

In response to Anonymous Referee #4 comments from October the 30th, 2018.

The paper by Kostinek et al. presents ground-based and in-flight performance assessments of a commercial trace gas analyzer (TILDAS, Aerodyne Research Inc.) after its adaptation for airborne operation. The subject is highly topical and targets a key issue that every scientist is facing when taking decision on analyzer selection. This can even be critical considering the stringent place and measurement-time limitations of flight campaigns. Here, the author's choice is on a dual-laser direct absorption spectrometer with multi-species (i.e., five compounds) detection capabilities deploying state-of-the-art mid-IR laser sources (both QCL and ICL). The in-flight intercomparison with CRDS-based instruments and flask samples is an important element of the manuscript that can be of interest for the community involved in airborne measurements. The manuscript is well written, and I recommend publication after addressing some comments and changes listed below.

Dear Referee,

Thank you very much for your careful review and the detailed, helpful comments. We greatly appreciate all your work involved with reviewing this manuscript. The comments include very interesting thoughts and insights. Especially those on instrument details sparked some new ideas to further improve the instrument performance in the future. The technical level of the specific comments is quite high. We hope to have answered to your full expectation.

General comments:

1. **The title should better reflect the content of the manuscript. Given that for the measurements the spectrometer is equally using both QCL and ICL devices, this should be weighted the same. Furthermore, the instrument was mainly adopted and not modified for airborne operation. Thus, my suggestion is to write: "Adaptation and performance assessment of a dual-laser mid-IR direct absorption spectrometer for ..."**

We agree, that the title should weigh QCL and ICL the same, we thus modified the title to include both after the "initial decision" phase. Based on your suggestion from above we further changed the title to "Adaptation and performance assessment of a Quantum / Interband Cascade Laser Spectrometer for simultaneous airborne in situ observation of CH₄, C₂H₆, CO₂, CO and N₂O"

2. **The abstract should focus on summarizing briefly the highlights and findings of the presented work. Thus, I suggest starting directly with L7, "Here we demonstrate..."**

We modified the abstract based on this comment:

"Tunable laser direct absorption spectroscopy is a widely used technique for in situ sensing of atmospheric composition. Aircraft deployment however, poses a challenging operating environment for instruments sensing climatologically-relevant gases in the Earth's atmosphere. Here, we demonstrate the successful adaption of a [...]"

3. **Although the introduction contains a brief hint about the large number of available measurement techniques for airborne atmospheric measurements, it is unfortunate that the authors completely refrain to motivate their choice for a particular analyzer. Clearly there are some benefits of having multi-species capabilities at slightly higher sampling rate, but how this compensates for the obvious limitations, such as cabin pressure dependence, frequent high-flow calibration requirements, tedious post-processing of the raw spectral data, high power and calibration gas consumption, etc.? A more elaborate discussion on advantages/disadvantages of the chosen approach would significantly improve the manuscript.**

We have added a brief statement in the introduction on the motivation for the particular analyzer used. As stated in the response to reviewer #2: "We consider it to be out of the scope of this paper to directly compare the two instruments against each other. Instead our goal is to demonstrate the suitability of the described instrument, given the calibration approach and post-processing described herein, for airborne observations with the ultimate goal of inferring local to regional fluxes. The instrument has advantages and drawbacks when directly compared to CRDS analyzers. One of the drawbacks is the reduced absorption path length. A big advantage is the large number of simultaneously sampled species using a single instrument. Depending on the scientific objective of the aircraft campaign, the additional measurements can either facilitate source attribution of observed methane enhancements (e.g. using ethane and/or nitrous oxide)), or

will allow to study specific scientific questions related to N₂O, since there is no dead time in between each single measurement. This is especially useful for measurements in close vicinity to sources where plumes are only weakly dispersed (spatially narrow). While there is a certain chance of missing narrow plume structures with sequentially probing instruments, this QCL/ICL spectrometer does not suffer from such a problem. This is further described in Sect. 5. We included the motivation for the choice:

"[...] This particular analyzer has been favored over other instruments for its simultaneous multi-species capability and its sampling pattern, allowing the detection and quantitative observation of spatially narrow plumes. [...]"

