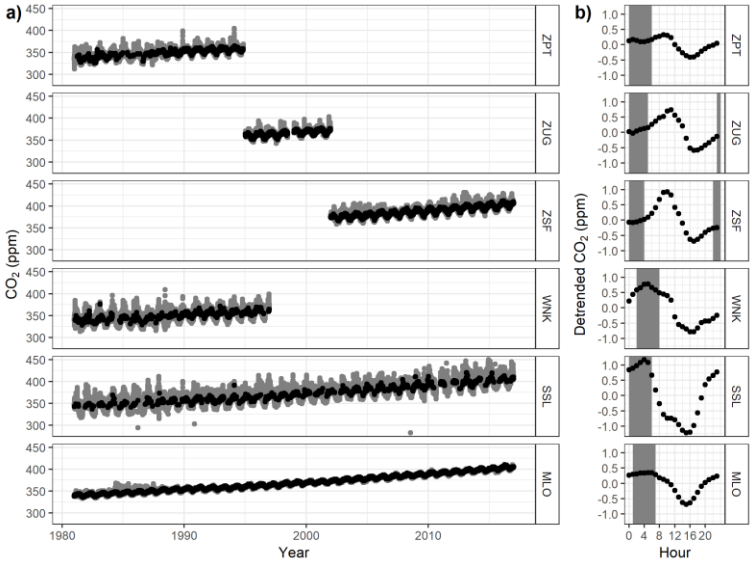

Figure 2: a) Time series plot of 30-min averaged CO_2 concentrations measured at Mount Zugspitze (ZPT, ZUG, and ZSF) and Wank (WNK), and hourly averaged CO_2 concentrations measured at Schauinsland (SSL) and Mauna Loa (MLO) with ADVS-selected results. b) Detrended mean diurnal cycles with starting time windows (in grey) for ADVS data selection.

Could you provide some statistics of the hours which are selected at Zugspitze as representative of the background according to ADVS method?

Authors: Yes, we added a graph of the resulting starting time window in Fig. 2b for each measurement site/location. A grey tone scale shows the frequency of ADVS-selected CO_2 data per hour in the total number of CO_2 data in Fig. 3. And a general discussion based on the diurnal variation is given in Sect 3.1, as the following.

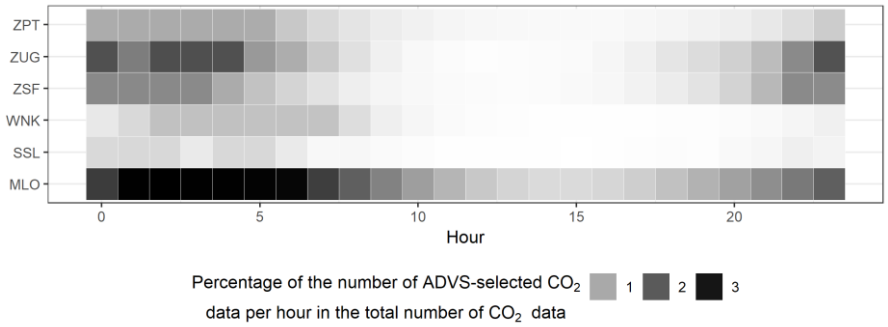

Figure 3: Frequency of the percentages of the number of ADVS-selected CO_2 data for each hour (0 to 23) in the total number of CO_2 data. In the shown greyscale grey means 1%, 2% and black means 3% of the data.

"…The resulting ADVS-selected CO_2 data showed a clear linkage of the percentage of selected data and the altitude of the measurement site. Among the continental stations, the percentage increased with altitude. Lower percentage indicates higher data variability due to lower elevation and proximity to local sources and sinks. At Schauinsland, the percentage of CO_2 data by the ADVS selection was 6.3% while the percentages at Mount Zugspitze reached 9.9% (ZPT), 19.5% (ZUG), and 13.6% (ZSF), respectively. A moderate percentage of 6.3% was also derived at Mount Wank. However, regarding the elevated mountain station Mauna Loa on the island of Hawaii, a much higher percentage (40.0%) of CO_2 data was selected by ADVS as representative of its background concentration mainly due to the very limited nearby anthropogenic sources as well as mostly clean, well-mixed air arriving there. A similar result for an island mountain station can be found in Yuan et al. (2018) where a percentage of 36.2% was computed for the CO_2 measurements at the station Izaña on Tenerife Island (28°19′ N, 16°30′ E, 2373 m a.s.l.). This can also be explained by the detrended mean diurnal cycles shown in Fig. 2(b) and Fig. 3. The mean diurnal cycle at MLO only exhibits a clear trough during daytime, especially starting from 12:00h local time (LT), which is believed to be influenced by the vegetation activity (photosynthesis) in the surroundings. The same effect can be seen at WNK and SSL, but with larger magnitudes and earlier occurrences of the minima because of their lower locations closer to CO_2 sinks. In contrast, at these two sites the CO_2 maxima in the diurnal cycles were not as clearly noticeable as at Mount Zugspitze due to anthropogenic sources and high biogenic respiration. At the three locations of Mount Zugspitze, the CO_2 peaks in the mean diurnal cycles are driven by the late-morning convective upslope wind, which was relatively obvious at both ZUG and ZSF. However, from the perspective of data selection, a significantly higher percentage of CO_2 data was selected at ZSF compared with ZPT although there is only a small difference in altitude of around only 70 m. This proves that ZSF is capable to capture more background conditions than ZPT during the day. Nevertheless, based on the starting time window computed for ADVS selection, we found that, in general, most stations exhibited similar starting time windows beginning around midnight and the ADVS data selection was applied systematically by including more data around these hours (see Fig. 3), which confirmed our assumption of background conditions during midnight for the ADVS data selection (Yuan et al., 2018)…"

2.5. STL decomposition Missing monthly values were substituted by spline interpolation: do you allow an interpolation of large data gaps like several consecutive months?

Authors: No, such large data gaps of several consecutive months are not allowed. And that is the reason why we previously decided to apply STL decomposition only on the original CO_2 data sets without ADVS data selection to evaluate the trend and seasonality. Besides, for the global trend data sets applied by the same STL decomposition technique, there are only monthly values available which cannot be selected by ADVS. Regarding the original CO_2 data sets, there is only one such large data gap for consecutive six months, which occurred at ZUG from July to December of 1998. Thus we performed the STL decomposition separately before and after this time period.

For improvement, we decided now to also apply STL decomposition to the ADVS-selected data at stations at Mount Zugspitze and Mauna Loa, as there are no large data gaps in the monthly averages from ADVS-selected data at these sites/locations. These results are implemented and discussed throughout the manuscript.

"…especially for measurement sites at lower elevations": I am confused about which sites you are referring to. Low altitude sampling locations at Zugspitze, or other sites like Schauinsland? Can you be more specific about the data gaps at stations, since it would make much more sense to use background data (after ADVS selection) for the seasonal and trend analysis, especially when comparing at other large scale time series.

Authors: More descriptions have been added in the text and also mentioned in the previous answer. Here the measurement sites at lower elevations refer to WNK and SSL. For a detailed illustration on each component of STL decomposition, we now included all the decomposed plots in Supplement S3.

3.1. Trend and seasonality "Only the mean annual growth rate between 1995 and 2001 at the ZUG site is much lower than the other sites due to missing values in 1998": Not clear for me why the 6 months data gap in summer 1998 decreases so much the total trend over the period 1995 to 2001. Please clarify.

Authors: Sorry for the confusion. What we want to point out is that because of the data gap in 1998 at ZUG, the annual growth rates of 1998 and 1999 are not accounted for in the mean annual growth rate calculation. However, for all of the other measurement sites, a clear anomalous peak in CO_2 annual growth rate is shown which can be attributed to a strong El Niño event. Therefore, we have rephrased this paragraph as the following.

"…This can be explained by the missing monthly values in 1998 and thus in turn the annual growth rates of 1998 and 1999 were left out for the average. However, the annual growth rates of these two years reached anomalous peaks at most sites (see details later in Sect. 3.6)…"

"Amplitudes of 15.44 and 14.89 ppm": For most signals I would suggest rounding the values to one decimal place.

Authors: Thank you very much for your suggestion. We have rounded all the values across the manuscript and rewrote the content accordingly.

The comparison of the seasonal cycles would be much more meaningful with background selected data. By the way do you use also all data (without selection) at SSL, WNK and MLO sites, or do you use the data selected by the station's managers at those sites? Please clarify. It could be interesting to see if the ZSF site remains more influenced by the air from the valleys, compared to ZPT and ZUG, once you have selected the nighttime values at all sites.

Authors: As mentioned above, we have now included the ADVS-selected data sets for the comparison of the seasonal cycles at Mount Zugspitze and Mauna Loa and similar results were found.

For sites SSL and WNK, all data were used for the analyses. There, no pre data selection routines have been performed. Therefore we added at the end of Sect. 2.2,

"…The CO_2 data from these measurement sites and from Mount Zugspitze locations were considered as validated data set (Level 2: calibrated, screened, artefacts and outliers removed), without any further data processing prior to the selection of representative data…"

Regarding the comparison among ZSF, ZPT, and ZUG, the results of seasonal cycles are similar for the ADVS-selected data sets, that for ZSF clearly higher CO_2 levels were observed from January to March and lower CO_2 levels were observed from July to September (see Fig. 7).

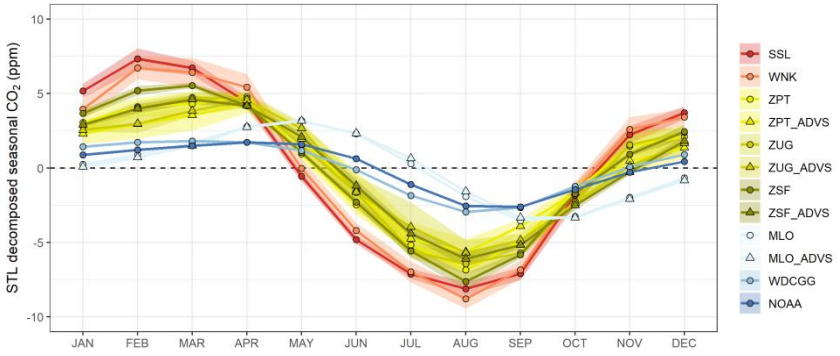

Figure 6: Mean CO_2 seasonal cycles from the STL seasonal component at each measurement site or location. Uncertainties at a 95% confidence interval are shown by the shaded areas with corresponding color.

"there are slight differences in seasonal amplitudes (ZPT: 10.86 ppm; ZUG: 11.14 ppm; ZSF: 13.09 ppm) among the three sites": I would not call a 2 ppm signal a slight difference ! A major signal to look at for such long term time series in North Hemisphere would be a possible trend in the amplitude of the seasonal cycle which could indicate a trend in the way the biosphere is interacting with atmospheric CO2. Graven et al., 2013 described for example increasing trends of the seasonal CO2 amplitude of 0.32 % per year at Mauna Loa and 0.60 % per year at Point Barrow. Considering a mean amplitude of about 12 ppm you could expect a trend of 1.4 to 2.5 ppm over the 36 years period of measurement at Zugspitze (assuming the MLO and BRW trends).

Authors: Thank you very much for the correction and information. We leave out the "slight" in the sentence. And with the new offset adjustment, the results are,

"…Despite the close proximity, there are differences in their seasonal amplitudes (ZPT: 11.9 ± 1.2 ppm; ZUG: 11.2 ± 1.0 ppm; ZSF: 13.3 ± 0.7 ppm). Good agreement is shown between CO_2 seasonal cycles from April to June and from October to December. However, significantly higher levels of CO_2 were evident at ZSF from January to March as well as lower levels from July to September. After data selection with lower seasonal amplitudes of 10.3 ± 1.3 ppm (ZPT_ADVS), 10.3 ± 1.2 ppm (ZUG_ADVS), and 10.9 ± 0.6 ppm (ZSF_ADVS), similar differences of the CO_2 levels in the seasonal cycles could be observed…"

Figure 3: the significant differences you show on figure 3b with the 3 sampling locations should prevent you from mixing those three dataset together as you do in figure 3a.

Authors: Thank you for the insight. As mentioned above, we have separated the three locations in all figures.

3.2. Inter-annual variations Abnormal high percentage at Zugspitze in 2000: I do not understand the sentence on line 5/6 suggesting that a careful and intensive selection was performed in 2000. Is the selection process different from the other years?

Authors: Sorry for the confusion. The original CO_2 data at ZUG was provided by the previous station manager Dr. H-E. Scheel, IFU. By direct cooperation, we learnt at that time that due to temporary systematic local effects of inflow of in-situ air to the sampling unit the CO_2 data at ZUG in 2000 had to be intensively selected by the operator. However the CO_2 data was only available in the format after this intensive selection so that such abnormal high percentage was derived.

Again, due to the differences between the three sampling locations (especially ZSF which is more influenced by air uplifted from the valleys) I think you should differentiate them in figure 4.

Authors: Done.

3.3. Weekly periodicity I would suggest to discuss short-term variabilities (weeks and daily) before trend and inter-annual variations.

Authors: Thank you for the suggestion. We have changed the order of the subsections in the results and discussion. Now we follow that,

- Sect. 3.1 ADVS selection and diurnal variation
- Sect. 3.2 Weekly periodicity
- Sect. 3.3 Case study on atmospheric CO, NO, and passenger numbers at Zugspitze
- Sect. 3.4 Trend
- Sect. 3.5 Seasonality

- Sect. 3.6 Inter-annual variation

I do not see the interest of comparing the weekly variations at Zugspitze to the one observed at Mauna Loa.

Authors: We decided to keep the comparison of the weekly periodicity between Mount Zugspitze and Mauna Loa. The reason is that this method of calculating the MSR values for evaluating the weekly cycle was developed by using the Mauna Loa CO_2 data (Cerveny and Coakley, 2002). The results show different weekly characteristics between ZSF and MLO, but not for the previous time periods with ZPT and ZUG.

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Author comments on "On the diurnal, weekly, seasonal cycles and annual trends in atmospheric CO_2 at Mount Zugspitze, Germany during 1981–2016" *by* Ye Yuan et al.

Ye Yuan on behalf of all co-authors

Answers to **Anonymous Referee #2 (RC2)**

The referee comments are shown in black. The answers are shown in blue.

General Comments

This paper outlines a set of CO2 data records collected over >30 years at locations within the German alps, specifically the methods used and trends observed. These long-term continental records, although more complicated to interpret than coastal records, are important. As such details of these records, like those given in this paper, should be published and the records themselves made publicly available. Unfortunately, there is a distinct lack of detail when it comes to the calibration approach used, in particular for the older data records. This needs to be rectified before publication. The paper also has a number of sentences which are confusing to read and would benefit greatly from the Copernicus copy editing service or the help of a native English speaker. I have attempted to note these in the technical corrections section and offered some suggestions for how they could be clarified. I feel that only with the addition of significant detail in relation to the calibration approach and a revision of the language used should the paper should be published.

Authors: We would like to thank Anonymous Referee #2 for the efforts to review this manuscript and to provide very helpful comments and detailed remarks. All the referee's comments have been carefully examined and addressed in the revised manuscript as well as supplement. Besides, we have improved the manuscript with English proofreading.

Specific Comments

Abstract

Examining weekend-weekday variability in order to comment on which fluxes are driving CO2 signals is a powerful tool. This, along with the outcomes of such a study should be highlighted in the abstract. At the moment the reference to it is rather vague, "indicating potential CO2 sources", and could easily be strengthened.

Authors: Thank you very much for the point. We have rephrased now in the abstract,

"…For a comprehensive site characterization of Mount Zugspitze, analyses of CO_2 weekly periodicity and diurnal cycle were performed to provide evidence for local sources and sinks, showing clear weekday to weekend differences with dominantly higher CO_2 levels during the daytime of the weekdays. A case study of atmospheric trace gases (CO and NO) and passenger numbers to the summit indicate that closeby CO_2 sources did not result from tourist activities but obviously from anthropogenic pollution in the near vicinity. Such analysis of local effects is an indispensable requirement for selecting representative data at orographic complex measurement sites…"

2.1 Measurement sites

There needs to be a description of the sampling method. Was there a small mast at these locations with an intake cup or were the instruments just measuring the air around them?

Authors: Done. We have included more details for the instrumental setup and restructured all the content of sampling method into section of instrumental setup and data processing.

Regarding sampling system, the text added in the manuscript is the following,

"…At ZUG the sampling line consisted of a stainless steel tube with an inner core of borosilicate glass and a cylindrical stainless steel top cup against intake of precipitation. The inlet with the structure of a small mast ended approximately 4 m on the top of the laboratory building, which is situated on the Zugspitze summit platform (see Fig. 1b). Inside the laboratory a turbine with a fast real-time fine control ensured a constant sample inflow of 500 l/min of in-situ air. The borosilicate glass tube (about 10 cm diameter) continued inside the laboratory, providing a number of outlets from where the instruments could get the sample air for their own analyses…"

"…At ZSF the same construction principle was applied for atmospheric sampling. There, the mast ends about 2.5 m above the pavement of the research terrace at the 5^{th} floor in an altitude of 2670 m a.s.l…"

2.2 Data processing

If you're presenting data from the first two time periods then you need to give information on how that data (or wasn't calibrated). If they weren't calibrated then say so, and in the discussion provide an estimate of the size of the error that this will drive in the data. The GC calibration method is unclear to me. From the description it appears that you have a single working standard, the concentration of which is adjusted based on the station standards, and that this working standard is measured once every 15 mins. This will account for instrumental drift but does that mean you're assuming a linear detector response? Using GC to measure CO2 is usually a more linear approach than many other CO2 measurement techniques but it's not exactly linear. The effect of this non-linearity needs discussed and outlined in the text. There is no information on the CRDS calibration process. If CRDS data is presented in the paper (it's not clear if it is) then this information needs to be provided.

