

# ***Author comments on “On the diurnal, weekly, seasonal cycles and annual trends in atmospheric CO<sub>2</sub> at Mount Zugspitze, Germany during 1981–2016” by Ye Yuan et al.***

Ye Yuan on behalf of all co-authors

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

The referee comments are shown in black. [The answers are shown in blue.](#)

General Comments

10 This paper outlines a set of CO<sub>2</sub> 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

15 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.](#)

20

Specific Comments

Abstract

Examining weekend-weekday variability in order to comment on which fluxes are driving CO<sub>2</sub> signals is a powerful tool.

25 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 CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 closely CO<sub>2</sub> 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?

10 **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<sup>th</sup> 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 CO<sub>2</sub> is usually a more linear approach than many other CO<sub>2</sub> 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.)

5 “...The CO<sub>2</sub> 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<sub>2</sub> in N<sub>2</sub>) were used for calibration every day at different hours. The CO<sub>2</sub> 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...”

10 “...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<sub>2</sub> concentrations was taken at every 25<sup>th</sup> 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...”

15 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<sub>2</sub> concentrations of the working standard as precisely as possible. The target was provided by the University of Heidelberg and had a slightly higher CO<sub>2</sub> 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<sub>2</sub> is via a CH<sub>4</sub> equivalent by the use of FID. In the GC, the collected CO<sub>2</sub> is converted to CH<sub>4</sub> on a nickel catalyzer at a temperature of 400°C at the presence of hydrogen gas. The measurement of CH<sub>4</sub> with FID is known as linear and in this case no problems with non-linearity will occur.

### 2.3 Offset adjustment

30 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 CO<sub>2</sub> in N<sub>2</sub> 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:

5 “...However, for the three-year parallel CO<sub>2</sub> measurements at ZPT and ZUG (1995–1997), clear offsets of  $-5.8 \pm 0.4$  ppm (CO<sub>2, ZPT</sub> minus CO<sub>2, ZUG</sub>,  $1 \cdot SD$ ) 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<sub>2</sub>/N<sub>2</sub> vs. CO<sub>2</sub>/air, the so called “carrier gas correction (CGC)” (Bischof, 1975; Pearman and Garratt, 1975). It is known from previous studies that the measured CO<sub>2</sub> concentration, when using CO<sub>2</sub>/N<sub>2</sub> mixtures as reference, is usually underestimated by several ppms for the  
10 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<sub>2</sub> 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  
15 correction factor

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

was applied to the ZPT data while  $C_{ZPT}$  denotes the CO<sub>2</sub> concentrations at ZPT. Because of the same calibration mixtures, an additional adjustment was applied to the CO<sub>2</sub> concentrations at WNK by calculating the CO<sub>2</sub> 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  
20 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<sub>2</sub> measurements at ZPT and ZUG (1995–1997) we obtain an offset of –  
25  $5.8 \pm 0.4$  ppm (CO<sub>2, ZPT</sub> minus CO<sub>2, ZUG</sub>,  $1 \cdot SD$ ). 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<sub>2</sub>/N<sub>2</sub> mixtures vs. CO<sub>2</sub>/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<sub>2</sub>/N<sub>2</sub> for ZPT and CO<sub>2</sub>/natural air for ZUG). Experiments implied that the CO<sub>2</sub> concentration in air when using CO<sub>2</sub>/N<sub>2</sub> mixtures as references is usually underestimated by several ppms for the URAS instruments. On the other hand, the measurement of CO<sub>2</sub> concentration in air is not affected if CO<sub>2</sub>/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<sub>2</sub> 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 <sub>2</sub> in N <sub>2</sub>
ZUG	1995–2001	Hartmann & Braun URAS 3G (NDIR)	WMO X85 scale	CO <sub>2</sub> 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 <sub>2</sub> in natural air
WNK	1981–1996	Hartmann & Braun URAS 2T (NDIR)	WMO X74 scale	CO <sub>2</sub> in N <sub>2</sub>

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<sub>2</sub> 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<sub>2</sub> concentration (Griffith, 1982; Manning and Pohl, 1986a). Carrier gas effects were determined experimentally by comparing analyser values (apparent CO<sub>2</sub> concentration  $C_a$ ) with true (mano-metrically determined) CO<sub>2</sub> concentration (true CO<sub>2</sub> concentration  $C_t$ ). Two terms were used here as the carrier gas shift ( $\Delta$ ) and the correction factor ( $G$ ).