4. **In the same context, it is also not obvious in the present form, why the authors decided for an extensive calibration scheme and additional data post-processing instead of developing a purged and sealed enclosure around the instrument. Apparently, most of the relevant drifts or biases are due to ambient air (H₂O mainly) absorptions outside the multi-pass cell.**

We do agree that a pressure-stabilized and zero-air-flushed compartment would certainly be a significant improvement. However, this might be a simpler task for ground- or lab-based instruments but it is far more challenging for airborne instrumentation. With the current setup we are at the absolute mass limit to be able to acquire FAA certification. An additional pressurized compartment would at least mean some additional weight, not to mention the required flushing gas. It is also unsure if such a compartment would solve most of the problems. We fear that this might improve things but not completely solve all related problems because of the very sensitive apparatus involved and the harsh environment aircraft deployment poses. In this context we agree with Alan Fried, who commented on this in a previous review: "For example, some of the dependence is due to the changing mixing ratios for the species under study in the open-air path. Additional dependencies result from movement of optical windows and other components and are instrument dependent. Also, we find that the rate of cabin pressure change is an important factor, and this is specific to the particular aircraft and the flight pattern employed."

5. **Considering that the spectral retrieval software of the manufacturer has been around for more than 20 years, supporting a large number of custom-built instruments applied in a wide range of applications, one would assume that the software experienced a continuous development and incorporates many fine-tuning/customizing features in order to optimize also the fitting process. Therefore, it is highly interesting and valuable if the custom retrieval software (JFIT) significantly improves the performance. This must, however, be more clearly documented by a side-by-side comparison of the results of both software packages. Especially, the additional shift parameters introduced by JFIT and its co-allocation to various segments of the spectral window seems rather subjective and should be quantified in terms of performance improvements. The authors refer to Fig.8 (p13) to show that the tuning rate of the lasers is stable, which seems to be in contradiction with the many shift parameters introduced in JFIT.**

The spectral retrieval software provided by the manufacturer certainly is a very powerful tool and as you say, it implements lots of tuning and tweaking features that can be used for optimization of the retrieval process. We do not claim to provide a better software package, instead we purposely wrote our own retrieval software mainly to learn about possible modifications and to be able to easily adapt our code to new problems. The handling of the shift parameters is one such example. We are not sure of how that could have been done other than writing our own software. We think that it makes perfect sense to split the shift parameters on the spectral axes. Even though spectral shifts seem perfectly co-linear tiny shifts can have significant influence on the retrieved mixing ratios.

6. **Similarly, the discussion of the water vapor correction should contain further details about the observed biases and drifts in the whole range of water concentrations experienced during flights. Measuring water concentration at absolute level is challenging, so the authors should show the observed correlation between generated humidity and spectroscopically measured water mixing ratios. Also, some discussion is required to make clear how the additionally introduced broadening effect improves the measurements, and compare this to the impact of the significant spectral instability (10-3 cm⁻¹) and potential temperature fluctuations of the sampled gas and of the cabin during flights.**

We are aware that measuring water concentrations at absolute levels certainly is a difficult task. We purposely do not

mention water vapor in the title because for us water vapor is just a side product used to enable reporting dry-air mixing ratios. The referred section mainly describes how the water vapor foreign broadening coefficient is obtained. This does not involve measuring water vapor at absolute levels, instead it is only necessary to span the range of atmospheric H₂O. The correlation for actual atmospheric measurements can be seen from the lowest panel in Fig. 10. We slightly modified the section to make this more clear and also to discuss how the broadening effect improves the measurements.