Authors: Thank you very much for your comment. We have now included a more detailed description on the instrumental setup for all measurement locations as mentioned in the previous answer. (This is the same as the comment regarding instrumental setup and data processing for Anonymous Referee #1.)

"…The CO_2 measurement at ZPT was continuously performed with different, consecutively used instrument models (i.e., the URAS-2, 2T, and 3G) of nondispersive infrared (NDIR) technique. The measured values were corrected by simultaneously measured air pressure with a hermetically sealed nitrogen-filled gas cuvette due to no flowing reference gas used. Two commercially available working standards (310 and 380 ppm of CO_2 in N_2) were used for calibration every day at different hours. The CO_2 concentration in this gas bottle was compared in short intervals with a reference standard provided by UBA which was adjusted to the Keeling standard reference scale…"

"…The measurement and calibration were performed with a URAS-3G device and an Ansyco mixing box. The mixing controller allowed automatic switching for up to four calibration gases and sampling air by a self-written calibration routine using Testpoint software. The linear two-point calibration enveloping the actual ambient values with low and high CO_2 concentrations was taken at every 25th hour. Every six months the working standards were checked and re-adjusted, when required, to the standard reference scale by inter-comparison measurements with the station standards…"

Regarding the GC measurement, there has been used a working standard and a target. The working standard was supplied by a German specialist Deuste-Steiniger. Before practical use it has been measured approximately 800 to 1000 times against a group of 6 station reference standards, provided by NOAA for the time of 9 months. This longer time for intercomparison was needed to determine and exclude a possible drift of the standard and to adjust the CO_2 concentrations of the working standard as precisely as possible. The target was provided by the University of Heidelberg and had a slightly higher CO_2 concentration. The role of the target is to ensure a consistency of the measurement accuracy over the time. The target was measured every day about 25 times. The working standard was re-checked every two months with intercomparison measurements against the station reference standards from NOAA. If required, values of the measurements will have to be corrected. Actually the measurement of CO_2 is via a CH_4 equivalent by the use of FID. In the GC, the collected CO_2 is converted to CH_4 on a nickel catalyzer at a temperature of 400°C at the presence of hydrogen gas. The measurement of CH_4 with FID is known as linear and in this case no problems with non-linearity will occur.

2.3 Offset adjustment

The offset noted between ZPT and ZUG is very large – typically 6ppm – and concerning. However, it's difficult to comment on the offset adjustment used to correct for this as no information is given on how these sites are calibrated. Without further information it is impossible to know whether the offsets are driven solely by the use of CO2 in N2 calibration standards or other issues. It's also possible that, considering that they are different locations, that they were measuring air of different composition and part of this offset was true signal. Was any data filtering (e.g. wind speed/direction) completed prior to the comparison?

Authors: First of all, no pre-data filtering were done before the comparison. And we have now included a detailed analysis on the offset adjustment. Please see the following text. (This is the same as the comment regarding offset adjustment for Anonymous Referee #1.)

In manuscript:

"…However, for the three-year parallel CO_2 measurements at ZPT and ZUG (1995–1997), clear offsets of –5.8 ± 0.4 ppm ($CO_{2,\ ZPT}$ minus $CO_{2,\ ZUG}$, $1 \cdot SD$) were observed. The major reason for this bias is assumed to be the pressure-broadening effect in the used gas analyzers and the different gas mixtures used in the standards, CO_2/N_2 vs. CO_2/air, the so called "carrier gas correction (CGC)" (Bischof, 1975; Pearman and Garratt, 1975). It is known from previous studies that the measured CO_2 concentration, when using CO_2/N_2 mixtures as reference, is usually underestimated by several ppms for the URAS instruments, and such offsets vary from different types of analyzers (Pearman, 1977; Manning and Pohl; 1986). The carrier gas effect varies even between the same type of analyzer as well as with replacement of parts of the analyzer (Griffith et al., 1982; Kirk Thoning, personal communication, August 1, 2018). Due to lack of information and impossible on-site experiments with previous calibration standards, an offset adjustment to the CO_2 data set at ZPT was made for further analyses based on the offsets in data computed in the overlapping years instead of a physically derived correction. A single correction factor

$$G = 0.956 + 0.00017 \cdot C_{ZPT} \qquad (1)$$

was applied to the ZPT data while C_{ZPT} denotes the CO_2 concentrations at ZPT. Because of the same calibration mixtures, an additional adjustment was applied to the CO_2 concentrations at WNK by calculating the CO_2 differences between ZPT and WNK. A detailed description on the offset adjustment of CGC with potential errors is given in the supplement. Two similar CGCs by Manning and Pohl (1986) at Baring Head, New Zealand and Cundari et al. (1990) at Mt. Cimone, Italy, were comparable in magnitude to our offset adjustment…"

In supplement:

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, i.e. CO_2/N_2 mixtures vs. CO_2/air mixtures. In Table S2, 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.

Table S1: Detailed description of atmospheric CO_2 measurement techniques (NDIR = Nondispersive infrared, GC = Gas chromatography, and CRDS = Cavity ring-down spectroscopy).

ID	Time period	Instrument (Analytical method)	Scale	Calibration gas
ZPT	1981–1997	1981–1984: Hartmann & Braun URAS 2 (NDIR) 1985–1988: Hartmann & Braun URAS 2T (NDIR) 1989–1997: Hartmann & Braun URAS 3G (NDIR)	WMO X74 scale	CO_2 in N_2
ZUG	1995–2001	Hartmann & Braun URAS 3G (NDIR)	WMO X85 scale	CO_2 in natural air
ZSF	2001–2016	2001–2016: Hewlett Packard Modified HP 6890 Chem. station (GC) 2012–2013: Picarro EnviroSense 3000i (CRDS)	WMO X2007 scale	CO_2 in natural air
WNK	1981–1996	Hartmann & Braun URAS 2T (NDIR)	WMO X74 scale	CO_2 in N_2

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).

$$\Delta = C_a - C_t \quad (1)$$

$$G = C_t / C_a \quad (2)$$

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),

$$\Delta = C_{ZPT,a} - C_{ZUG,t} \quad (3)$$

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

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

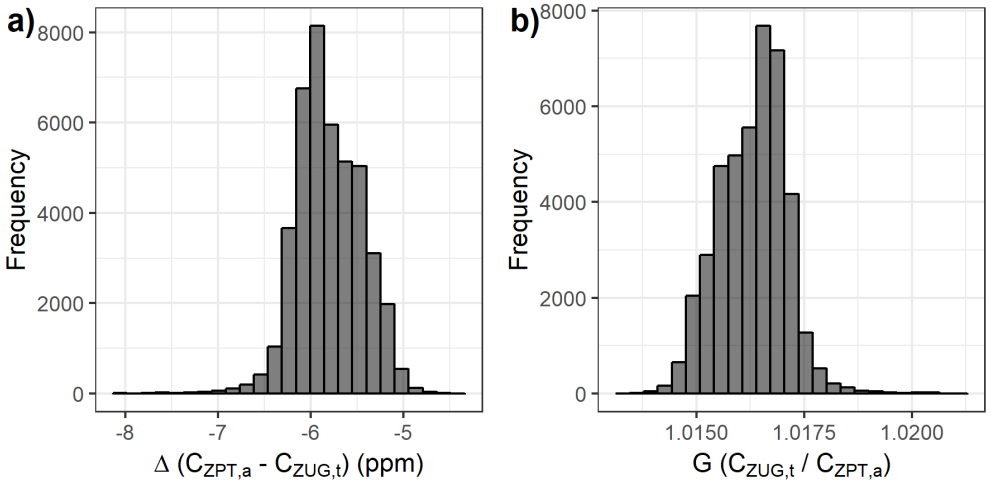

Figure S2: a) Histogram for the offsets (Δ) between CO_2 measurements at ZPT and ZUG for the period of 1995–1997. b) Histogram of the correction factor (G) between CO_2 measurements at ZPT and ZUG for the period of 1995–1997.

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.

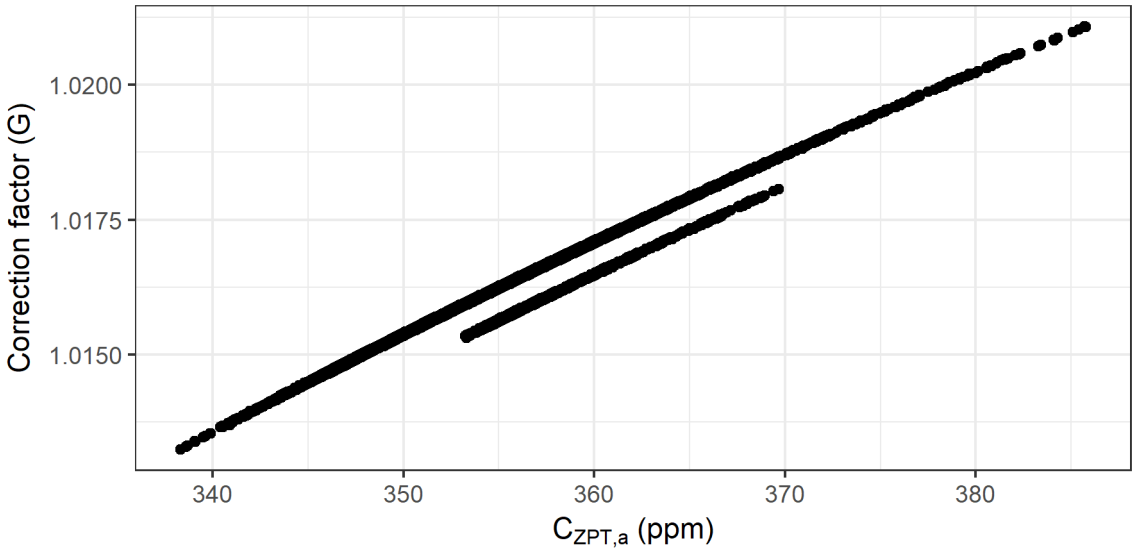

Figure S3: Computed correction factor G against CO_2 concentrations at ZPT from 1995 to 1997.

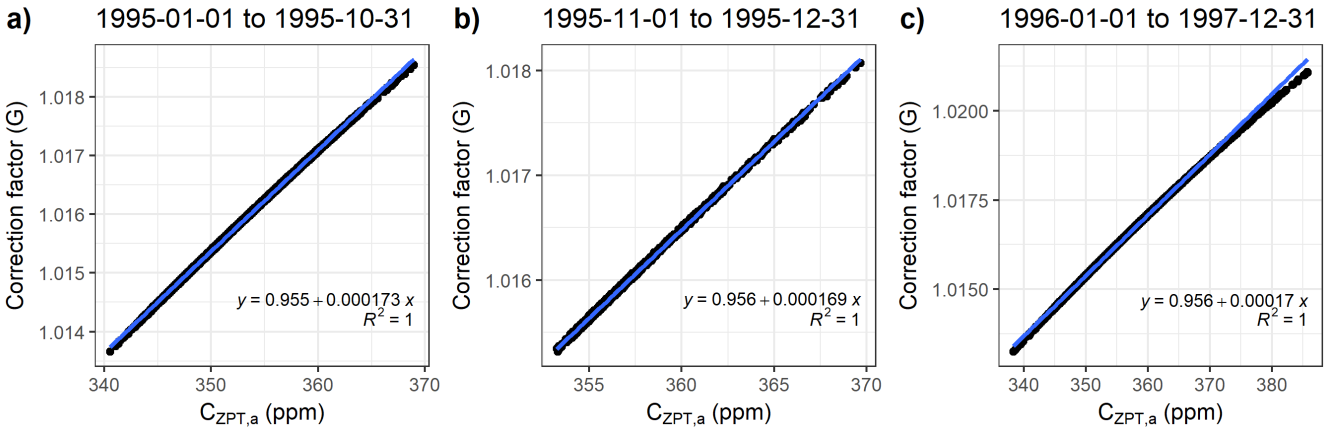

Figure S4: Computed correction factor G against CO_2 concentrations at ZPT from 1995 to 1997 with three separate time blocks.

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

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

And the adjusted CO_2 concentrations at ZPT can be expressed as

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

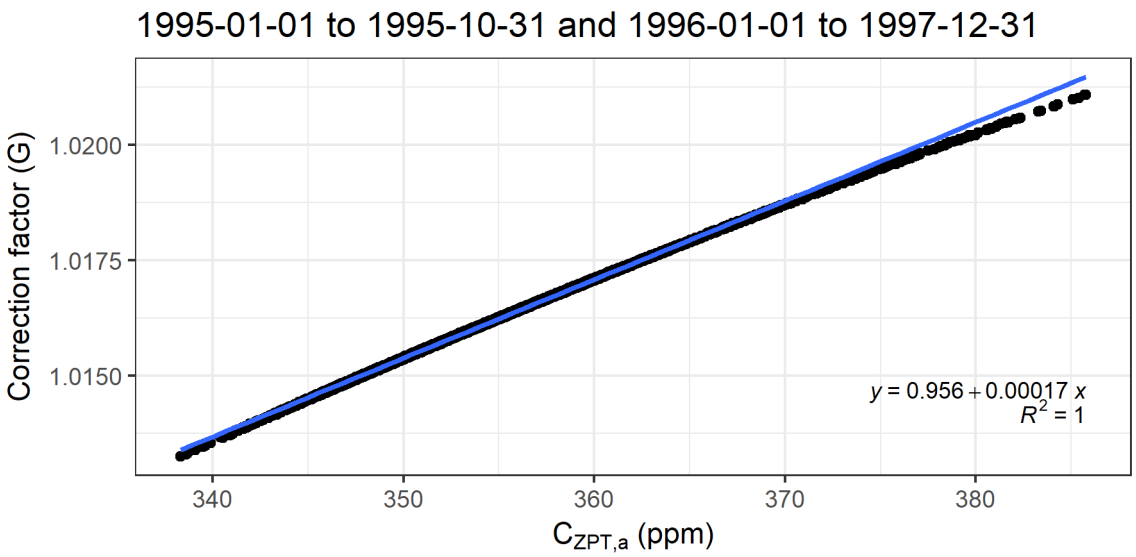

Figure S5: Computed correction factor G against CO_2 concentrations at ZPT from two separate time blocks, used for offset adjustment on the CO_2 data set at ZPT.

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

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

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 S1). 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

$$C_{WNK,a} - C_{ZPT,a} \approx C_{WNK,t} - C_{ZPT,t}. \quad (8)$$

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

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

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.

Technical and editorial corrections

The below comments are made in reference to specific areas of the text identified as page no./line no.

1/17 In this context there is no need for the definite article before "Mauna Loa" and "global means". This error occurs throughout text. For example "in good agreement with the Mauna Loa station and the global means" should read "in good agreement with Mauna Loa and global means"

Authors: Thank you very much for pointing this out. We have changed it throughout the manuscript.

1/18 It's important to include some estimate of the variability of the seasonal amplitude to give an indication of how stable it is.

Authors: Thank you very much for the suggestion. Now we have included the variability for the seasonal amplitude throughout the manuscript.

"…The peak-to-trough difference of the mean CO_2 seasonal cycle is 12.4 ± 0.6 ppm at Mount Zugspitze (after data selection: 10.5 ± 0.5 ppm), which is much lower than at nearby measurement sites at Mount Wank (15.9 ± 1.5 ppm) and Schauinsland (15.9 ± 1.0 ppm), but following a similar seasonal pattern…"

1/20-22 This sentence is confusing and vague.

Authors: We have rephrased it as following,

"…For a comprehensive site characterization of Mount Zugspitze, analyses of CO_2 weekly periodicity and diurnal cycle were performed to provide evidence for local sources and sinks, showing clear weekday to weekend differences with dominantly higher CO_2 levels during the daytime of the weekdays. A case study of atmospheric trace gases (CO and NO) and passenger numbers to the summit indicate that closeby CO_2 sources did not result from tourist activities but obviously from anthropogenic pollution in the near vicinity. Such analysis of local effects is an indispensable requirement for selecting representative data at orographic complex measurement sites…"

1/31-2/1 Please change “Apart from the sites located either in the Antarctica or along coastal/island regions, continental mountain stations also offer excellent options to observe the background atmospheric levels due to high elevations that are least unaffected…” to “Along with sites located in Antarctica or along coastal/island regions, continental mountain stations offer excellent options to observe background atmospheric levels due to high elevations that are less affected…”

Authors: Done.

2/2-4 This sentence is superfluous, please remove. “Presently, there are 31 Global Observatories coordinated by the Global Atmosphere Watch (GAW) network, focusing on monitoring the physical and chemical state of the atmosphere on a global scale.”

Authors: Done.

2/7 Please change “lidar” to “LIDAR” it’s an acronym.

Authors: Done.

2/15 Change “…what extend that elevated…” to “…what extent elevated…”

Authors: Done.

2/33 Confusing “Weekly CO2 periodicities were evaluated with the diurnal cycles for the Mount Zugspitze sites”. Do you mean that the weekly periodicity was evaluated by examining diurnal cycles or that the weekly periodicity was evaluated and diurnal cycles were also evaluated? I think the former but it could be read both ways.

Authors: We have rephrased the sentence as,

“…Short-term variations of weekly CO_2 periodicities and diurnal cycles were evaluated for Mount Zugspitze…”

3/1-2 Again “In addition, we perform an atmospheric CO and NO case study together with the amount of passengers at Zugspitze in 2016 as potential indicators for weekday–weekend influences.” is confusing. I’m guessing you mean “A case study combining atmospheric CO and NO measurements and records of passenger numbers was used to examine weekday-weekend differences”?