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

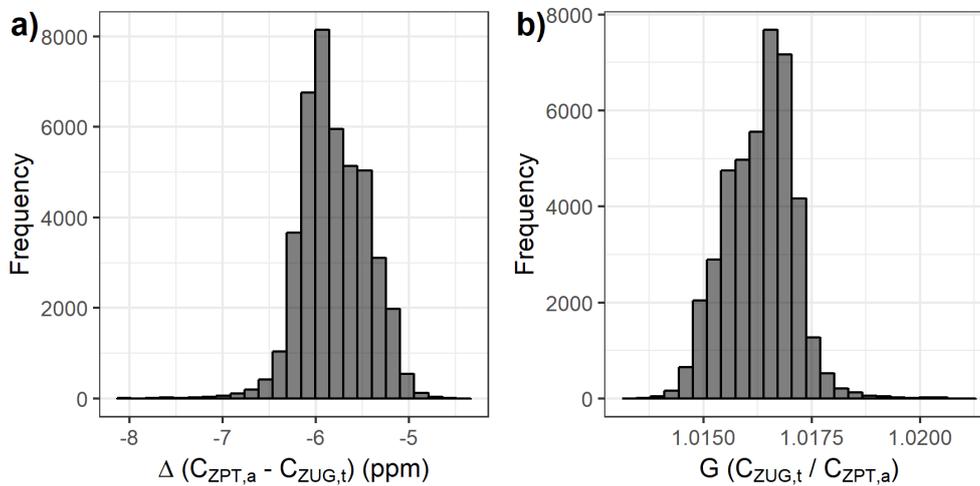
$$G = C_t / C_a \quad (2)$$

In our case, given that CO<sub>2</sub> 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<sub>2</sub> measurements at ZUG to be the true value ( $C_{ZUG,t}$ ) and the CO<sub>2</sub> 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 ( $\Delta$ ) between CO<sub>2</sub> measurements at ZPT and ZUG for the period of 1995–1997. b) Histogram of the correction factor ( $G$ ) between CO<sub>2</sub> 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  $\text{CO}_2$  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  $\pm 0.08$  ppm. Within the interval from 340 ppm to 370 ppm of atmospheric  $\text{CO}_2$  concentrations, the same calculation applied shows an error range in the adjusted values from  $\pm 0.06$  to  $\pm 0.09$  ppm.

