Atmospheric Measurement Techniques Discussions

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Reply on RC2

Antje Hoheisel et al.

Author comment on "Comparison of atmospheric CO, CO2 and CH4 measurements at Schneefernerhaus and the mountain ridge at Zugspitze" by Antje Hoheisel et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-298-AC2, 2023

General Comments:

- [Referee #2] As a general comment, I would recommend the authors to provide specific recommendations to the user of the ZSF dataset. As an instance, can potential user (still) use the daytime data from 2002 to 2014 in front of the possible impact of a potential leak in the sampling system? Can you provide recommendation for the fitness of this dataset for specific purposes (e.g. trend calculation, use in inversion modeling, model validation, etc etc)? Similar recommendation should be mirrored in distribution databases like the WDCGG.
  As concerning the ZSF dataset in the WDCGG, it is not completely clear to me if the data available by the WDCGG are the ZSF QC or the ZSF with local pollution (with suitable flags). A clarification to potential users can be really useful.
  [Hoheisel et al.] Thank you for pointing this out. We agree that this is important. However, in our study we focus on the comparison between the ambient air measurements from Schneefernerhaus and from the mountain ridge. In this comparison, no difference was found between weekends and weekdays in terms of diurnal cycles or mean values for the individual days of the week. As these findings do not agree with the results of Yuan et al. (2019), we analysed the CO_2 time series between 2002 and 2021 with regard to these two effects. We can show that the differences between weekend and weekday no longer occur since 2015 and thus also during our comparison measurement. A more detailed analysis of the long-term CO_2 time series between 2002 and 2021 with regard to trend, annual variation and the use of the data for inversion experiments or model validation was not carried out in this comparison study of the two sampling locations. However, in the next update of the data in the WDCGG it is planned to point out the differences between weekdays and weekends and to recommend interpreting the daily values with caution.
  Regarding the last comment, we have added the following sentence to section 2.4 Data flagging and correction for clarification:
  "The half-hourly, hourly, daily and monthly averages of CO, CO_2 and CH_4 mole fractions at Schneefernerhaus reported to national and international databases such as the World Data Centre for Greenhouse Gases (WDCGG) are also based on one-minute averaged data where local pollution events have been flagged as invalid in addition to artefacts and outliers."

Detailed Comments and Questions:

ABSTRACT:

- [Referee #2] Line 2: please provide the geographical location of Zugspitze
  [Hoheisel et al.] We now have included the geographical location:
  "The CO, CO_2 and CH_4 mole fractions have been measured since 2002 at the Environmental Research Station Schneefernerhaus, which is located approximately 300m below the summit of Mount Zugspitze in the German Alps."
- [Referee #2] Line 11: please, be more specific: what anthropogenic sources?
  [Hoheisel et al.] We understand the referee's comment. However, in contrast to the CO, CO_2 and CH_4 peaks where the sources are identifiable, in the case of the CO_2 difference in the mean diurnal cycles between Schneefernerhaus and mountain ridge in winter, the exact cause cannot be determined with absolute certainty. The different theories are explained in more detail in the sections 3.5 and 3.6 and involve local or regional anthropogenic sources. In the abstract, we have therefore decided to refer only generally to anthropogenic sources to keep it short.

INTRODUCTION

- [Referee #2] Line 17-18: please provide references for the cited stations. Among the continental mountain site also Mt. Cimone (active since 1979 can be cited).
  [Hoheisel et al.] We included the references for the cited stations and Mount Cimone. In addition, we included the countries to the station's name as suggested by Referee#1. We changed the sentence to:
  "Historically, most measurement stations are located on coasts, such as Mace Head, Ireland (Bousquet et al.,1996), island mountains, such as Mauna Loa, Hawaii (Keeling et al., 1976) or Izana, Spain (Navascues and Rus, 1991; Gomez-Pelaez et al., 2019) or continental mountains, such as Mount Cimone, Italy (Ciattaglia, 1983), Jungfraujoch, Switzerland (Sturm et al., 2005; Schibig et al., 2016) or Schauinsland, Germany (Schmidt et al., 2003)."
- [Referee #2] Line 28: please specify GAW acronym
  [Hoheisel et al.] Yes, we changed it to "Global Atmosphere Watch (GAW) program".