Authors: Thank you very much. It has been rephrased.

3/8-11 This is confusing. Please change “The measurements were collected at a southward-facing balcony in a pedestrian tunnel (Reiter et al., 1986) from the summit of Mount Zugspitze to the Schneefernerhaus (ZPT, 4725âAˇ š N, 1059âAˇ š E, slightly below the summit), which was a hotel until 1992 when it was rebuilt into an environmental research station. From 1995 until 2001, a new set of measurements began at the summit (ZUG, 4725âAˇ š N, 1059âAˇ š E, 2960 m a.s.l.) at a sheltered laboratory on the terrace using a URAS-3G device.” to “The measurements were collected at a southward-facing balcony of a pedestrian tunnel (Reiter et al., 1986) which joined the summit of Mount Zugspitze to the Schneefernerhaus

situated Xm below the summit (ZPT, 4725âA˘ š N, 1059âA˘ š E). The Schneefernerhaus was a hotel until 1992 when it was rebuilt into an environmental research station. From 1995 until 2001, a new set of measurements were made at a sheltered laboratory on the terrace of the summit (ZUG, 4725âA˘ š N, 1059âA˘ š E, 2960 m a.s.l.) using a URAS-3G device."

Authors: Done.

3/15-18 This section ("Zugspitzplatt, a glacier … shown in Fig 1. (Gantner et al., 2003)" interrupts the flow of the site descriptions. It's also unclear why it's included – I'm guessing to highlight that there are visitors nearby? Please move it to the end of the paragraph and provide more context.

Authors: We have re-structured this section. This section now only describes about the surrounding environment of the measurement locations. More detailed descriptions about instrumental setup and data processing were moved to the next section.

3/20-21 Confusing. Were the CRDS measurements made as well as the GC measurements i.e in parallel? Or instead of due to the instrumental failure? It's unclear.

Authors: We have rephrased this information in the data processing. The CRDS measurements started in 2011 and were performed in parallel with the GC system. We only use the CRDS data for 2012 and 2013 because GC data were not available.

"…Measurements of CO_2 at Schneefernerhaus continued thereafter to the present with a modified HP 6890 by using gas chromatography (GC) with an intermediate upgrade in 2008 (Bader, 2001; Hammer et al., 2008; Müller, 2009). In 2012 and 2013, because of an instrumental failure of the GC, CO_2 data were recorded with a cavity ring-down spectrometer (CRDS, Picarro EnviroSense 3000i) connected to the same air inlet, which had been installed in parallel since 2011…"

4/3 What were the concentrations of the working standards? I don't need the exact value for each cylinder but a general description would be useful. E.g. "near-ambient"

Authors: Thank you for the remark. "Near-ambient" was added.

4/5-6 Confusing. The GC data acquisition system doesn't "produce" the calibration values. By their very definition acquisition systems can only acquire data. Do you mean that using the GC system chromatograms were measured every 5 minutes with the working standard measured every third chromatogram?

Authors: The HP6890 GC measurement takes five minutes for one chromatogram. The typical sequence is sample, sample standard. With the chemstation software an automated realtime integration of chromatogram peaks was performed continuously. Together with the GC organizer software of the University of Heidelberg every two to four days the calculation of in situ CO_2 concentrations was performed. For continuous quality assurance the GC was checked daily for flows, retention times, gas pressures, and the structure of chromatograms.

4/8 What is a “pollution list”?

Authors: In the Environmental Research Station Schneefernerhaus we have a “central logbook for local pollution from working activities in the Research Station”. It is a strict rule, that every worker, crafter or colleague writes in the start- and end-time and the activity. This enables the scientists to do a well-organized data flagging of time sequences with air pollution.

4/8 “Simultaneous measurements of identical gas” Do you really mean that you have simultaneous measurements of CO2 made using another instrument at the same location? If so how were they made and why aren’t they reported here?

Authors: As mentioned above, a second CRDS measurement started in 2011 in parallel. But we only used the CRDS data of CO_2 for 2012 and 2013 due to the instrumental failure of GC.

4/12 If the working standard is measured every 15 minutes how often was the second target measured?

Authors: Every day for about 25 times.

4/18 This is a really large offset, typically 6ppm. Please give the mean offset here so that readers don’t have to look in the supplementary.

Authors: Done.

5/1-2 It would be useful to refer to this 36-year data record as a “compound” data record as it’s actually composed of data collected at three different locations. Using this terminology would make later sections of paper clearer.

Authors: Done. We have rephrased this combing the comment from Anonymous Referee #1, using “composite”.

“…In this study, we took CO_2 measurements during the corresponding time intervals at ZPT (1981–1994), ZUG (1995–2001), and ZSF (2002–2016) to assemble a composite time series for Mount Zugspitze over 36 years…”

6/11 Was this done on the raw data or the ADVS filtered data?

Authors: The MSR weekly periodicity analysis was done on the calibrated and quality assured data set (Level 2), which here is named “raw data” that have not been selected by ADVS.

6/23 Change “over the entire 36 year period” to “of the 36-year compound record”

Authors: Done.

6/25-26 “In general, the mean annual growth rates over the entire 36 year period at all sites agree within a range of 1.8 ppm yr–1”. Which sites are you referring to here? The Zugspitze sites don’t cover a 36-year period e.g. ZPT is only 16 years long. If you’re referring to SSl, MLO and the global mean as referenced in the previous sentence than this sentence is redundant please remove it.

Authors: This refers to the 36-yr composite record of atmospheric CO_2 at Mount Zugspitze. The reason is that we have done the offset adjustment between ZPT and ZUG, and also the offset between ZUG and ZSF in 2001 is within ±0.1 ppm. This evidence makes us think that it is applicable to compare the mean annual growth rate of overall 36 years with other measurement stations. Of course, we also showed the mean annual growth rate at each measurement locations at each separate time blocks.

7/1-2 Please change "Möller (2017) also mentioned that growth rates at both German stations and the MLO from 1981 to 1992 were identical." To "Möller (2017) also mentioned that 1981 to 1992 growth rates at both German stations and MLO were identical."

Authors: Done.

7/8 Please change "that minimize in August" to "that reach a minimum in August".

Authors: Done.

7/10-11 Please change "Sampled air is more frequently mixed with air from lower levels, which is characterized by lower CO2 concentrations that also minimize in August." To "As such, in Summer sampled air is more frequently mixed with air from lower levels, which is characterized by lower CO2 concentrations, enhancing the August minimum."

Authors: Done.

7/17 Please change "The MLO is" to "Mauna Loa data are" or "The Mauna Loa CO2 record is"

Authors: Done.

7/18 Please change "which agree" to "which agrees"

Authors: Done.

7/18-19 Please change "Moreover, global means exhibited the lowest seasonal amplitudes of 4.33 ppm (NOAA) and 4.76 ppm (WDCGG)." To "Global means exhibited the lowest seasonal amplitudes, 4.33 ppm (NOAA) and 4.76 ppm (WDCGG)."

Authors: Done.

7/19-23 I know what you're trying to say but this section really isn't written clearly. Please correct it.

Authors: Done. We have rephrased it as,

"…Compared with WDCGG, NOAA global mean fits better the seasonal cycle of MLO supporting the presence of a typical Marine Boundary Layer (MBL) condition for the levels of background CO_2 in the atmosphere. On the other hand, the WDCGG global mean includes continental characteristics for its calculation, thus exhibiting a slightly more continental signature which can be equally seen in the seasonal cycles at continental sites, such as Mount Zugspitze…"

7/27-28 Please change “Apart from this, significantly higher levels of CO2 at ZSF from January to March and lower levels from July to September cannot be neglected.” To “However, significantly higher levels of CO2 are evident at ZSF from January to March and lower levels from July to September.”

Authors: Done.

8/6-7 I’m confused. You state that there are an abnormally high percentage of validated data points for the year 2000 but then say there are only 4634 points but there are 15000 for the other years. Do you mean 15000 total for the remaining years or 15000 per year? If it’s per year then that’s seems wrong.

Authors: Sorry for the misunderstanding. The abnormally high percentage refers to the percentage of ADVS-selected data in the validated data in that year. At ZUG in 2000, an intensive data filtering had to be performed. Hence, the number of validated data points is much lower than in other years. But because this intensive data filtering resulted in a comparably low data variability, the data selection ADVS gave a considerably better relative percentage of representative data in 2000.

8/11-12 In figure 4b please colour code the sections of the compound Mt Zugspitze record for the different sites to make it easy to identify which years are ZPT, ZUG or ZSF. This would make relating this section to the figure far easier.

Authors: Done. Now we have separated these three measurement locations in all figures.

8/20 Please change “can also be illustrated for” to “are also evident in”

Authors: Done.

11/1-2 “Seasonal amplitude at … compared with global sites” This sentence doesn’t make sense. Please correct.

Authors: Done. We have rephrased as,

“…Regarding the seasonal amplitude, Mount Zugspitze is significantly more influenced by biogenic activity, mostly in the summer compared with Mauna Loa and global means…”

Figure 2 Please plot the data from the different sites as different colours in the bottom left hand plot to make it clear which site is being used at which time.

Authors: Done. We have separated the three measurement locations.

Figure 4 – Please add the abbreviations used in the text e.g. SSL or WNK to the titles of the plots to make comparisons between the text and the figure easier. Please colour code the sections of the compound Mt Zugspitze record for the different sites to make it easy to identify which years are ZPT, ZUG or ZSF.

Authors: Done. We have changed the labels in the figures to the abbreviations used in the text and separate the Zugspitze measurement locations.

Figure 5 – Match the site colour coding from figure 4 to this figure.

Authors: Done.

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

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Abstract. A continuous, 36-year measurement ~~record~~ composite of atmospheric carbon dioxide (CO_2) at three measurement ~~sites~~ locations of Mount Zugspitze, Germany was studied. For a comprehensive site characterization of Mount Zugspitze, analyses of CO_2 weekly periodicity and diurnal cycle were performed to provide evidence for local sources and sinks, showing clear weekday to weekend differences with dominantly higher CO_2 levels during the daytime of the weekdays. A case study of atmospheric trace gases (CO and NO) and passenger numbers to the summit indicate that closeby CO_2 sources did not result from tourist activities but obviously from anthropogenic pollution in the near vicinity. Such analysis of local effects is an indispensable requirement for selecting representative data at orographic complex measurement sites. The CO_2 trend and seasonality were then analyzed by background data selection and decomposition of ~~decomposing~~ the long-term time series into trend and seasonal components. The mean CO_2 annual growth rate over the ~~36~~ 36-year period at Zugspitze is 1.8 ± 0.4 ppm yr^{-1}, which is in good agreement with ~~the~~ Mauna Loa station and ~~the~~ global means. The peak-to-trough ~~amplitude~~ difference of the mean CO_2 seasonal cycle is ~~11.67~~12.4 ± 0.6 ppm at Mount Zugspitze (after data selection: 10.5 ± 0.5 ppm), which is ~~significantly less~~much lower than at nearby measurement sites at Mount Wank (15.9 ± 1.5 ppm) and Schauinsland (15.9 ± 1.0 ppm), but ~~which~~ following a similar seasonal pattern~~s~~. ~~To characterize this mountain site better, analyses of weekly periodicity and the diurnal cycle were performed to provide evidence of local sources and sinks of CO_2. Together, with an atmospheric trace gas (CO and NO) and the number of site visitor case study, clear weekday–weekend differences were detected, indicating potential CO_2 sources in the near vicinity.~~

1. Introduction

Long-term records of atmospheric carbon dioxide (CO_2) improve our understanding of the global carbon cycle, as well as long- and short-term changes, especially at remote background locations. The longest continuous measurements of

atmospheric CO_2 ~~trace back to~~started in 1958 at Mauna Loa, Hawaii, ~~taken~~ initiated by investigators of the Scripps Institution of Oceanography (Pales and Keeling, 1965). The measurements were performed on the north slope of the Mauna Loa volcano at an elevation of 3397 m above sea level (a.s.l.), thus at long distances from CO_2 sources and sinks~~, situated on the north slope of the Mauna Loa volcano at an elevation of 3397 m above sea level (a.s.l.)~~. Later, additional measurement sites were established for background studies of global atmospheric CO_2, such as the South Pole (Keeling et al., 1976), Cape Grim, Australia (Beardsmore and Pearman, 1987), Mace Head, Ireland (Bousquet et al., 1996), and Baring Head, New Zealand (Stephens et al., 2013). ~~Apart from the~~Along with sites located ~~either~~ in ~~the~~ Antarctica or along coastal/island regions, continental mountain stations ~~also~~ offer excellent options to observe ~~the~~ background atmospheric levels due to high elevations that are ~~least~~ less ~~un~~affected by local influences, for example, Mount Waliguan, China (Zhang et al., 2013), Mount Cimone, Italy (Ciattaglia, 1983), Jungfraujoch, Switzerland, and Puy de Dôme, France (Sturm et al., 2005). ~~Presently, there are 31 Global Observatories coordinated by the Global Atmosphere Watch (GAW) network, focusing on monitoring the physical and chemical state of the atmosphere on a global scale.~~

Although mountainous sites experience less impact from local pollution and represent an improved approach to background conditions compared with stations at lower elevations, we cannot fully dismiss the influence of local to regional emissions. This influence ~~depends~~ largely depends on air-mass transport and mixing within the moving boundary layer height. ~~Based on lidar~~ LIDAR measurements show that~~,~~ air~~, during the daytime,~~ from the boundary layer is orographically lifted to approximately 1–1.5 km above typical summit heights during daytime in the warm season (Carnuth and Trickl, 2000; Carnuth et al., 2002). ~~Based on a~~A 14-year record of atmospheric CO_2 at Mount Waliguan (3816 m a.s.l.), China, reveals significant diurnal cycles and depleted CO_2 levels ~~were observed~~ during ~~the~~ summer that are mainly driven by biological and local influences from adjacent regions, although the magnitude and contribution of these influences are smaller than those at other continental or urban sites (Zhang et al., 2013). At the Mt. Bachelor Observatory (2763 m a.s.l.), U.S.A., atmospheric CO_2 variations were studied in the free troposphere and boundary layer separately, where wildfire emissions were observed to drive CO_2 enhancement at times (McClure et al., 2016). However, it still remains unclear ~~as~~ to exactly what extent ~~that~~ elevated mountain sites are influenced by local activities and how to ~~better~~ characterize better local sources and sinks at such ~~sites~~stations. It is difficult to make quantitative conclusions on the anthropogenic and biogenic contributions to these measurements (Le Quéré et al., 2009). Analyzing weekly periodicity may be a potential indicator since periodicity represents anthropogenic activity patterns during one week (seven days) without the influence of natural causes (Cerveny and Coakley, 2002). From the prespective of modeling and satellite observational system, studies have shown that the weekly variability has implications on the quantification and verification of anthropogenic CO_2 emissions, as well as diurnal variability (e.g., Nassar et al., 2013; Liu et al., 2017). Regarding in-situ measurements, ~~The~~ results from Ueyama and Ando (2016) clearly indicate~~d~~ the presence of elevated weekday CO_2 emissions compared with weekend and/or holiday CO_2 emissions at two urban sites in Sakai, Japan. Cerveny and Coakley (2002) detected significantly lower CO_2 concentrations on weekends than on weekdays at Mauna Loa, which was assumed to result from anthropogenic emissions from Hawaii and nearby sources.