"[...] partial pressure of water vapor p_{H_2O} and the water broadening coefficient γ_{H_2O} . The former can be computed from the measured water vapor concentration. The latter can be empirically determined. Not including the self and water foreign broadening leads to relative errors in the range of 0-2% for the described setup, depending on the species of interest. While small for C₂H₆ and CH₄ with < 0.03%, the influence on retrieved CO is rather large with ~ 2%. In order to obtain γ_{H_2O} two MFCs are used to modify mixing ratios of water vapor in a clean and dry calibration gas. This does not involve measuring water vapor at absolute levels, instead it is only necessary to span the range of atmospheric H₂O. An additional downstream pump allows, in combination with a manually-controlled needle-valve, tuning the absolute pressure at the instrument inlet to simulate altitude changes. For these tests, the QCLS instrument has been operated at low flow rates of approx. 1 SLPM due to limitations on the two mass flow controllers. The water broadening coefficient γ_{H_2O} has been adjusted iteratively until reported dry-air mixing-ratios of the species of interest remained constant for the set of water vapor mixing ratios. [...]"

7. **Since the instrument is a unique platform, where two different mid-IR laser sources are operated side-by-side, a more detailed comparison of performances and noise characteristics of QCL/ICL would certainly be an added value to the manuscript.**

We sincerely agree, that this would be a very interesting analysis and a nice added value to the manuscript. However, this kind of study is out of the scope of this paper. This is something that should be carried out by laser experts and not as an addendum to this paper. We think this to deserve a publication on its own.

Specific comments:

1. **Pg2, L27: need more clarification what is meant by sequential and truly concurrent sensing. Otherwise, there should be a short note about the importance/benefit of measuring at 0.5 Hz instead of 2 Hz.**

In this context "concurrent sensing" is used to describe the fact, that the individual species are measured quasi-simultaneously. The laser sweeps over the absorption lines with a frequency of 1.5kHz, resulting in a sampling of the spectral absorption of all targeted species at the same frequency. This is to be seen as opposed to "sequential" measurements, where one species is sampled after the other. Further details on the "sequential" approach are given in Section 5. To clarify this, we changed the relevant sentence to:

"[...] Unlike many established instruments measuring different species sequentially (one species after the other), the described spectrometer allows for concurrent sensing of the selected species and faster response times. Fast system response times are valuable to resolve the high variability in trace gases near strong sources. [...]"

2. **Pg2, L25: a reference to the paper at this stage is enough; especially, that Section 2 starts with the same information.**

The relevant sentence was redundant and has been removed in a revised version of the manuscript.

3. **Pg2, L29-31: How to interpret these cited works? In the present context, they give the impression that there is no open question regarding the suitability of QCLS for airborne measurements.**

We rephrased the corresponding text in the introduction to:

"[...] . Santoni et al. (2014) describe the successful deployment and evaluation of a similar airborne spectrometer (Harvard QCLS) for more than 500 flight hours. In contrast, Pitt et al. (2016) reported a severe cabin pressure dependency of their N₂O and CH₄ measurements using a commercial instrument (Aerodyne QCLS). By implementing a pressure-differentiated calibration method they were able to correct the corresponding data set, but had to omit roughly half of the measured data. Recently, Gvakharia et al. (2018) reported on a similar, clear cabin pressure dependency for their N₂O,

CO₂ and CO measurements (based on an Aerodyne QCLS). They suggested a fast calibration procedure to overcome these dependencies while maintaining a $\geq 90\%$ duty cycle. [...]"

4. **Pg2, L32: the main objective of the paper is missing. What is the final goal of this investigation? Which measurement data and for what purpose are they going to be used? Is the data quality adequate to answer the research questions?**

We added the missing objective:

"[...] The instrument is shown to provide airborne observations of high quality at high sampling rate with multi-species sensitivity as required for assessing greenhouse gas fluxes with a regional focus. [...]"

5. **Pg3, Sect 2.1: this section needs some re-work, e.g. statement like "optics compartment contains all optical elements" is redundant, while Laser#1 and #2 without clear definition has no sense. I suggest giving the driving specifications of the lasers (current and temperature) as well as their optical power output. Specify the exact detector type.**

We have reworked this section to include the above mentioned:

"[...] The spectrometer is split into an electronics compartment and an optics compartment. The electronics compartment includes an embedded computing system, thermoelectric cooling (TEC) controllers, power supplies, etc.. The optics compartment includes the lasers, the sample cell, the pressure controller, etc..