EXPERIMENTAL SET-UP

- [Referee #2] Please, can you provide more description about the management of the calibration and target gas injections? Looking to the setup reported in figure A1, it seems that they are simultaneously sampled by all the three instruments. Is it correct? Did you intercompare the instrument when simultaneously sampling ambient air from the ZSF inlet?
  [Hoheisel et al.] Yes, it is correct, that the calibration and target gases are simultaneously sampled by all three analysers. The working standards and the target are measured every three days for 15 minutes and the WMO reference gases of NOAA every two months for 30 minutes. A more detailed description of the usage of calibration and target gases is given in section 2.3 Calibration and quality control. To improve the reading flow, we have now noted this in the text in section 2.2. Experimental setup:
  "In addition to the ambient air of Schneefernerhaus or the mountain ridge, the analysers simultaneously measure the same calibration and target gases for quality control (see Sect. 2.3 for further details)."
  We also compared the CO, CO_2 und CH_4 mole fractions in ambient air from the Schneefernerhaus inlet measured simultaneously with all analysers for 15 days in July 2020. The average difference between the hourly averaged CO, CO_2 and CH_4 mole fractions measured with the CRDS G2301&OA-ICOS EP30 and CRDS G2401 are -0.04±0.58 ppb (mean±sd) in CO, 0.04±0.02 ppm in CO_2 and 0.3±0.2 ppb in CH_4. We included this comparison in the manuscript in section 2.3 Calibration and quality control, too.

- [Referee #2] How the air inlet at ZGR is designed? Is it equipped with heater, rainguard, filters?
  [Hoheisel et al.] The air inlet at ZGR is not heated, has no filter but is protected from rain. We included: *"The air inlet at the mountain ridge is protected from rain, but not heated."*
- [Referee #2] Line 94: specify the inner diameter, I think it is more important than the o.d.
  [Hoheisel et al.] We agree that it would be helpful to specify the inner diameter. As soon as we get the value, we will change this if still possible.
- [Referee #2] Line 95: "a part of the air flow is dried using the same drying system as the ..", Why only "a part"? I cannot see an overflow before the cold trap (figure A1).
  [Hoheisel et al.] Figure A1 shows the setup only schematically, but it shows that the inlet line is purged by a pump. A small part of the air is taken from the main inlet line via a T-piece and purged via the cold trap.
- [Referee #2] Line 98: if the residence time is 6':40", why was the data shifted by 6 minutes and not 7 minutes? Do you monitor the flow stability over the time?
  [Hoheisel et al.] The residence time from the intake at Schneefernerhaus to the analyser is 35s and from the mountain ridge 6min and 40s. Therefore, we shifted the minutely averaged mountain ridge data by 6 minutes, to compare them with the Schneefernerhaus data. The air flow through the long intake line up to the mountain ridge is not monitored.
- [Referee #2] Line 101 – 104. All this section need a more robust explanation and discussion. How did you assess the offset of 5.2 ppb (which is rather large, indeed)? Did you perform an instrument characterization for the impact of the water vapor influence (e.g. https://doi.org/10.5194/amt-5-2555-2012)? The impact of the not efficient water vapor correction must change as a function of the water vapor levels. Why did you not apply a correction function based on the actual water vapor value? How the overall measurement uncertainty was affected by using this fix offset? The same points are valid for the offsets related with the pump within the flow path. Which was the reason of the artifacts by the 2 pumps? Did you note any impact on CO2 and CH4? All these points should be clarified in the text.
  [Hoheisel et al.] We appreciate the recommendation and include a more detailed description of the corrections in section 2.3 Calibration, correction and quality control. If the pump is installed in the direct flow path, the membrane used in the pump causes the CO mole fraction to increase.

CALIBRATION

- [Referee #2] In general, how often the NOAA calibration gases have been reassigned? How stable were the target gas measurements? Are you able to provide a quantification of the uncertainty based on the target gas results? Please, provide a better description of the calibration strategy (how many cycles, injection duration …). Providing this information will represent a valuable source of info for interested readers.
  [Hoheisel et al.] We appreciate the recommendation. The same four NOAA calibration gases were used for the duration of the two-year comparison measurement. They are measured every two months for 30 minutes each (one cycle). We have also added more details in the paragraph on target gas measurement:
  "In addition to calibration cylinders, a target cylinder is simultaneously measured every three days by all analysers for quality control. The calibrated target measurements of CO, CO_2 and CH_4 were stable over time and there is no significant mean difference between the G2301/EP30 and G2401 analyses for all three species. Table 1 shows the average and standard deviation of the CO, CO_2 and CH_4 mole fractions for the two-year comparison for each analyser and their difference."