In this study, we present a ~~continuous~~composite~~,~~ 36-year record of atmospheric CO_2 measurements (1981–2016) at Mount Zugspitze, Germany (2962 m a.s.l.). The objective of this study is to ~~produce a consistent overall analysis of CO_2 trend and seasonality, and~~ achieve an improved measurement site characterization with respect to historical CO_2 data in terms of diurnal and weekly cycles, and to produce a consistent overall analysis of CO_2 trend and seasonality. The CO_2 measurements were performed at three locations on Mount Zugspitze: at a pedestrian tunnel (ZPT), at the summit (ZUG), and at the Schneefernerhaus (ZSF) on the southern face of the mountain. In addition, CO_2 measurements were taken at the nearby lower mountain station, Wank Peak (WNK), but for a shorter time period. Short-term variations of weekly CO_2 periodicities and diurnal cycles were evaluated for Mount Zugspitze. In addition, a case study combing atmospheric CO and NO measurements and records of passenger numbers was used to examine weekday-weekend influences. Then ~~T~~the results for the CO_2 annual growth rates and seasonal amplitudes were studied separately via trend-seasonal decomposition and compared with CO_2 data for the comparable time period (1981–2016) at the GAW Regional Observatory Schauinsland, Germany (SSL) and the GAW Global Observatory Mauna Loa, Hawaii (MLO), as well as the global CO_2 means calculated by the NOAA/ESRL and the World Data Centre for Greenhouse Gases (WDCGG). ~~Weekly CO_2 periodicities were evaluated with the diurnal cycles for the Mount Zugspitze sites. In addition, we perform an atmospheric CO and NO case study together with the amount of passengers at Zugspitze in 2016 as potential indicators for weekday–weekend influences.~~

2. Experimental methods and data

2.1. Measurement ~~sites~~locations

Mount Zugspitze is located approximately 90 km southwest of Munich, Germany. The nearest ~~populated city~~major town is Garmisch-Partenkirchen (GAP, 708 m a.s.l.~~, see Fig. 1~~). Measurements of CO_2 were first performed between 1981 and 1997 ~~with different, consecutively used instrument models (i.e., the URAS 2, 2T, and 3G), using nondispersive infrared (NDIR) technique. The measurements were collected~~ at a southward-facing balcony in a pedestrian tunnel (ZPT, 47°25′ N, 10°59′ E, 2710 m a.s.l) ~~(Reiter et al., 1986) from~~ situated about 250 m below the summit of Mount Zugspitze, which joined the ancient summit station of the first Austrian cable car ~~the summit of Mount Zugspitze~~ to the Schneefernerhaus (Reiter et al., 1986).~~(ZPT, 47°25′ N, 10°59′ E, slightly below the summit), which~~ The Schneefernerhaus was a hotel until 1992 when it was rebuilt into an environmental research station. From 1995 until 2001, a new set of measurements ~~began at the summit~~were made at a sheltered laboratory on the terrace of the summit (ZUG, 47°25′ N, 10°59′ E, ~~2960~~ 2962 m a.s.l.)~~ at a sheltered laboratory on the terrace using a URAS 3G device~~. These two measurement periods were performed by the Fraunhofer-Institute for Atmospheric Environment Research (IMK-IFU), and, since 1995 these measurements have been carried out on behalf of the German Environmental Agency (UBA). Since 2001, to continue contributing to the GAW Programme, CO_2 measurements have been performed at the Environmental Research Station Schneefernerhaus (ZSF, 47°25′ N, 10°59′ E, 2656 m a.s.l.). Approximately 100 m below the Schneefernerhaus, ~~Zugspitzplatt, a~~the glacier plateau Zugspitzplatt ~~approximately 100 m below the Schneefernerhaus~~ can be reached from the valley via cable cars or cogwheel

trains. The Zugspitzplatt descends eastward via a moderate to steep slope across the Knorrhütte towards the Reintalangerhütte as shown in Fig. 1 (Gantner et al., 2003). ~~Measurements of CO_2 at Schneefernerhaus continued thereafter to the present with a modified HP 6890 by using gas chromatography (GC) method with an intermediate upgrade in 2008 (Bader, 2001; Hammer et al., 2008; Müller, 2009). In 2012 and 2013, an instrumental failure occurred, such that measurements of CO_2 required parallel measurements with a cavity ring down spectrometer (CRDS, Picarro EnviroSense 3000i) connected to the same air inlet.~~

~~Additional atmospheric CO_2 measurements throughout the GAP area were performed between 1978 and 1996 at the Wank summit (WNK, 47°31′ N, 11°09′ E, 1780 m a.s.l.) using a URAS 2T instrument. The Wank Observatory is located in alpine grasslands just above the tree line (Reiter et al., 1986; Slemr and Scheel, 1998). A more detailed description can be found in Table 1. Detailed information on the CO_2 measurements at Schauinsland (SSL, 47°55′ N, 7°54′ E, 1205 m a.s.l.) and Mauna Loa, Hawaii (MLO, 19°28′ N, 155°35′ W, 3397 m a.s.l.), which we use to compare with the results of this study, can be found in Schmidt et al. (2003) for SSL and Thoning et al. (1989) for MLO.~~

2.2. Instrumental setup and ~~D~~data processing

CO_2 mole fractions were processed separately because of different measurement ~~sites~~ locations and time periods at Mount Zugspitze as described above. Information ~~for~~ on the first ~~and second~~ time period~~s~~ (ZPT) ~~were~~ was ~~mainly~~ collected based on personal communication with corresponding staff, ~~and~~ logbooks, and literature research (Reiter et al., 1986). The CO_2 measurement at ZPT was continuously performed with different, consecutively used instrument models (i.e., the URAS-2, 2T, and 3G) of nondispersive infrared (NDIR) technique. The measured values were corrected by simultaneously measured air pressure with a hermetically sealed nitrogen-filled gas cuvette due to no flowing reference gas used. Two commercially available working standards (310 and 380 ppm of CO_2 in N_2) were used for calibration every day at different hours. The CO_2 concentration in this gas bottle was compared in short intervals with a reference standard provided by UBA which was adjusted to the Keeling standard reference scale.~~The data calibration and filtering procedures described in detail focus on CO_2 measurement performed at ZSF.~~

At ZUG the sampling line consisted of a stainless steel tube with an inner core of borosilicate glass and a cylindrical stainless steel top cup against intake of precipitation. The inlet with the structure of a small mast ended approximately 4 m on the top of the laboratory building, which is situated on the Zugspitze summit platform (see Fig. 1b). Inside the laboratory a turbine with a fast real-time fine control ensured a constant sample inflow of 500 l/min of in-situ air. The borosilicate glass tube (about 10 cm diameter) continued inside the laboratory, providing a number of outlets from where the instruments could get the sample air for their own analyses. The measurement and calibration were performed with a URAS-3G device and an Ansyco mixing box. The mixing controller allowed automatic switching for up to four calibration gases and sampling air by a self-written calibration routine using Testpoint software. The linear two-point calibration enveloping the actual ambient values with low and high CO_2 concentrations was taken at every 25th hour. Every six months the working standards were

checked and re-adjusted, when required, to the standard reference scale by inter-comparison measurements with the station standards.

At ZSF the same construction principle was applied for atmospheric sampling. There, the mast ends about 2.5 m above the pavement of the research terrace at the 5th floor in an altitude of 2670 m a.s.l. Measurements of CO_2 at Schneefernerhaus continued thereafter to the present with a modified HP 6890 by using gas chromatography (GC) with an intermediate upgrade in 2008 (Bader, 2001; Hammer et al., 2008; Müller, 2009). In 2012 and 2013, because of an instrumental failure of the GC, CO_2 data were recorded with a cavity ring-down spectrometer (CRDS, Picarro EnviroSense 3000i) connected to the same air inlet, which had been installed in parallel since 2011. ~~At ZSF,~~The GC calibrations were carried out at 15 minute intervals using working standards (near-ambient), which had been calibrated with station standards from the GAW Central Calibration Laboratory (CCL) operated by the NOAA/ESRL Global Monitoring Division. The GC data acquisition system (see Supplementary Fig. S1) produced a calibration value every 15 minutes and two values from the sampled air based on one chromatogram every five minutes. Calibration factors and metadata were used to convert raw data into the final data product. Invalid and unrepresentative data due to local influences were flagged according to a pollution list. The measurement quality was controlled by comparison with simultaneous measurements of identical gas (CRDS) or with measurements of other trace substances and meteorological data, and additional support from station logbooks and checklists. The data were flagged according to quality control results. In principle, the acquisition system stores all measured data (flagged or not) and never discards them. Drifts in the working standards were controlled by a quasi-continuously measured second target and a regular two-month inter-comparison between the working standard and NOAA station standards, performing corrections as needed. ~~Averaged 30-min values were generated by calculating the arithmetic mean of the remaining data with a minimum of 2/3 of all the data.~~Calibration for CRDS was performed automatically with three different concentrations every 12 hours. Until 2013 the calibrations were performed automatically every 24 hours with one concentration, very close to the ambient value. Every two months the concentrations were re-checked to the station reference standards.

Additional atmospheric CO_2 measurements throughout the GAP area were performed between 1978 and 1996 at Mount Wank summit (WNK, 47°31′ N, 11°09′ E, 1780 m a.s.l.) using a URAS-2T instrument. The Wank Observatory is located in an alpine grassland just above the tree line (Reiter et al., 1986; Slemr and Scheel, 1998). Detailed information on the CO_2 measurements at Schauinsland (SSL, 47°55′ N, 7°54′ E, 1205 m a.s.l.) and Mauna Loa, Hawaii (MLO, 19°28′ N, 155°35′ W, 3397 m a.s.l.), which we use to compare the results of this study with, can be found in Schmidt et al. (2003) for SSL and Thoning et al. (1989) for MLO. The CO_2 data from these measurement sites and from Mount Zugspitze locations were considered as validated data set (Level 2: calibrated, screened, artefacts and outliers removed), without any further data processing prior to the selection of representative data.

2.3. Offset adjustment

According to ~~the~~ NOAA CMDL (http://ds.data.jma.go.jp/wcc/co2/co2_scale.html), no significant offsets are documented between the calibration scales WMO X74 and WMO X85 and the current WMO mole fraction scale. However, for the three-year parallel CO_2 measurements at ZPT and ZUG (1995–1997), ~~we observe significant~~ clear offsets of –5.8 ± 0.4 ppm ($CO_{2,\ ZPT}$ minus $CO_{2,\ ZUG}$, $1 \cdot SD$) were observed. ~~($CO_{2,\ ZUG}$ minus $CO_{2,\ ZPT}$, detailed offset plots can be found in Supplementary Fig. S2). We assume that this offset exists due to pressure broadening effects on the analyzers.~~ The major reason for this bias is assumed to be the pressure-broadening effect in the used gas analyzers and the different gas mixtures used in the standards, CO_2/N_2 vs. CO_2/air, the so called "carrier gas correction (CGC)" (Bischof, 1975; Pearman and Garratt, 1975). It is known from previous studies that the measured CO_2 concentration, when using CO_2/N_2 mixtures as reference, is usually underestimated by several ppms for the URAS instruments, and such offsets vary from different types of analyzers (Pearman, 1977; Manning and Pohl; 1986). The carrier gas effect varies even between the same type of analyzer as well as with replacement of parts of the analyzer (Griffith et al., 1982; Kirk Thoning, personal communication, August 1, 2018). ~~As Table 1 shows, different calibration gases were used at ZPT (CO_2 in N_2) and ZUG (CO_2 in natural gas). However, due~~ Due to ~~a~~ lack of information and impossible on-site experiments with previous calibration standards, an ~~potential~~ offset adjustment to the CO_2 data set at ZPT was made for further analyses ~~was made~~ based on the offsets in data computed in the overlapping years instead of a physically derived correction~~to the ZPT CO_2 record based on differences in the overlapping years~~. A single correction factor

$$C = 0.956 + 0.00017 \cdot C_{ZPT} \quad (1)$$

was applied to the ZPT data while C_{ZPT} denotes the CO_2 concentrations at ZPT. Because of the same calibration mixtures, an additional adjustment was applied to the CO_2 concentrations at WNK by calculating the CO_2 differences between ZPT and WNK. A detailed description on the offset adjustment of CGC with potential errors is given in the supplement. Two similar CGCs by Manning and Pohl (1986) at Baring Head, New Zealand and Cundari et al. (1990) at Mt. Cimone, Italy, were comparable in magnitude to our offset adjustment. ~~For the adjustment, we used the mean offset from these three years (5.802 ± 0.004 ppm) and added this to the ZPT data. The data measured at WNK were also calibrated similarly based on the same X74 scale used at ZPT as well as using CO_2 in N_2 gases, such that an identical value was added to the WNK data. Nevertheless, the results of this study still need to be viewed with caution, especially for the ZPT historical data and parameters such as the annual growth rates. Various analyzers were used during different periods, which could potentially cause variations as well as uncertainty in the offset adjustment.~~

On the other hand, there were 9 consecutive months, from April to December 2001, of parallel atmospheric CO_2 measurements at both ZUG and ZSF, based on which an inter-comparison between the two series was made. The ~~mean~~ offset between these two records attained an average of 0.1 ± 0.4 ppm ~~0.11 ± 0.03 ppm~~ (~~$CO_{2,\ ZSF}$ minus~~ $CO_{2,\ ZUG}$ minus $CO_{2,\ ZSF}$, $1 \cdot SD$), which ~~is still in good agreement between ZUG and ZSF with respective to~~fulfills the requirement of the GAW

Data Quality Objective (DQO, ±~~–~~0.1 ppm) for atmospheric CO_2 in the Northern Hemisphere. Therefore, no adjustments regarding this offset were applied to the data sets.

In this study, ~~CO_2 time series analyses for Mount Zugspitze sites are organized in the following ways. We~~ we took CO_2 measurements during the corresponding time intervals at ZPT (1981–1994), ZUG (1995–2001), and ZSF (2002–2016) to assemble a composite time series for Mount Zugspitze over ~~full~~ 36 years ~~time series~~. ~~For site characterization,~~Nevertheless, we always treat measurements from each ~~site~~ location separately for further analyses ~~with respect to weekly and diurnal analyses~~. At WNK, as well as at SSL and MLO, we used measured CO_2 data ~~between~~ starting from 1981 ~~and 1996 (~~for time consistency with measurements at Mount Zugspitze~~, which began in 1981)~~.

2.4. ADVS data selection

Adaptive Diurnal minimum Variation Selection (ADVS), a recently published, novel statistical data selection strategy, was used to ensure that the data were clean and consistent with respect to the state of a locally unaffected lower free troposphere at the measurement sites (Yuan et al., 2018). ADVS, which was originally designed to characterize mountainous sites, selects data based on diurnal patterns with the aim of selecting optimal data that can be considered representative of the lower free troposphere. To achieve this, variations in the mean diurnal CO_2 were first evaluated and a time window was selected based on minimal data variability around midnight, at which point data selection began. The data outside the starting time window were examined on a daily basis both forward~~s~~ and backward~~s~~ in time for the day under consideration, by applying an adaptive threshold criterion. The selected data results represent background CO_2 levels at the different measurement sites.

ADVS data selection was applied to all CO_2 records based on the same threshold parameters, followed by examining the starting time window and calculating ~~the calculation of~~ the percentages of the ADVS-selected data. Figure 2(a) shows the CO_2 time series before and after ADVS data selection. ~~The percentages of ADVS-selected data are 3.7% for SSL, 6.5% for WNK, 13.5% for Zugspitze, and 37.9% for MLO. Lower percentages indicate higher data variability due to lower elevation and proximity to local sources and sinks.~~We also evaluated the starting time windows resulting from ADVS data selection with the detrended mean diurnal cycles as described in Yuan et al. (2018) for each measurement site in Fig. 2(b). The number of ADVS-selected data is summarized as percentage per hour in the total number of all CO_2 data in Fig. 3. A detailed description and discussion is given in Sect. 3.1.

2.5. Mean symmetrized residual

Weekly periodicity was calculated using the "Mean Symmetrized Residual" (MSR) method, which was originally applied to atmospheric CO_2 data (Cerveny and Coakley, 2002). The MSR method focuses on variations in mean values by the days of the week. Daily deviations from the seven-day (consecutive) averages are calculated to account for the most likely emission cycles. Then, the MSR values are derived by averaging the differences for each single day. Additionally, only the MSR values with no data gaps in all the seven differences are considered as valid. Finally, all the MSR values are aggregated into

overall mean values for each day of the week. In addition, the MSR values are standardized so that the sum of all the seven values is equal to 0 (Cerveny and Coakley, 2002).

2.5~~6~~. STL decomposition

The Seasonal-Trend Decomposition technique (STL) was applied to decompose the CO_2 time series into trend, seasonal and remainder components individually (Cleveland et al., 1983; Cleveland et al., 1990), which, in previous studies, has been a commonly applied method (e.g., Stephens et al., 2013; Hernández-Paniagua et al., 2015). Locally weighted polynomial regressions were iteratively fitted to all monthly values in both an outer and an inner loop. According to Cleveland et al. (1990) and Pickers and Manning (2015), we set the trend and seasonal smoothing parameters to 25 and 5, respectively. The CO_2 time series at each site / location were aggregated into monthly averages and, then, decomposed by STL. Missing monthly values were substituted by spline interpolation.

To study the trend and seasonality, we firstly intended to apply STL decomposition to the ADVS-selected time series. However, due to multiple occurrences of consecutively missing values in the ADVS-selected monthly averages, especially for measurement sites at lower elevations (WNK and SSL), ~~we found that~~ it was more practical to use the original CO_2 time series without ADVS data selection for STL decomposition, to preserve time series continuity (Pickers and Manning, 2015). ~~Nevertheless, there~~ There is one missing six-month time interval at ~~Zugspitze~~ ZUG in 1998 (July to December). Thus~~, for Zugspitze,~~ STL was performed separately for the time periods before (~~1981~~1995.01–1998.06) and after (1999.01–~~2016~~2001.12) the gap~~, and the decomposed results were combined afterwards (see Supplementary Fig. S3)~~. Nevertheless, we still applied STL decomposition to the ADVS-selected data sets from Mount Zugspitze and Mauna Loa, since these selected time series were applicable. Only at ZPT, due to greatly missing data at the beginning (1981 and 1982) of the ADVS-selected data set, we only used the ADVS-selected results starting from 1983. Individual figures of each STL-decomposed component at all stations can be found in the supplement.

For annual growth rates~~,~~ we did not include the WNK time series due to shorter time periods of available data. Monthly trend components were first aggregated into annual mean values. Then, the annual CO_2 growth rates were calculated as the difference between the CO_2 value of the current year and the value from the previous year (Jones and Cox, 2005). The mean seasonal cycle was aggregated directly from the monthly seasonal components by month. To observe potential deviations on the regional and global scale, we compared the trend and seasonality derived from the STL decomposed components respectively at Zugspitze with other measurement sites. We included the globally averaged marine surface monthly mean data from ~~the~~ NOAA (www.esrl.noaa.gov/gmd/ccgg/trends/) and data for the global mean mole fractions from ~~the~~ WDCGG (WMO, 2017) as references, and processed these data based on the identical STL decomposition routine. All the statistical analyses described above (including ADVS, MSR, and STL) were performed in the R environment (R Core Team, 2018).