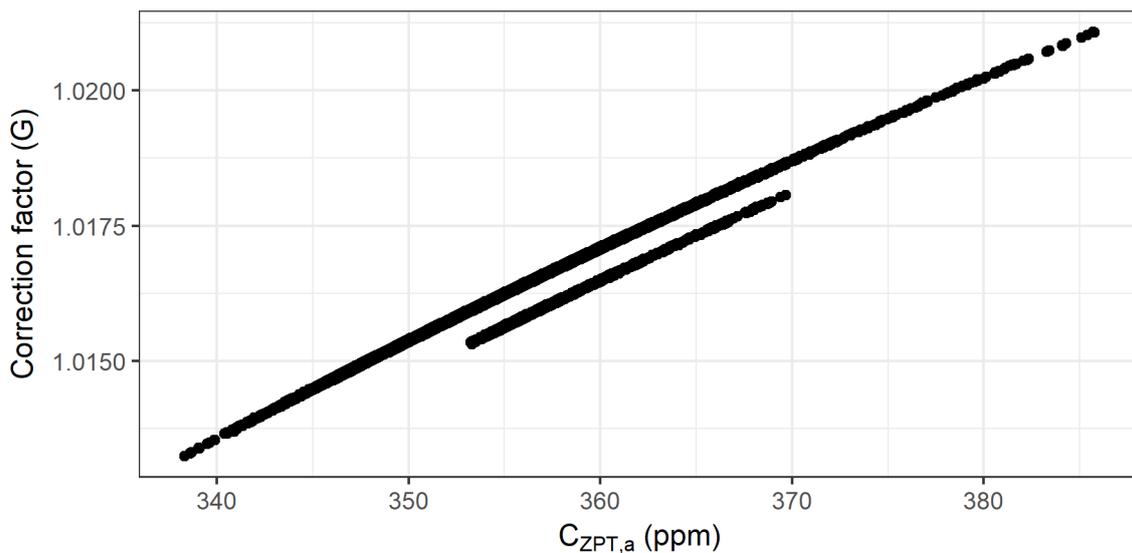
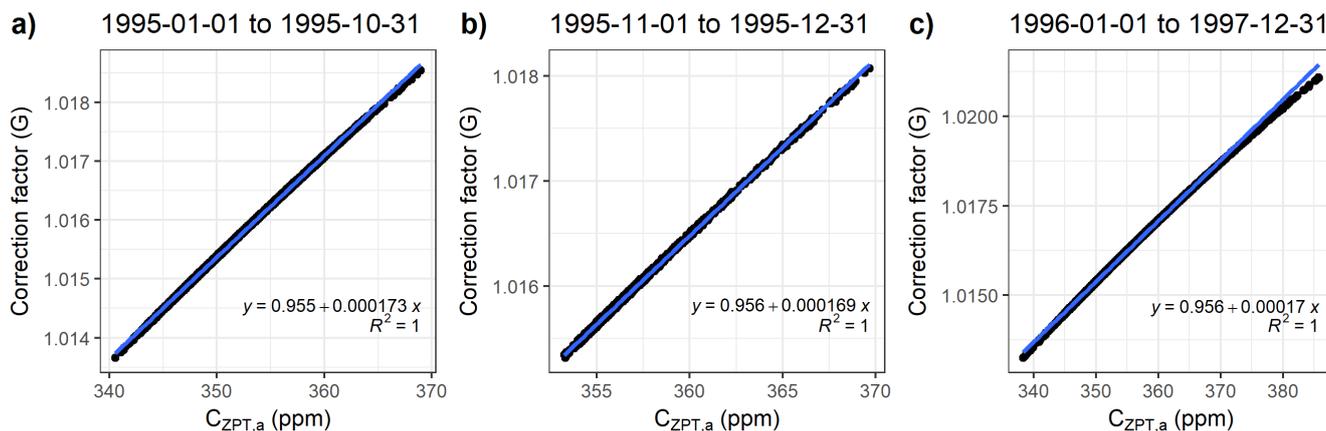


Figure S3: Computed correction factor  $G$  against  $\text{CO}_2$  concentrations at ZPT from 1995 to 1997.



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

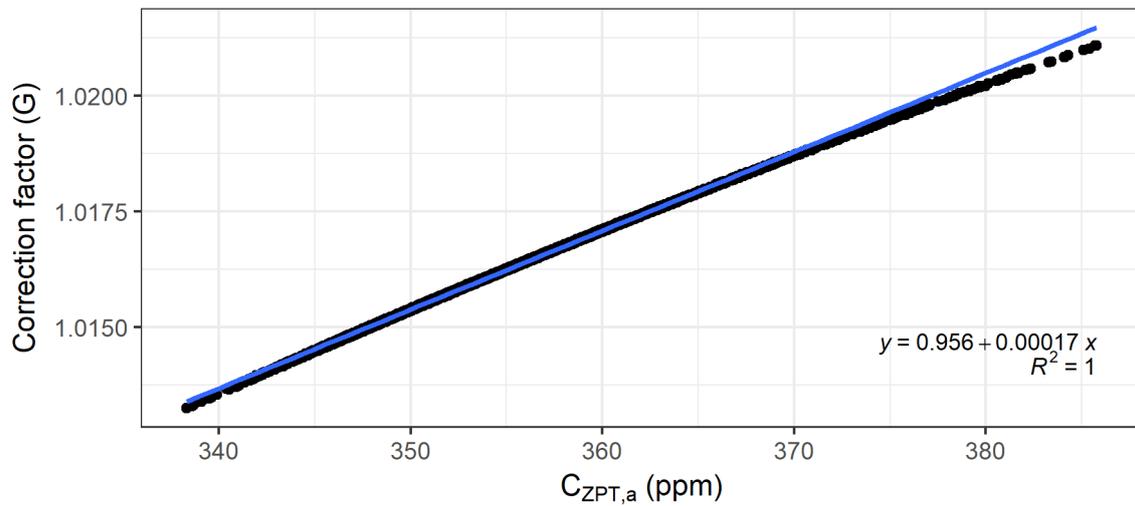
Therefore, for the shifted time block (1995-11-01 to 1995-12-31), we used the correction factors by the linear regression function in Fig. S4b. Since the rest of the time blocks showed nearly identical results, we combined the data together and made a new linear regression. Based on this regression function, we made the following offset adjustment for all the remaining  $\text{CO}_2$  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  $\text{CO}_2$  concentrations at ZPT can be expressed as