RESULTS AND DISCUSSION

- [Referee #2] Line 166: I would expect that very local pollution events like those related with the use of snowblower were traced better by NO peaks (rather than NO2). Can you comment on this?
  [Hoheisel et al.] At Schneefernerhaus, the UBA measures NO and NO_2 in the ambient air. In both time series, the use of snow blowers or snow groomers is clearly visible in the form of measurement spikes and an increasing trend during the day.
- [Referee #2] Line 172: which kind of specific tests have been performed? Are you able to completely rule out the possibility of icing on the sampling inlet affecting the sampling efficiency? Please, explain more.
  [Hoheisel et al.] We are glad to provide you with further details on the tests carried out. To exclude the possibility that these inverse spikes are caused by the analyser or the setup, two tests were carried out. First, during an event in which inverse spikes are measured at Schneefernerhaus, the two analysers G2301 and G2401 are exchanged. Thus, analyser G2301 first measures the ambient air of the Schneefernerhaus and later that of the mountain ridge. Analyser G2401 first measures the ambient air of the mountain ridge and later that of the Schneefernerhaus. In all measurements at the Schneefernerhaus, inverse spikes occur for both analysers, while in the measurements at the mountain ridge, no spikes are detected for either analyser. Therefore, analyser G2301 is not responsible for the occurrence of inverse CH_4 spikes in the time series at Schneefernerhaus. In a second test, CRDS analyser G2301 measures the ambient air at Schneefernerhaus using the normal setup described in Section 2.2. However, the CRDS analyser G2401 uses a completely different setup with a stainless steel intake line that starts at the same point as the glass intake line for the normal setup. The CH_4 mole fractions measured with both analysers but different setups show strong inverse CH_4 spikes. Therefore, the experimental setup is not responsible for the inverse CH_4 spikes, too.
  We also added further details in the manuscript:
  "Two tests were performed during such events with inverse CH_4 spikes. Firstly, we have exchanged the analysers and secondly, we have used an independent intake line that receives ambient air from the same location on the terrace at Schneefernerhaus. Since the inverse CH_4 spikes were measured with both sampling lines to the Schneefernerhaus terrace and with both analysers when measuring ambient air from the Schneefernerhaus, but not with both analysers when measuring ambient air from the mountain ridge, these spikes are neither an artefact nor caused by the analyser, the measurement setup or the inlet."
  Regarding the possible impact of icing at the sampling inlet, we can exclude this as a cause, since on the one hand the intake at the Schneefernerhaus is heated and on the other hand the air flow through the analyser did not show any irregularities during the occurrence of the spikes.
- [Referee #2] Line 177: this is an interesting experiment. How did you measure the direction of the flow inside the tunnel? I would suggest to change Figure 4 with an example from the experiment in Nov 2020 showing the CH4 near the tunnel entrance with simultaneous measurements at ZSF. Did the CO2 vary during the inverse CH4 peaks?
  [Hoheisel et al.] The flow direction inside the tunnel was measured with a 1D anemometer (of the company Thies) which was installed a few meter within the tunnel. We now have added the instrument type: *"For 15 days in November 2020, the CH_4 mole fraction was measured with a CRDS 300i analyser (Picarro, Inc., Santa Clara, CA) inside the tunnel near the opening. The measured mole fraction of CH_4 strongly depends on the direction of the tunnel air flow, which was measured in the tunnel with a 1D anemometer."*
  We appreciate the recommendation regarding Figure 4. In order to continue to give a good idea of the inverse CH_4 spikes, we have not replaced Figure 4, but included a figure which shows the measurements in the tunnel in more detail.
  So far we have not detected any peaks in the CO_2 time series that correlate with the inverse CH_4 spikes. This was to be expected, as the CO_2 measurements in the tunnel

have shown that the CO_2 mole fraction in the tunnel entrance does not change much between periods when air is blowing uphill or downhill.