~~**2.6. Mean Symmetrized Residual**~~

~~Weekly periodicity significance was calculated using the "Mean Symmetrized Residual" (MSR), which was originally applied to atmospheric CO_2 data (Cerveny and Coakley, 2002). In doing so, we were cautious when choosing the most appropriate statistical analysis (Daniel et al., 2012; Sanchez-Lorenzo et al., 2012). The MSR method focuses on variations in mean values by the days of the week. Daily deviations from the seven day (consecutive) averages are calculated to account for the most likely emission cycles. Then, the MSR values are derived by averaging the differences for each single day. Additionally, only the MSR values with no data gaps in all the seven differences are considered as valid. Finally, all the MSR values are aggregated into overall mean values for each day of the week. In addition, a standardized adjustment is also done so that the sum of all the seven values is equal to 0 (Cerveny and Coakley, 2002). All the statistical analyses described above (including STL, ADVS, and MSR) were performed in the R environment (R Core Team, 2018).~~

3. Results and discussion

3.1. ADVS selection and diurnal variation

The resulting ADVS-selected CO_2 data showed a clear linkage of the percentage of selected data and the altitude of the measurement site. Among the continental stations, the percentage increased with altitude. Lower percentage indicates higher data variability due to lower elevation and proximity to local sources and sinks. At Schauinsland, the percentage of CO_2 data by the ADVS selection was 6.3% while the percentages at Mount Zugspitze reached 9.9% (ZPT), 19.5% (ZUG), and 13.6% (ZSF), respectively. A moderate percentage of 6.3% was also derived at Mount Wank. However, regarding the elevated mountain station Mauna Loa on the island of Hawaii, a much higher percentage (40.0%) of CO_2 data was selected by ADVS as representative of its background concentration mainly due to the very limited nearby anthropogenic sources as well as mostly clean, well-mixed air arriving there. A similar result for an island mountain station can be found in Yuan et al. (2018) where a percentage of 36.2% was computed for the CO_2 measurements at the station Izaña on Tenerife Island (28º19′ N, 16º30′ E, 2373 m a.s.l.). This can also be explained by the detrended mean diurnal cycles shown in Fig. 2(b) and Fig. 3. The mean diurnal cycle at MLO only exhibits a clear trough during daytime, especially starting from 12:00h local time (LT), which is believed to be influenced by the vegetation activity (photosynthesis) in the surroundings. The same effect can be seen at WNK and SSL, but with larger magnitudes and earlier occurrences of the minima because of their lower locations closer to CO_2 sinks. In contrast, at these two sites the CO_2 maxima in the diurnal cycles were not as clearly noticeable as at Mount Zugspitze due to anthropogenic sources and high biogenic respiration. At the three locations of Mount Zugspitze, the CO_2 peaks in the mean diurnal cycles are driven by the late-morning convective upslope wind, which was relatively obvious at both ZUG and ZSF. However, from the perspective of data selection, a significantly higher percentage of CO_2 data was selected at ZSF compared with ZPT although there is only a small difference in altitude of around only 70 m. This proves that ZSF is capable to capture more background conditions than ZPT during the day. Nevertheless, based on the starting time

window computed for ADVS selection, we found that, in general, most stations exhibited similar starting time windows beginning around midnight and the ADVS data selection was applied systematically by including more data around these hours (see Fig. 3), which confirmed our assumption of background conditions during midnight for the ADVS data selection (Yuan et al., 2018).

3.2. Weekly periodicity

For a better characterization of the differences among the measurement locations at Mount Zugspitze, the mean CO_2 weekly cycles were analyzed as a function of mean MSR values (see Fig. 4a). The mean MSR values at the MLO for the corresponding time intervals were also calculated. Most weekly cycles exhibited no clear peaks or patterns for both sites. However, the magnitude of MSR data variability is mostly higher at Zugspitze with a maximum on Thursdays. The only significant weekday-weekend difference is observed at ZSF in terms of the 95% confidence interval, which shows weekly maxima and weekly minima on Thursday and Saturday, respectively (peak-to-trough difference: 0.76 ppm). Gilge et al. (2010) observed similar phenomena when studying O_3 and NO_2 concentrations at Alpine mountain stations including Zugspitze. Clear weekly cycles, with enhanced O_3 levels on working days, were observed at ZSF in summer, with weekly maxima and minima on Thursday and Sunday, respectively. For NO_2, maximum mixing ratios on working days and minimum ratios on Sundays at neighboring stations were observed, generally suggesting an anthropogenic impact at all elevations.

We obtained more insights into the weekly CO_2 cycle at Mount Zugspitze by comparing the mean diurnal cycles of weekdays and weekends (see Fig. 4b). Detrended mean diurnal cycles at ZSF, from Sunday to Saturday, were calculated by subtracting the daily averages from the daily data between 2002 and 2016. In the morning around 9 to 10 a.m. LT the CO_2 levels at ZSF are higher on weekdays than weekends, while CO_2 diurnal patterns during the rest of the week are relatively stable. Such weekly cycles are not observable at ZPT and ZUG nor at WNK and SSL (see Supplementary Fig. S18). At ZPT, there are less variations in the diurnal cycle compared to ZSF, indicating that this location does not receive the effect of regular local anthropogenic working activities and hence it is more representative of lower free tropospheric conditions regarding this aspect. The weekday-weekend differences at ZSF are possibly due to local working patterns, whereas the absence of this pattern at lower sites may indicate influences from a more regional reservoir. In fact, ZSF is closed on the weekends and, thus, influenced by less immediate anthropogenic activities.

3.3. Case study on atmospheric CO, NO, and passenger numbers at Zugspitze

To study further the potential sources and sinks for such weekday-weekend differences in the CO_2 diurnal cycles at ZSF, we analyzed atmospheric CO and NO data at ZSF and the daily, combined number of cable car and train passengers to Zugspitzplatt and to the Zugspitze Summit in 2016. Atmospheric CO and NO are known to be good indicators of local anthropogenic influences due to highly variable short-term signals and are thus helpful to identify potential CO_2 sources (Tsutsumi et al., 2006; Sirignano et al., 2010; Wang et al., 2010; Liu et al., 2016). In this study, we used atmospheric NO due

to its short lifetime based on rapid atmospheric NO_2 formation with resulting altitude-dependent O_3 surplus, indicating the presence of sources at closer distances. The CO and NO data shown in Fig. 5 include data that was flagged during data processing, because for the delivery to GAW World Data Centers the logged and recognized work dependent concentration peaks are flagged. A clear weekday-weekend difference is observed for both CO and NO. Only weekdays are characterized by multiple short-term atmospheric CO events and higher atmospheric NO peaks during the daytime (mostly around 9 a.m. LT), which fits perfectly with daytime peaks in CO_2 diurnal cycles. A general fluctuating pattern in NO throughout the week is thought to originate from heating of the Zugspitzplatt and changing work with combustion engines. On the other hand, the daily number of passengers at Zugspitze (see Fig. 5c) shows a clear weekday–weekend pattern with higher number of passengers on the weekends. However, increased numbers of passengers on the weekends do not correspond to higher levels of CO and CO_2, indicating that measured CO_2 levels are not significantly influenced by tourist activities nearby. Instead, it is more likely that anthropogenic working activities are the main driver of weekly periodicity.

3.~~1~~4. Trend ~~and seasonality~~

Based on the STL decomposed results, the mean annual growth rate ~~over~~ of the ~~entire~~ 36-year composite record ~~36-year period~~ at Mount Zugspitze from the three measurement locations is 1.8 ± 0.4 ~~1.78 ± 0.34~~ ppm yr^{-1}, which is consistent with the SSL (1.8 ± 0.4 ~~1.84 ± 0.39~~ ppm yr^{-1}), MLO (1.8 ± 0.2 ~~1.82 ± 0.21~~ ppm yr^{-1}), and global means (NOAA: 1.8 ± 0.2 ~~1.79 ± 0.21~~ ppm yr^{-1}; WDCGG: 1.8 ± 0.2 ~~1.84 ± 0.20~~ ppm yr^{-1}). The mean annual growth rates from the ADVS-selected data sets at Mount Zugspitze and Mauna Loa also result in the identical value of 1.8 ppm yr^{-1}. ~~In general, the mean annual growth rates over the entire 36-year period at all sites agree within a range of 1.8 ppm yr^{-1}.~~ Then, we divided the entire time period (1981–2016) into three time blocks corresponding to the different locations at Mount Zugspitze in order~~, i.e., ZPT, ZUG, and ZSF, to calculate the mean annual CO_2 growth rates~~ to observe potential differences with respect to other sites separately (see Table ~~2~~1). The results show good agreement of each location of Mount Zugspitze with other measurement sites (also for the ADVS-selected results) as well as a clearly increasing trend of the annual growth rates over these three time blocks. ~~The mean annual growth rates at all Zugspitze sites agree with those for the other sites, which in general, show clear, increasing trend over the time blocks.~~ Only the mean annual growth rate between 1995 and 2001 at ~~the~~ ZUG ~~site~~ is ~~much~~ obviously lower than at the other sites. This can be explained by the missing monthly values in 1998 and thus in turn the annual growth rates of 1998 and 1999 were left out for the average. However, the annual growth rates of these two years reached anomalous peaks at most sites (see details later in Sect. 3.6). ~~due to missing values in 1998 so that the annual growth rates for 1997 and 1998 are left out.~~ Möller (2017) also mentioned that 1981 to 1992 growth rates at both German stations and ~~the~~ MLO ~~from 1981 to 1992~~ were identical.

3.5 Seasonality

For the overall seasonality, Figure ~~3~~6~~a~~ presents the mean seasonal cycles for the STL decomposed seasonal components. We observed similar patterns in the SSL and WNK seasonal cycles, with mean peak-to-trough ~~amplitudes~~ differences of

~~15.44~~15.9 ± 1.0 and ~~14.89~~15.9 ± 1.5 ppm, respectively. The composite data set at Mount Zugspitze ~~sites have~~ results in a lower amplitude (~~11.67~~12.4 ± 0.6 ppm), but ~~also~~ still ~~have~~ exhibits a similar seasonality influenced by active biogenic processes (mainly photosynthesis) ~~during the~~in summer ~~(seasonal minima in August)~~ compared with ~~the~~ SSL and WNK (Dettinger and Ghil, 1998). As vegetation grows with rising temperatures (approaching summer), CO_2 levels decrease due to more and more intense photosynthetic activities ~~that minimize~~ till a minimum in August. In addition, with rising temperatures, locally influenced air masses reach ~~the~~ Mount Zugspitze ~~sites~~ more often due to "alpine pumping" (Carnuth et al., 2002; Winkler et al., 2006). As such, ~~Sampled~~ air sampled in summer is more frequently mixed with air from lower levels, which is characterized by lower CO_2 concentrations ~~that also minimize in August~~, intensifying the August minimum. Anthropogenic activities and plant respiration dominate the increases in concentration in the winter (January to April). This influence appears to be stronger at SSL and WNK than at ~~the elevated~~Mount Zugspitze ~~site~~. Lower levels of CO_2 and a one-month delay, from February to March, ~~for~~ of the seasonal maximum at Mount Zugspitze are in agreement with the expectation of thermally driven orographic processes that drive the upward transport of CO_2 from local sources, as well as limited human access to ~~the~~ Mount Zugspitze ~~site~~ and the ~~almost non-existent presence~~prevailing absence of biogenic activities at such high elevations. Regarding the resulting seasonal cycles based on ADVS-selected Zugspitze data sets, similar patterns were observed but with a lower amplitude (10.5 ± 0.5 ppm) as well as a two-month shift of the seasonal maximum to April.

The ~~MLO~~ Mauna Loa CO_2 record is characterized by a seasonal maximum in May and a minimum in September with a peak-to-trough ~~amplitude~~ difference of ~~6.73~~6.8 ± 0.1 ppm, which agrees with observations from Dettinger and Ghil (1998) and Lintner et al. (2006). The ADVS-selected results for MLO also show a similar pattern with a lower amplitude of 6.6 ± 0.1 ppm. ~~Moreover, global~~ Global means exhibited the lowest seasonal amplitudes, ~~of 4.33~~4.4 ± 0.1 ppm (NOAA) and ~~4.76~~4.8 ± 0.0 ppm (WDCGG). Compared with WDCGG, ~~The~~ NOAA global mean fits better ~~towards~~ the ~~MLO~~ seasonal cycle of MLO~~, compared with the WDCGG, indicating~~ supporting the presence of a typical Marine Boundary Layer (MBL) condition for the levels of background CO_2 in the atmosphere. ~~The~~ On the other hand, the WDCGG global mean includes continental characteristics for its calculation,~~and,~~ thus~~, exhibits~~ exhibiting a slightly more continental signature~~,~~ which can be equally seen ~~from~~ in the seasonal cycles ~~for~~ at ~~the~~ continental sites, such as ~~at~~ Mount Zugspitze. April and October appear to be the important months that indicate the switch of either CO_2 source to sinks or vice versa for the continent.

We then ~~separately~~ examine~~,~~ in more detail~~,~~ the seasonal cycles at ZPT, ZUG, and ZSF ~~(see Fig. 3b)~~. Despite the close proximity, there are ~~slight~~ differences in their seasonal amplitudes (ZPT: ~~10.86~~11.9 ± 1.2 ppm; ZUG: ~~11.14~~11.2 ± 1.0 ppm; ZSF: ~~13.09~~13.3 ± 0.7 ppm) ~~among the three sites~~. ~~Figure 3b shows good~~ Good agreement is shown between CO_2 ~~concentrations~~ seasonal cycles from April to June and from October to December. ~~Apart from this~~However, significantly higher levels of CO_2 were evident at ZSF from January to March ~~and~~ as well as lower levels from July to September ~~cannot be neglected~~. After data selection with lower seasonal amplitudes of 10.3 ± 1.3 ppm (ZPT_ADVS), 10.3 ± 1.2 ppm (ZUG_ADVS), and 10.9 ± 0.6 ppm (ZSF_ADVS), similar differences of the CO_2 levels in the seasonal cycles could be observed. ~~Similarly, as Fig. 3a shows, these~~ These results indicate that factors such as elevation and ~~site~~ measurement

surroundings ~~have a strong influence on determining~~strongly determine the air-mass composition ~~in view of~~via local~~,~~ vertical transport. The amount of air-mass transport via orographic lifting affects the three ~~sites~~ locations differently. The lower elevation station, ZSF, apparently captures more mixed air masses ~~when measuring CO_2 levels, which follows~~due to a daytime up-valley flow along the Reintal (Gantner et al., 2003)~~,~~ as well as a slightly southeastern flow from the Inntal ~~that reaches the ZSF site~~ (see Fig. 1) that is less frequent for the higher ~~elevation sites~~locations (ZPT or ZUG). In addition, comparably postponed seasonal maxima at ZUG and ZPT from March to April show delayed onset of convective upwind air-mass transport and changing Planetary Boundary Layer (PBL) compositions.

3.~~2~~6. Inter-annual variation

To study the inter-annual variability, we focused on the percentages of ADVS selection, the growth rates, and the seasonal amplitudes~~ annually~~. The annual percentages from ADVS data selection are shown for years without missing monthly averages (see Fig. ~~4a~~7a). ~~Therefore, 1982, 1994, and 1998 for the Zugspitze sites, 1996 for WNK, and 1981, 1982, 2010, 2011, and 2014 for SSL were excluded.~~ An ~~abnormally~~ exceptionally high percentage at Zugspitze in 2000 resulted from careful and intensive filtering of the original CO_2 data. The total number of validated 30-min data points in 2000 is 4634, while the amount of data for other years ~~is approximately 15000~~ranges from 8754 to 15339 (except for 1998, with only 6-month data, the total number of 30-min CO_2 data is 6441). As described in the previous section, the ~~mean~~ annual growth rates are plotted in Fig. ~~4b~~7b. The annual CO_2 seasonal amplitudes are calculated as the difference between the yearly maximum and minimum monthly CO_2 values from the STL decomposed seasonal components (see Fig. ~~4c~~7c).

Focusing on the annual percentages from ADVS-selected representative data after 1990, we calculated the mean annual percentages at ~~the~~ Mount Zugspitze ~~sites~~locations, for the time periods between 1990 and 2001 (2000 was not included for ZUG), and 2002 and 2016. We observe significantly higher percentages ~~at a 95% confidence interval,~~ at ZPT and ZUG (~~20.59~~18.5 ± ~~4.12~~2.4%) ~~compared with values~~than at ZSF (13.6~~3~~ ± 1.1~~0~~%) at a 95% confidence interval~~,~~. ~~which~~ These percentages are different from ~~the~~ SSL (4.2~~0~~ ± 0.5~~3~~ vs. 4.2~~0~~ ± ~~0.58~~0.6%) and ~~the~~ MLO (~~41.10~~43.5 ± 1.4~~2~~ vs. ~~38.42~~42.1 ± ~~1.87~~1.6%). A likely explanation is that there are systematically different air-mass transport characteristics reaching each of these ~~sites~~locations. Higher percentages at ZPT and ZUG indicate that these ~~sites~~ locations are capable of capturing more air masses that have traveled over long distances along the mountains. These air masses trap air that ascends from many Alpine valleys, but also from remote source regions up to intercontinental scale (Trickl et al., 2003; Huntrieser et al., 2005). On the other hand, ~~the~~ ZSF is dominated by mixing air masses that have traveled along the Zugspitzplatt area, which contain higher levels of CO_2 due to daily, local anthropogenic sources during winter and convective upwind during seasons without snow cover that are characterized by lower concentrations of CO_2 at lower altitudes. Such patterns in the data are also evident in ~~can also be illustrated for~~ the annual growth rates and seasonal amplitudes. The overall patterns at ~~the~~ Mount Zugspitze ~~sites~~ agree with ~~the~~ SSL and WNK. However, ~~the~~ SSL and WNK exhibit ~~much~~ more variation in the annual growth rates and higher seasonal amplitude levels (see Fig. ~~4b~~ 7b and ~~4c~~7c). In addition, slightly higher seasonal amplitudes for the WDCGG

global mean compared with the NOAA one can be explained by the WDCGG global mean calculation method~~s~~, which includes more continental stations (WMO, 2017).