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

1995-01-01 to 1995-10-31 and 1996-01-01 to 1997-12-31



**Figure S5: Computed correction factor  $G$  against  $\text{CO}_2$  concentrations at ZPT from two separate time blocks, used for offset adjustment on the  $\text{CO}_2$  data set at ZPT.**

- 10 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 ( $\text{CO}_2$  minimum and maximum at ZPT for this period), which agrees well with Griffith et al. (1982) as
- 15 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<sub>2</sub> data at WNK based on the adjusted CO<sub>2</sub> data at ZPT because the same CO<sub>2</sub>/N<sub>2</sub> mixtures were used for calibration (see Table S1). The time period of CO<sub>2</sub> measurements at WNK used in this study is 1981–1996, which is completely covered by CO<sub>2</sub> measurements at ZPT. We assume that the differences in CO<sub>2</sub> 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<sub>2</sub> concentrations at WNK can be expressed as

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

Finally the offset adjustment at WNK was done by calculating the differences in CO<sub>2</sub> concentrations between WNK and ZPT raw data and then adding it to the adjusted CO<sub>2</sub> concentrations at ZPT to compute the adjusted CO<sub>2</sub> 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:  $\pm 0.2$  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

10 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.

15 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.

20 “...The peak-to-trough difference of the mean CO<sub>2</sub> seasonal cycle is  $12.4 \pm 0.6$  ppm at Mount Zugspitze (after data selection:  $10.5 \pm 0.5$  ppm), which is much lower than at nearby measurement sites at Mount Wank ( $15.9 \pm 1.5$  ppm) and Schauinsland ( $15.9 \pm 1.0$  ppm), but following a similar seasonal pattern...”

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

**Authors:** We have rephrased it as following,

25 “...For a comprehensive site characterization of Mount Zugspitze, analyses of CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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...”

5 **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.

10 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.

15 2/33 Confusing “Weekly CO<sub>2</sub> 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<sub>2</sub> periodicities and diurnal cycles were evaluated for Mount Zugspitze...”

20 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.

25 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, 4725âAˆ ˆ N, 1059âAˆ ˆ 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, 4725âAˆ ˆ N, 1059âAˆ ˆ 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 X m below the summit (ZPT, 4725â° N, 1059â° 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, 4725â° N, 1059â° E, 2960 m a.s.l.) using a URAS-3G device.”

**Authors:** Done.

- 5 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.

10

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.

15

“...Measurements of CO<sub>2</sub> 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<sub>2</sub> 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 ...”

- 20 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?

25

**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<sub>2</sub> concentrations was performed. For continuous quality assurance the GC was checked daily for flows, retention times, gas pressures, and the structure of chromatograms.

30

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 CO<sub>2</sub> 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<sub>2</sub> for 2012 and 2013 due to the instrumental failure of GC.

10 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.

15 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 combining the comment from Anonymous Referee #1, using “composite”.

“...In this study, we took CO<sub>2</sub> 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...”

20 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.

25 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<sup>-1</sup>”. 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 SSI, 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<sub>2</sub> 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  
5 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.

10 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 CO<sub>2</sub> 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 CO<sub>2</sub> concentrations, enhancing the August minimum.”

15 **Authors:** Done.

7/17 Please change “The MLO is” to “Mauna Loa data are” or “The Mauna Loa CO<sub>2</sub> record is”

**Authors:** Done.

7/18 Please change “which agree” to “which agrees”

**Authors:** Done.

20 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.

25 **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<sub>2</sub> 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 CO<sub>2</sub> at ZSF from January to March and lower levels from July to September cannot be neglected.” To “However, significantly higher levels of CO<sub>2</sub> are evident at ZSF from January to March and lower levels from July to September.”

**Authors:** Done.

5 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  
10 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.

15 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,

20 “...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.

25 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.](#)