- [Referee #2] Line 205: from a user perspective, it is interesting to know the relationship between the local pollution event flagged in this work with the flags reported in the WDCGG datasets (e.g. Valid (background): 1, Valid (background): U, Invalid: N, Valid (background): O, Invalid: K, Valid (background): R, Invalid: H, Invalid: 3, see https://gaw.kishou.go.jp/search/file/0071-6031-1001-01-01-9999).
  [Hoheisel et al.] We can understand that this could be interesting from the user's point of view. Until joining ICOS and thus at the time of the comparison measurements, the one-minute averages were flagged. As described in section 2.4, artefacts, outliers and local pollution events are flagged as invalid and are not taken into account when averaging the one-minute averages to hourly averages. In the WDCGG, the hourly values are then reported as valid or invalid, as appropriate.
- [Referee #2] Line 213: how long the intercomparison was?
  [Hoheisel et al.] The comparison was done for 15 days. We included the duration in the manuscript:
  "A comparison of the CO, CO_2 and CH_4 mole fractions measured for 15 days with OA-ICOS EP30 or CRDS G2401 and CRDS G2301 using exactly the same air shows a standard deviation of hourly averages of 0.6ppb CO, 0.02ppm CO_2 and 0.2ppb CH_4"
- [Referee #2] Line 231: please correct "ppb".
  [Hoheisel et al.] Thanks, we changed it.
- [Referee #2] Figure 7: please explain what the error bars represent.
  [Hoheisel et al.] The error bars are the standard errors of the averages.
- [Referee #2] Line 242: I suppose that also thermal valley and slope winds play a role. This should be cited.
  [Hoheisel et al.] Yes, also thermal valley and slope winds play a role and we included it:
  "The diurnal cycles are mainly determined by the planetary boundary layer height and convective upslope winds (Yuan et al., 2019).
- [Referee #2] Line 244: this is actually not true. For CH4 and CO the seasonal peaks are occurring in spring (March-May). During the summer a relative minimum is evident likely due to lower combustion emissions (for CO) and enhanced OH removal (for CO and CH4).
  [Hoheisel et al.] Yes, in our effort to briefly explain several processes, we wrote the paragraph inaccurately and misleadingly. We have now changed the paragraph to:
  "The general pattern of the annual and diurnal cycles of CO, CO_2 and CH_4 measured at Schneefernerhaus and the mountain ridge are similar to those of other mountain stations in the Northern Hemisphere (Thoning et al., 1989; De Wekker et al., 2009). The diurnal cycles are mainly determined by the planetary boundary layer height and convective upslope winds (Yuan et al., 2019). Depending on the season and the time of day, the air masses of the free troposphere or the planetary boundary layer are measured. Since air from the planetary boundary layer is typically more polluted in CO and CH_4, higher values are measured during the day especially in summer. Since CO_2 uptake by the biosphere reduces the CO_2 mole fraction in the boundary layer, the CO_2 mole fraction measured at Zugspitze is lower during the day in summer."
- [Referee #2] Line 258: I think that the higher deviation during winter daytime (when vertical transport from the PBL is minimized) can be a point towards local influences.
  [Hoheisel et al.] That's right, we also assume that the difference between the CO_2 measurement at Schneefernerhaus and at the mountain ridge is due to the reduced vertical transport in winter. However, we have not been able to clarify whether the higher CO_2 mole fraction at Schneefernerhaus is due to local sources in the surroundings of Schneefernerhaus, or whether it is due to more regional sources such as heating, whereby the CO_2-enriched air masses come up the valley but not all the way to the mountain ridge.
- [Referee #2] Line 279 – 284. I'm confused. Figure C2 reported a significant deviation between weekday and weekend also in 2002-2007. Why is not this evident in Figure C1?

[Hoheisel et al.] Yes, also in the period 2002-2007 differences between the diurnal cycles at the weekend and during the week can be seen in Figure C2. However, these are not quite as large on average as between 2008 and 2014. In Figure C1, one can also notice a small tendency towards higher values during the week for 2002-2007 compared to the period 2015-2021. However, the changes are so small that the significance test for weekly dependence does not detect a significant weekend effect for the period 2002-2007. Furthermore, we would like to note that in order to determine the mean diurnal cycles, detrended values were used, i.e. in our case the mean night value was subtracted for each day. In Figure C2, therefore, mean weekday differences are not completely included.

- [Referee #2] The presence of a leakage in the sampling system in the period 2002-2014 can potentially have impact on the trend calculation and (considering that the impact is exceeding 1 ppm during daytime hours) on utilization of this dataset for inversion experiments (even if modelers are usually taking night-time data from mountain sites) or model validation. I would like to see recommendations to users about the use of this earlier ZSF dataset. These recommendations should be also provided in the national/international database using these data.
  [Hoheisel et al.] We agree that this is an important point. We have answered these comments of the referee in the context of the first general comment of the referee at the beginning.

CONCLUSIONS:

- [Referee #2] Line 298: "baseline" should be used instead of "background"
  [Hoheisel et al.] Yes, we changed it to "baseline".

APPENDIX C:

- [Referee #2] Line 326: how the 31-day moving window was defined? Did you perform sensitivity tests changing the length of the time window?
  [Hoheisel et al.] For each day, a 31-day moving average was calculated by averaging the daily means in the period of 15 days before and 15 days after that day.