Anomalies in the annual growth rates are frequently observed, which are possibly explained by climatic influences such as the El Nino-Southern Oscillation (ENSO), volcanic activity, and extreme weather conditions (Keeling et al., 1995; Jones and Cox, 2001; Francey et al., 2010; Keenan et al., 2016). One of the largest positive annual growth rate anomalies ~~occurs~~ occurred in 1998 and is clearly seen in all the records (aside from ~~the WNK and~~ ZUG ~~Zugspitze sites that have~~with missing values), which is attributed to a strong El Niño event (Watanabe et al., 2000; Jones and Cox, 2005). Similar signals are found in 1988, especially at ~~the~~ MLO and in ~~the~~ global means. Such anomalies are more clearly observed in the global and seaside time series. Regarding continental sites, inter-annual signals may be hidden by more intense land influences rather than global effects. Moreover, positive consecutive anomalies between 2002 and 2003 are clearly observed at ~~Zugspitze~~ ZSF and ~~the~~ SSL, which are potentially due to anomalous climatic conditions, such as the dry European summer in 2003 that led to an ~~increasd~~ increasing number of forest fires. These events are also observable in the MLO and global means ~~records~~ but at smaller scale~~s~~ (Jones and Cox, 2005). At all German sites, clear negative anomalies, due to violent eruptions of the El Chichón and Mt. Pinatubo volcanoes and the subsequent volcanic induced surface cooling effect~~,~~ are observed after stratospheric aerosol maxima above Garmisch-Partenkirchen in 1983 and 1992, respectively (Lucht et al., 2002; Frölicher et al., 2011; Frölicher et al., 2013; Trickl et al., 2013). This effect is only slightly visible in the MLO and global means ~~records~~ despite the fact that volcanic aerosol spread over the entire globe.

However, the reasons for some anomalies are still unclear. These include the negative anomalies during 1985 and 1986 at all Germans sites. Certain anomalies in the annual percentages and seasonal amplitudes also derive from extremely low ADVS selection percentages beginning at 1984 and continuing until 1990, with peaks in seasonal amplitudes between 1985 and 1986. This is the reason why we calculated the mean annual ADVS selection percentage beginning at 1990. We assume that local influences mask similar physical mechanisms ~~between~~ at the sites ~~do not occur due to local influences~~. However, annual percentages at the MLO also have similar characteristics. Therefore, it is still unclear what triggers such distinct inter-annual data variability across measurement sites. Another clear negative annual growth rate anomaly occurred in 2014 across all sites. Such anomalies still require further investigation, but are beyond the scope of this study.

~~3.3. Weekly periodicity and diurnal variation~~

~~To characterize site differences at Mount Zugspitze better, we analyzed the mean CO_2 weekly cycles as a function of mean MSR values (see Fig. 5a). The mean MSR values at the MLO for the corresponding time intervals were also calculated. Most weekly cycles exhibit no clear peaks or troughs patterns for both sites. However the magnitude of MSR data variability is much higher at Zugspitze with a maximum on Thursdays for several periods. The only weekday weekend pattern is observed at ZSF, which shows weekly maxima and weekly minima on Thursday and Saturday, respectively (peak to trough difference: 0.76 ppm), significantly different at the 95% confidence interval. Gilge et al. (2010) observed similar phenomena when studying O_3 and NO_2 concentrations at Alpine mountain stations including Zugspitze. Clear weekly cycles, with~~

enhanced O_3 levels on working days, were observed at ZSF in summer, with weekly maxima and minima on Thursday and Sunday, respectively. For NO_2, they continually observed maximum mixing ratios on work days and minimum ratios on Sundays at neighboring stations, generally suggesting that there is an anthropogenic impact at all elevations.

We obtained more insights into the weekly Zugspitze CO_2 cycle by comparing the mean diurnal cycles between weekdays and weekends (see Fig. 5b). Detrended mean diurnal cycles at ZSF, from Sunday to Saturday, were calculated by subtracting the daily averages from the daily data between 2002 and 2016. Morning CO_2 levels at ZSF (i.e., weekday peaks at around 9 - 10 a.m. LT) are higher on weekdays than weekends, while CO_2 levels during the rest of the week are relatively stable. Such weekly cycles are not observable at other Zugspitze sites, or at the WNK and SSL (see Supplementary Fig. S4). At ZPT, there is nearly no diurnal variation, indicating that this site has the closet characteristics to background conditions. The weekday–weekend differences at ZSF are possibly due to local working patterns, whereas the absence of this pattern at lower sites may indicate influences from a more regional reservoir. In fact, this measurement site is closed on the weekends and, thus, influenced by less anthropogenic activities.

3.4. Case study with atmospheric CO, NO, and the number of daily passengers at Zugspitze

To further study the potential sources and sinks for such weekday–weekend differences in the CO_2 diurnal cycles at ZSF, we analyzed atmospheric CO and NO data at ZSF and the daily, combined number of passengers from Zugspitzplatt and the summit of Zugspitze during 2016. Atmospheric CO and NO are known to be good indicators of local anthropogenic influences due to highly variable short-term signals and, thus, are helpful when attempting to identify potential CO_2 sources (Tsutsumi et al., 2006; Sirignano et al., 2010; Wang et al., 2010; Liu et al., 2016). In this study, we used atmospheric NO due to its short lifetime based on rapid atmospheric NO_2 formation with adjacent altitudinal dependent O_3 surplus, indicating the presence of sources at closer distances. The CO and NO data shown in Fig. 6 for the mean weekly cycle include data that was flagged during data processing, because for the delivery to GAW world data centers the logged and recognized work dependent concentration peaks are flagged. A clear weekday–weekend difference is observed for both CO and NO. Only weekdays are characterized by multiple short-term atmospheric CO events and higher atmospheric NO peaks during the daytime (mostly around 9 a.m. LT), which fits perfectly with daytime peaks in CO_2 diurnal cycles. A general increasing and decreasing pattern in NO throughout the week is thought to originate from heating at Zugspitzplatt and work with combustion engines. On the other hand, the daily number of passengers at Zugspitze (see Fig. 6c) shows a clear weekday–weekend pattern, as well as with the higher number of passengers on the weekends. However, increased numbers of passengers on the weekends do not correspond to higher levels of CO and CO_2, indicating that measured CO_2 levels are not significantly influenced by tourist activities at nearby sites. Instead, it is more likely that anthropogenic working activities are the main driver of weekly periodicity.

4. Conclusions

In this study, we presented a time series analysis of a 36-year CO_2 measurement record at Mount Zugspitze in Germany together with a thorough study of the weekly periodicity combined with diurnal cycles. Even though it is challenging to quantify local sources and sinks, this study shows that it is possible to gain information on variation in this regard. Compared with the GAW Regional Observatories at Schauinsland and Wank Peak, as well as the GAW Global Observatory at Mauna Loa, Mount Zugspitze proves to be a highly suitable site for monitoring background levels of air components ~~with~~ using proper data selection procedures. The ~~Long~~long-term trend at Zugspitze agrees well with that at Mauna Loa and global means~~, ,~~ ~~while seasonality~~ The seasonality and short-term variations show similar patterns, but are considerably less influenced by local to regional mechanisms than the lower elevation stations at Schauinsland and Wank Peak. Inter-annual variations also correlate well with anomalous global events. However, several anomalies still exist across most stations that lack clear explanations. These anomalies require further investigation possibly by analyzing correlations between extreme events and historical meteorological or hydrological data. Finally, we ~~observe~~ conclude that, at Zugspitze, we cannot neglect local to regional influences. Regarding ~~Seasonal~~ the seasonal amplitude, ~~at~~ Mount Zugspitze is significantly more influenced by biogenic activity, mostly in the summer~~, at regional sites~~ compared with ~~global sites~~Mauna Loa and global means. On the other hand, weekly periodicity analysis provides a clear picture of local CO_2 sources that potentially result from human working activities, especially at ZSF. Overall, this study provides detailed insights into long-term atmospheric CO_2 measurements, as well as site characteristics at Mount Zugspitze. We propose the application of this type of analysis as a systematic tool for the physical and quantitative classification of stations with respect to their lower free tropospheric representativeness. As an additional component in this analysis, weekly periodicity can be used to analyze anthropogenic influences. The systematic application of this approach to larger continental or global regions can serve as a basis for more quantitative analyses of global greenhouse gases trends such as CO_2. Based on the physical foundation of the methodology presented here, we suggest that these techniques can be applied to other greenhouse gases such as SF_6, CH_4, and aerosols.

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level of expertise and diligence. Former IFU staff members helped us to reconstruct details of the measurements. We would also like to thank the operating team at the Environmental Research Station Schneefernerhaus for supporting our scientific activities and to the Bavarian Ministry for Environment for supporting this High Altitude Research Station. Finally, our gratitude goes to the Bavarian Zugspitze Railway Company for the passenger data in 2016.

Data availability

NOAA global mean: ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_mm_gl.txt.

WDCGG global mean: https://ds.data.jma.go.jp/gmd/wdcgg/pub/global/2017/co2_monthly_20171030.csv.

CO_2 records (also including CO and NO) of all GAW Observatories which were used in this study can be found from the World Data Centre for Greenhouse Gases (WDCGG): https://ds.data.jma.go.jp/gmd/wdcgg/wdcgg.html.

The daily passenger number data for Zugspitze were provided by Bayerische Zugspitzbahn.

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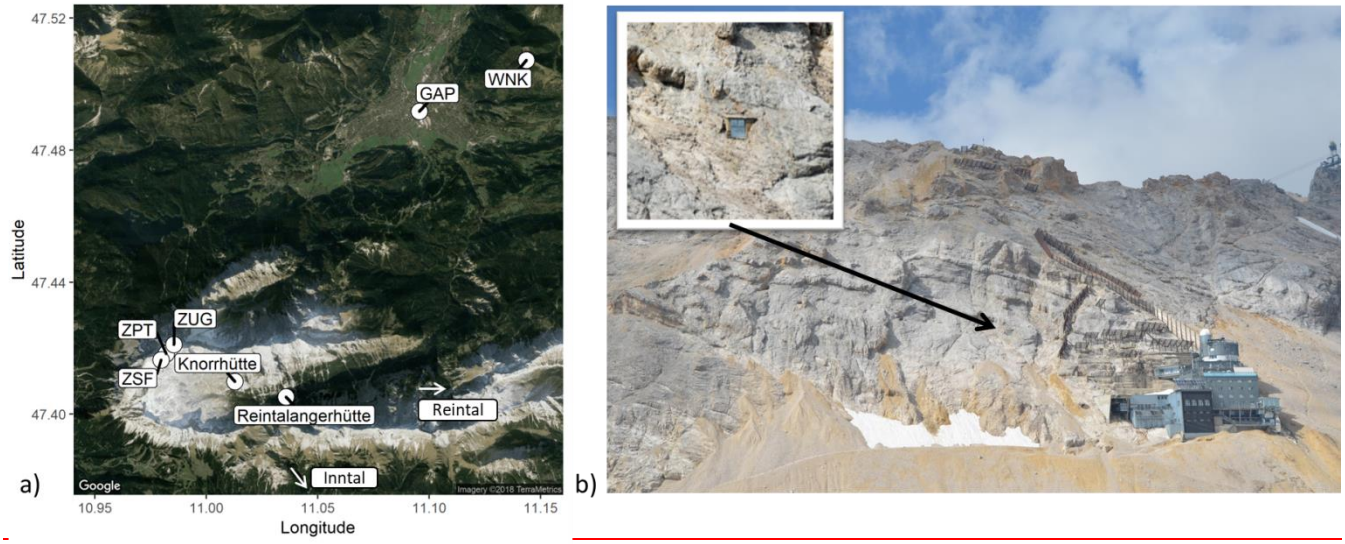
Table 1: Detailed description of atmospheric CO_2 measurements (NDIR = Nondispersive infrared, GC = Gas chromatography, and CRDS = Cavity ring-down spectroscopy).

Site ID	Time period	Instrument (Analytical method)	Scale	Calibration gas
ZPT	1981–1997	1981–1984: Hartmann & Braun URAS 2 (NDIR) 1985–1988: Hartmann & Braun URAS 2T (NDIR) 1989–1997: Hartmann & Braun URAS 3G (NDIR)	WMO X74 scale	CO_2 in N_2
ZUG	1995–2001	Hartmann & Braun URAS 3G (NDIR)	WMO X85 scale	CO_2 in natural air
ZSF	2001–2016	2001–2016: Hewlett Packard Modified HP 6890 Chem. station (GC) 2012–2013: Picarro EnviroSense 3000i (CRDS)	WMO X2007 scale	CO_2 in natural air
WNK	1981–1996	Hartmann & Braun URAS 2T (NDIR)	WMO X74 scale	CO_2 in N_2

Table ~~2~~1: Mean annual CO_2 growth rates in ppm yr^{-1} at the 0.95 confidence interval based on three time blocks for all measurement sites / locations studied (SSL – Schauinsland; WNK – Mount Wank; ZPT – pedestrian tunnel at Mount Zugspitze; ZUG – Zugspitze summit; ZSF – Zugspitze Schneefernerhaus; MLO – Mauna Loa; WDCGG and NOAA – global means). ADVS means the data were selected by ADVS method. This comparison refers to data from all years including the corresponding time period for all stations. Measurement sites or locations where data are not available for calculating the corresponding time blocks are shown as "–". ~~Only data for station Zugspitze from 1995–2001 are partly missing (i.e., 6-month missing data in 1998 and, thus, annual growth rates are not available for 1998 and 1999).~~

~~Time period~~	~~Schauinsland~~	~~Zugspitze~~	~~Mauna Loa~~	~~WDCGG Global~~	~~NOAA Global~~
~~1981–1994~~	~~1.45 ± 0.54~~	~~1.42 ± 0.69~~	~~1.43 ± 0.30~~	~~1.42 ± 0.36~~	~~1.40 ± 0.31~~
~~1995–2001~~	~~1.74 ± 1.11~~	~~1.49 ± 0.58~~	~~1.76 ± 0.51~~	~~1.78 ± 0.42~~	~~1.74 ± 0.45~~
~~2002–2016~~	~~2.23 ± 0.68~~	~~2.18 ± 0.40~~	~~2.19 ± 0.23~~	~~2.15 ± 0.22~~	~~2.16 ± 0.24~~

Time block	SSL	WNK	ZPT	ZPT_ADVS	ZUG	ZUG_ADVS	ZSF	ZSF_ADVS	MLO	MLO_ADVS	WDCGG	NOAA
1981–1994	1.5 ± 0.5	1.4 ± 1.1	1.5 ± 0.8	1.5 ± 1.4	–	–	–	–	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.4	1.4 ± 0.3
1995–2001	1.7 ± 1.1	–	–	–	1.3 ± 0.8	1.5 ± 0.5	–	–	1.8 ± 0.5	1.8 ± 0.5	1.8 ± 0.4	1.7 ± 0.5
2002–2016	2.2 ± 0.7	–	–	–	–	–	2.2 ± 0.4	2.2 ± 0.4	2.2 ± 0.2	2.2 ± 0.2	2.2 ± 0.2	2.2 ± 0.2



~~Figure 1: (a) Satellite map from Google and TerraMetrics (Kahle and Wickham, 2013) showing the study area and (b) a photograph showing the locations of the Mount Zugspitze sites in the Garmisch-Partenkirchen region (GAP) where atmospheric CO_2 measurements were taken. Zoomed photograph with the arrow shows the balcony for the measurement site ZPT.~~

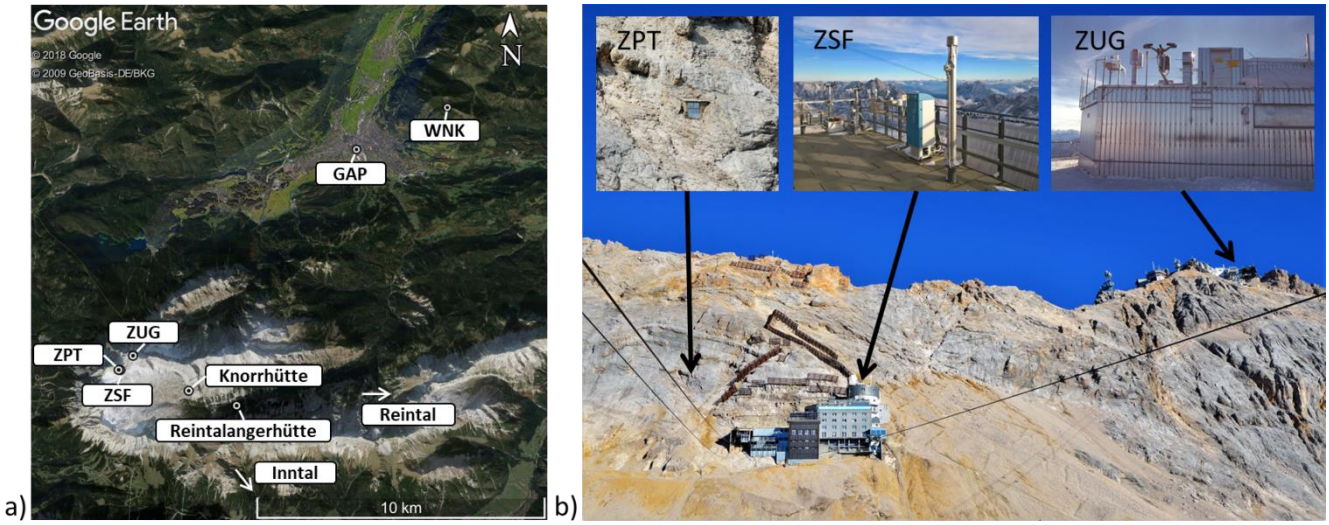
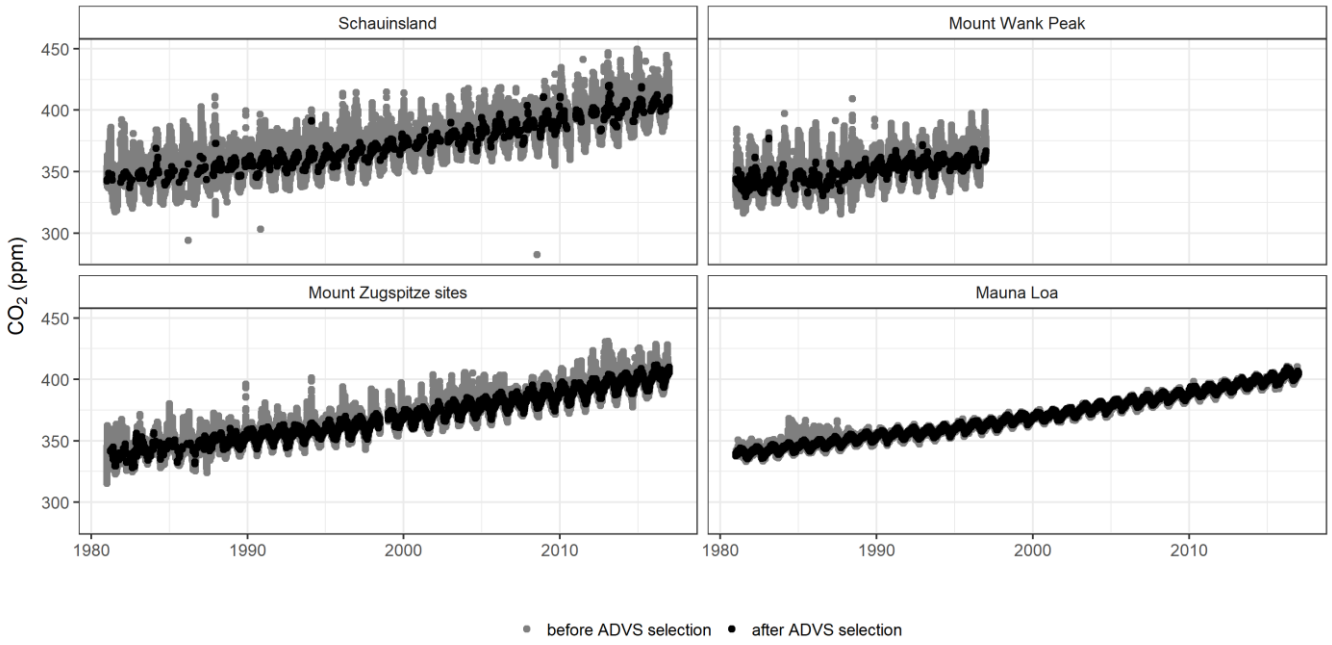


Figure 1: (a) Map showing the study area (GAP – Garmisch-Partenkirchen; WNK – Mount Wank; ZPT – pedestrian tunnel at Mount Zugspitze; ZUG – Zugspitze summit; ZSF – Zugspitze Schneefernerhaus). (b) A photograph showing the locations (ZPT, ZSF, and ZUG) at Mount Zugspitze where atmospheric CO_2 measurements were performed.



~~Figure 2: Time series plot of 30 min averaged CO_2 concentrations measured at the Wank and Zugspitze sites, and hourly averaged CO_2 concentrations measured at Schauinsland and Mauna Loa between 1981 and 2016 with ADVS-selected results.~~

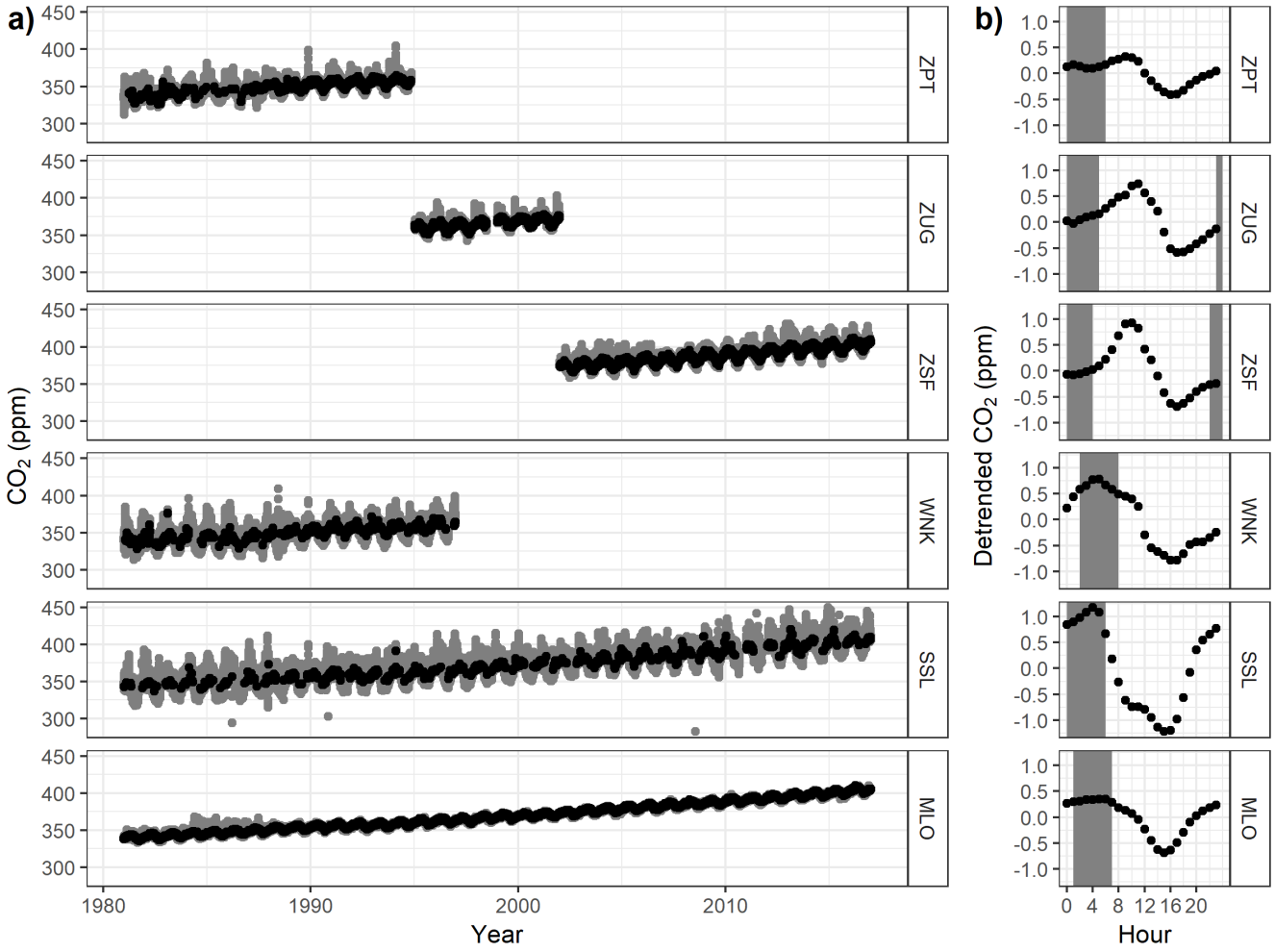


Figure 2: a) Time series plot of 30-min averaged CO_2 concentrations measured at Mount Zugspitze (ZPT, ZUG, and ZSF) and Wank (WNK), and hourly averaged CO_2 concentrations measured at Schauinsland (SSL) and Mauna Loa (MLO) with ADVS-selected results. b) Detrended mean diurnal cycles with starting time windows (in grey) for ADVS data selection.

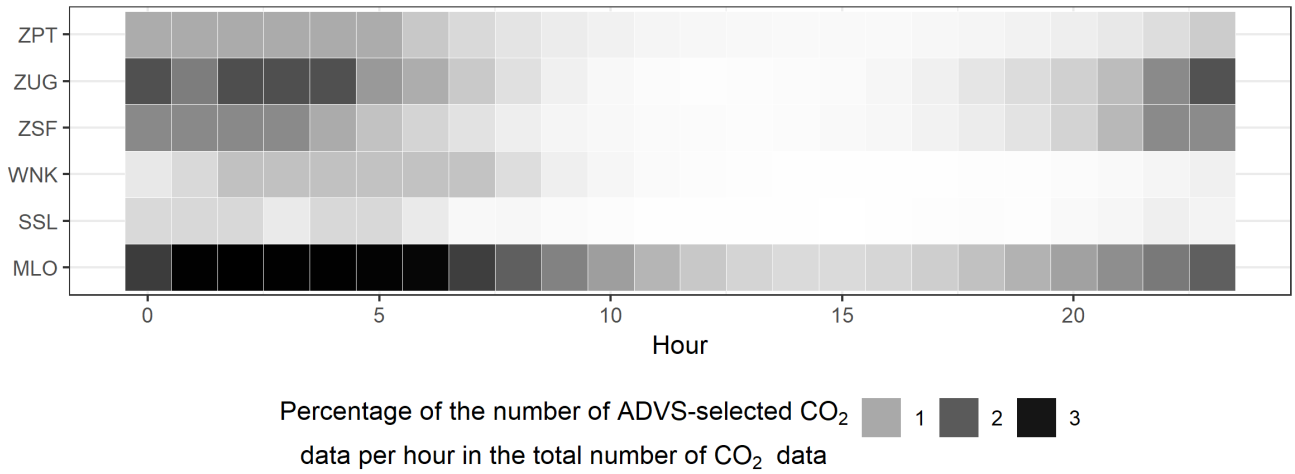


Figure 3: Frequency of the percentages of the number of ADVS-selected CO_2 data for each hour (0 to 23) in the total number of CO_2 data. In the shown greyscale grey means 1%, 2% and black means 3% of the data.

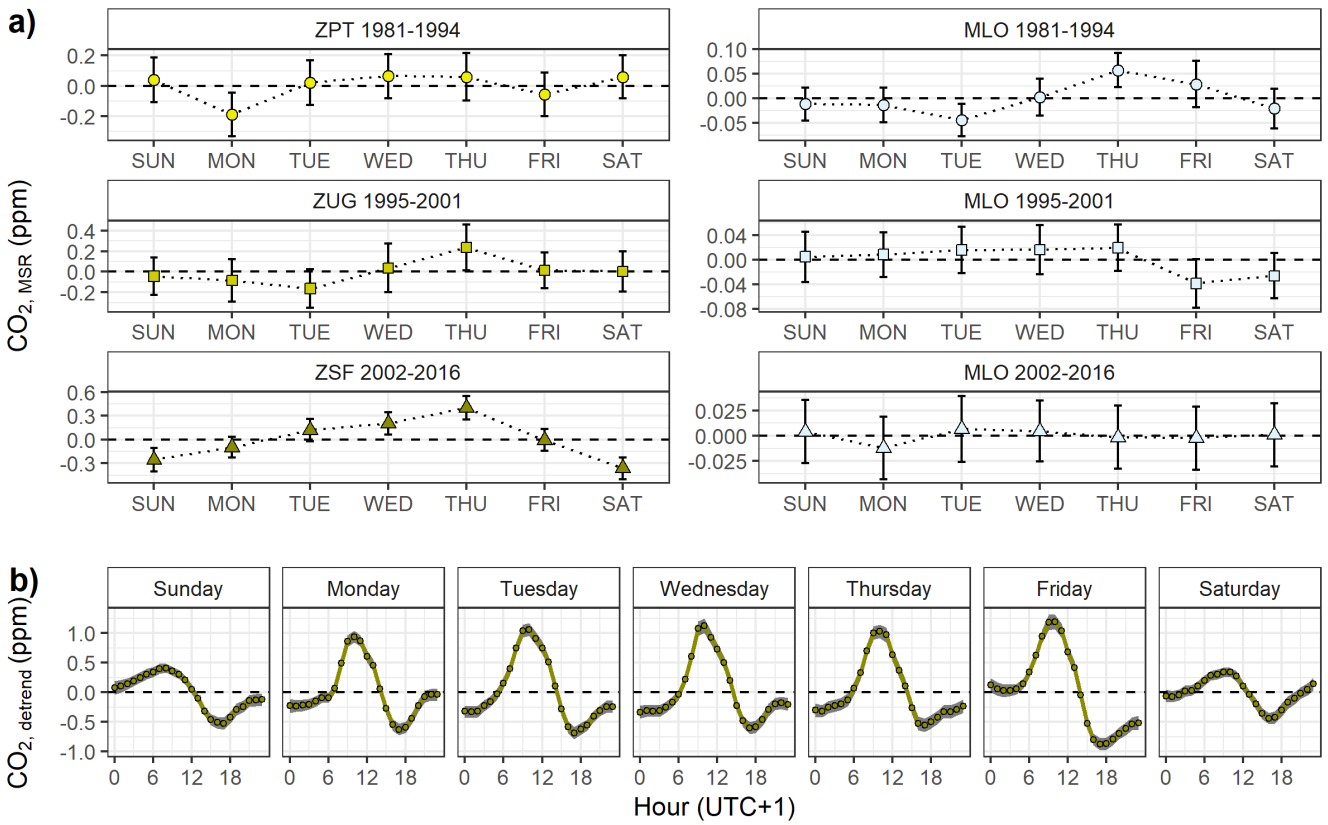


Figure 4: a) Mean MSR CO_2 values at Mount Zugspitze and MLO as a function of the weekday. Mean MSR values are adjusted such that they sum to 0. b) Detrended mean CO_2 diurnal cycles at ZSF by weekday from 2002 to 2016. Uncertainties at a 95% confidence interval are shown by the shaded areas.

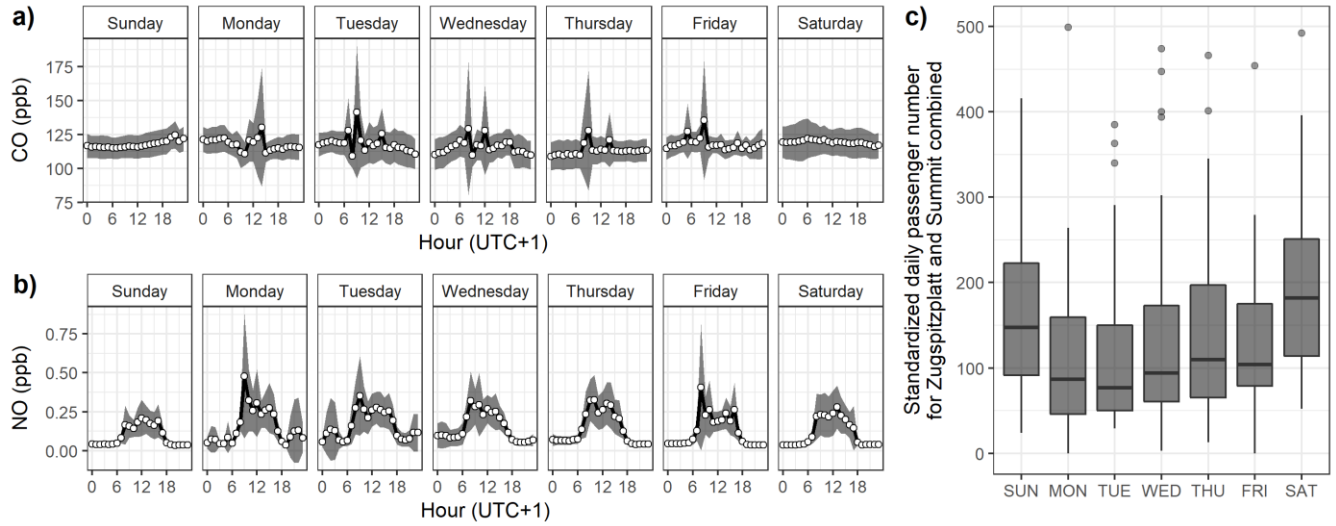
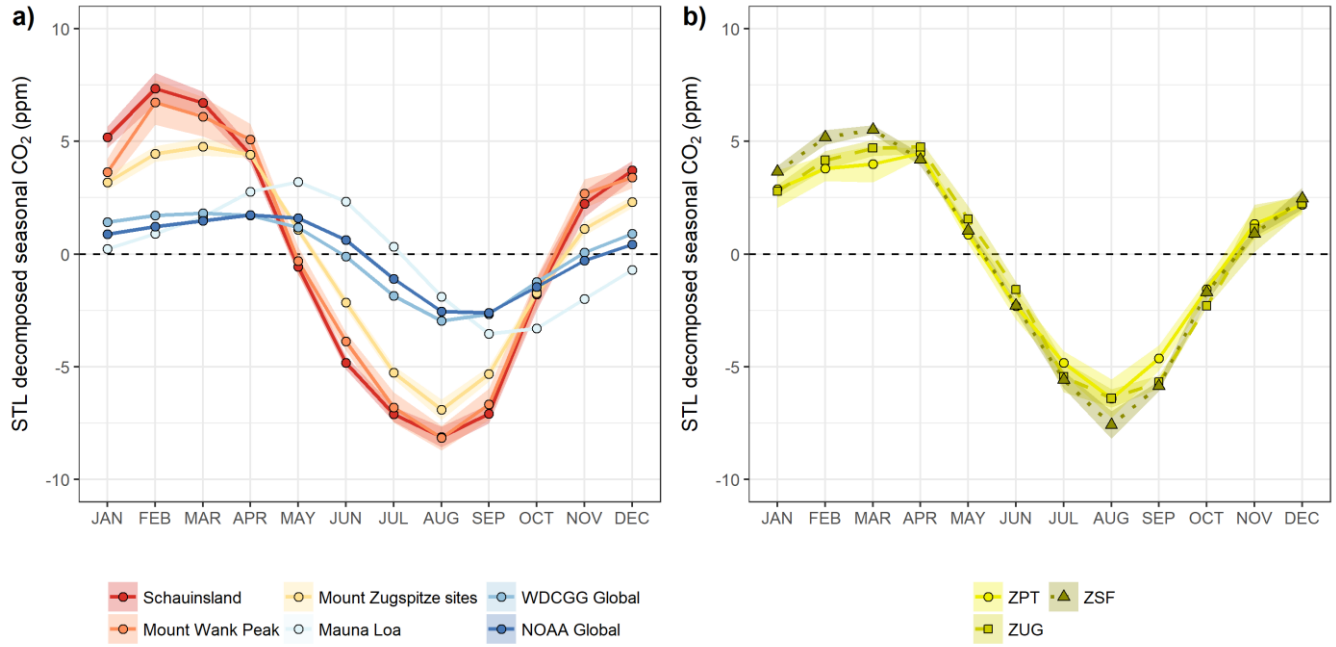


Figure 5: Mean diurnal plots at ZSF during 2016 by weekday for a) CO, b) NO, and c) the standardized daily passenger number at the Zugspitzplatt and Zugspitze summit combined.



~~**Figure 3: a) Mean CO_2 seasonal cycles from 1981 to 2016 (aside from WNK, which exists between 1981 and 1996). Uncertainties at a 95% confidence interval are shown by the shaded areas. b) Mean CO_2 seasonal cycles at ZPT (1981–1994), ZUG (1995–2001), and ZSF (2002–2016).**~~

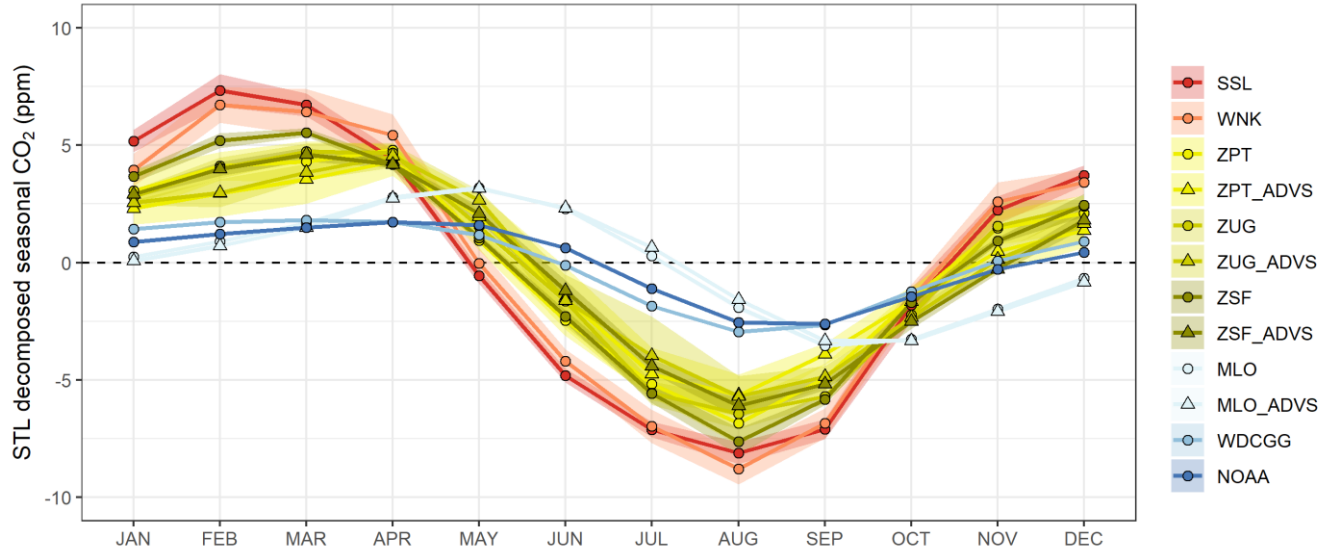
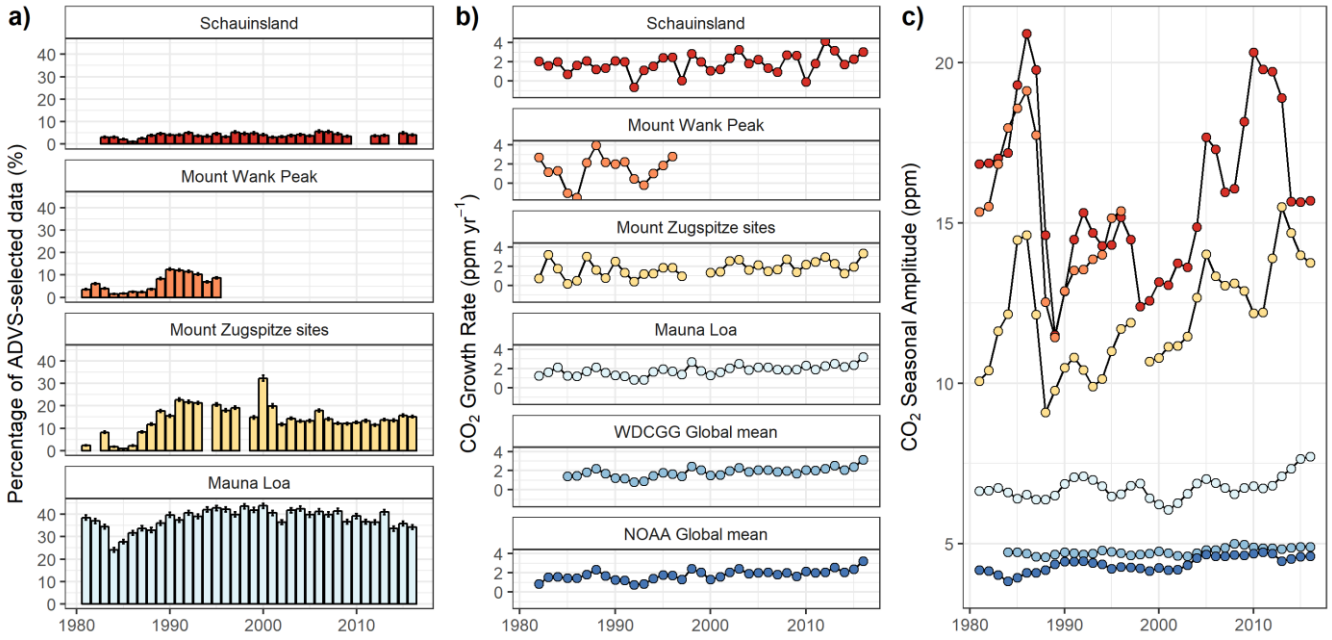


Figure 6: Mean CO_2 seasonal cycles from the STL seasonal component at each measurement site or location. Uncertainties at a 95% confidence interval are shown by the shaded areas with corresponding color.



~~**Figure 4: a) Annual ADVS selected percentages. b) Annual CO_2 growth rates for all sites and global means from the NOAA and the WDCGG. The calculated growth rates are shown at the beginning of the year. Since the time period starts in 1981, the values of growth rates start in 1982. WDCGG data is only available starting 1984. c) Annual CO_2 seasonal amplitudes.**~~

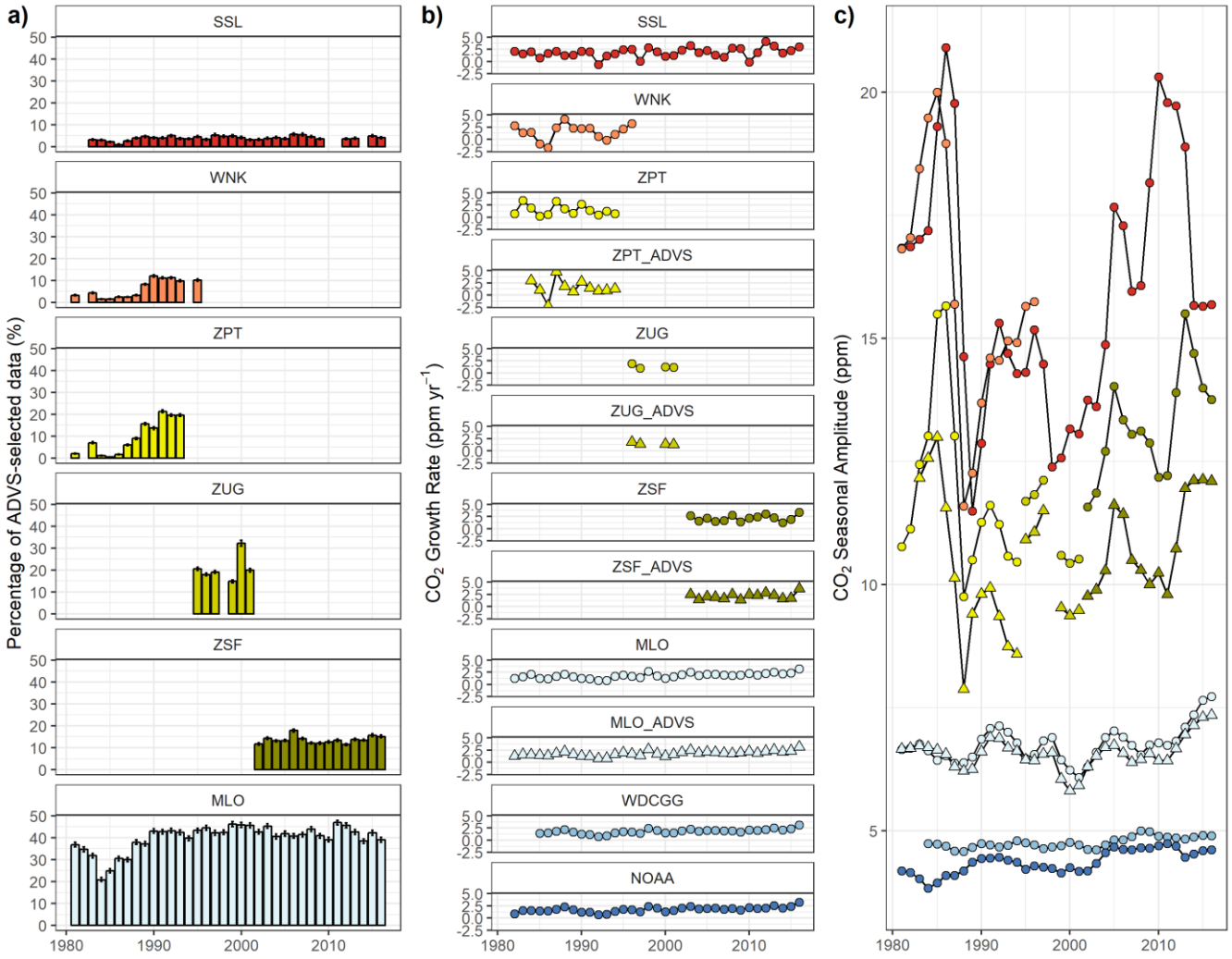
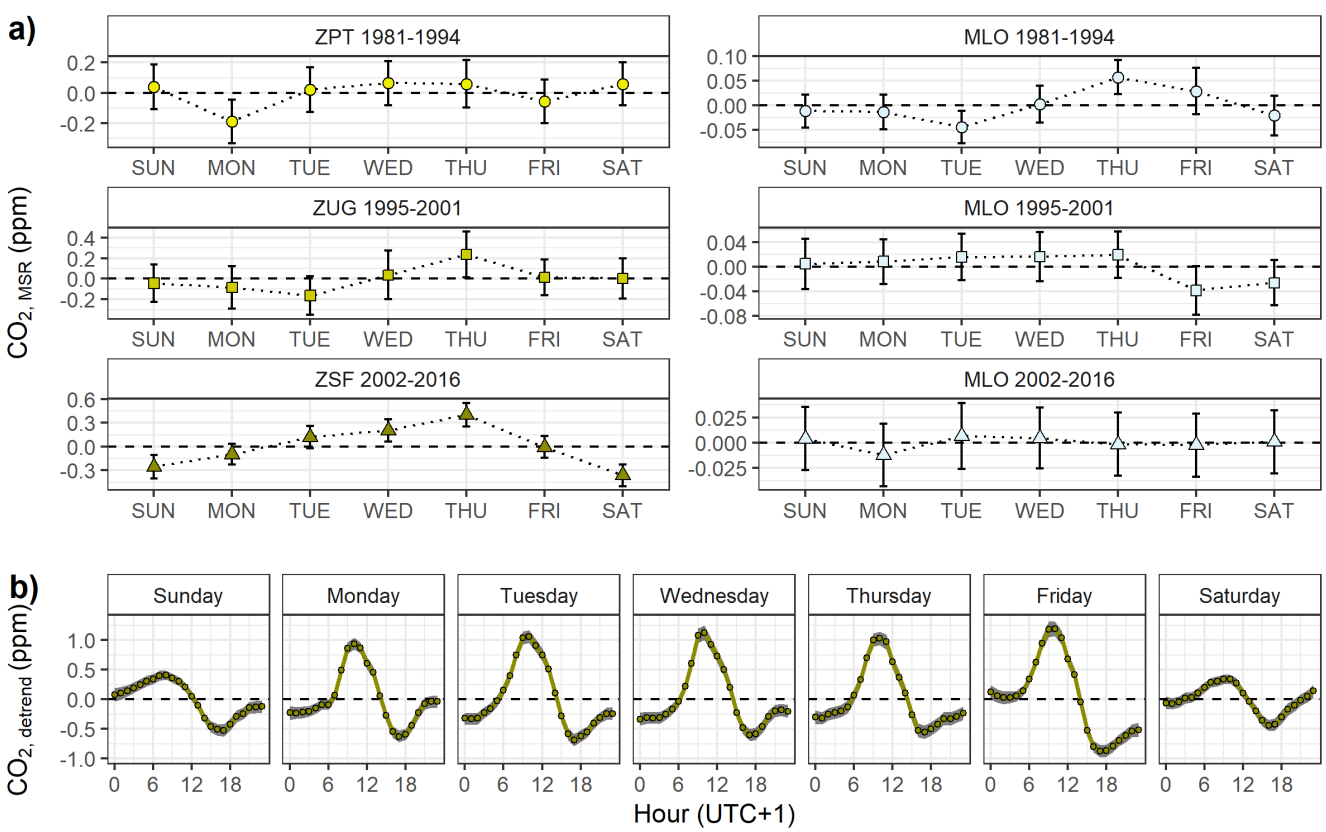
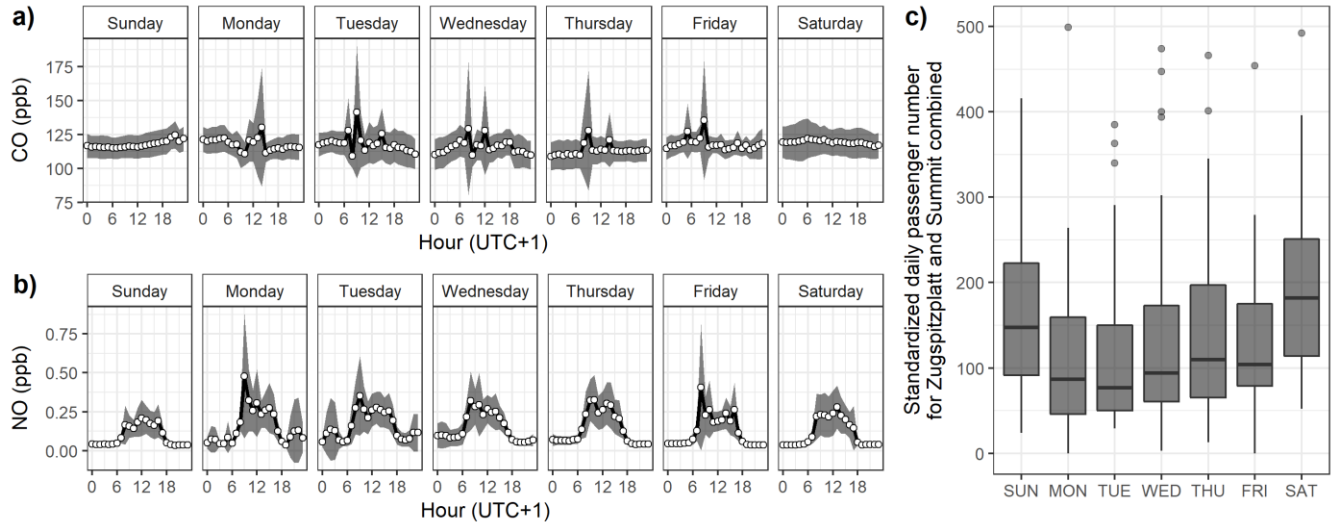


Figure 7: a) Annual ADVS-selected percentages. b) Annual CO_2 growth rates and global means from the NOAA and the WDCGG. The calculated growth rates are shown at the beginning of the year. Since the time period starts in 1981, the values of growth rates start in 1982. WDCGG data is only available starting 1984. c) Annual CO_2 seasonal amplitudes.



~~**Figure 5: a) Mean MSR CO_2 values at the Mount Zugspitze sites and MLO as a function of the week day. Mean MSR values are adjusted such that they sum to 0 at each site. b) Detrended mean CO_2 diurnal cycles at ZSF by week day from 2002 to 2016. Uncertainties at a 95% confidence interval are shown by the shaded areas.**~~



~~**Figure 6: Mean diurnal plots at ZSF during 2016 by week day for a) CO, b) NO, and c) the standardized daily passenger number at the Zugspitzplatt and Zugspitze summit combined.**~~