Fig. 1 shows a top-view photograph of the optics compartment. A combination of a continuous wave (CW) QCL and ICL measures mixing ratios of CH₄, C₂H₆, CO₂, CO, N₂O and H₂O simultaneously by direct absorption spectroscopy. The sample cell is an astigmatic Herriott cell with approximate physical dimensions of 15cm x 15cm x 50cm (WxHxL) made from aluminum. It provides an effective absorption path length of 204m with a net volume of 2.1L. Two laser light sources are tuned to a specific center wavelength by adjusting the temperature using Peltier elements contained in the lasers housing. Excess heat is removed through a liquid cooling/heating circuit (*SOLID STATE COOLING SYSTEMS, New York, USA*). Laser #1 is an Interband cascade laser manufactured by *nanoplus GmbH, Gerbrunn, Germany* with a peak output power of 9.5mW operated at 4.7°C and modulated between 2988.520cm⁻¹ and 2990.625cm⁻¹ using a linear current ramp of up to 40mA. Laser #2 is a quantum cascade laser manufactured by *ALPES Laser, St-Blaise, Switzerland* with a peak output power of 40mW operated at 1.5°C modulated between 2227.550cm⁻¹ and 2228.000cm⁻¹ using a linear current ramp of up to 300mA. The lasers are modulated sequentially at a fixed frequency of 1.5kHz. Laser #1 scans over absorption lines of CH₄, C₂H₆ and H₂O, Laser #2 sweeps over N₂O, CO₂ and CO lines. Each laser is sampled at 450 spectral points. Acquired spectra are co-added to yield a single output spectrum every half of a second. Before reaching the sample cell, the laser beam travels approximately 1.6m inside the instrument under ambient conditions. This will be referred to as the open-path of the instrument, which is heavily influenced by variations in cabin pressure, temperature and humidity during airborne operation. After passing through the sample cell, the combined output from both lasers hits a single TEC-cooled detector. A second, identical detector collects radiation from two auxiliary paths. The first auxiliary path contains a small, sealed reference cell filled with CH₄ and N₂O. This allows for spectral referencing during system startup. The second path introduces an etalon into the beam, allowing for experimental determination of the laser tuning rate, which relates laser supply current and emitted wavelength. [...]"

6. **Pg4, L1: obviously there are many hundreds of reflections within the multi-pass cell, which leads to significant decrease of optical power of the laser beam. What is the reflectivity of the mirrors and how much is the out-coupled ICL intensity?**

The sample cell has not been modified from its original state. The exact reflectivity of the mirrors employed by Aerodyne Inc. is therefore unknown to us just like we did not measure the out-coupled intensity. From our point of view, this quantity is not relevant for the purpose of this manuscript. It is high enough to provide sufficient signal-to-noise ratio on the acquired spectra.

7. **Pg4, L3: I doubt that the laser devices are directly coupled to the Peltiers. There should be a buffer heat-sink between.**

The laser devices are supplied by the manufacturer in a TO66 housing with the TECs already built in. This is what is

meant with "[...] Peltier elements directly attached to the laser [...]". We modified the relevant sentence accordingly:
"[...] Both lasers are tuned to a specific center wavelength by adjusting the temperature using Peltier elements contained in the laser housing. [...]"

8. **Pg8, L15: the relative frequency changes seem to be the same, which is also illustrated by Fig8. So what is the real benefit for using five different shift parameters?**

Even very subtle perturbations from the co-linearity of these shift parameters result in large changes in retrieved mixing ratios. Apart from that, the shift parameters provide a means for observing spectral stability, that would not be available otherwise.

"[...] This allows to properly model frequency changes and provides a means for observing spectral stability. Typical shift parameters for ground-based operation are given [...]"

9. **Pg9, L1: how large were the temperature fluctuations within the optical compartment? What was their effect on the spectral retrieval?**

The optical compartment is temperature stabilized by means of a recirculating chiller. As a consequence typical temperature fluctuations inside the optical compartment are on the order of ~ 0.3 K. We did not observe a correlation between retrieved mixing ratios and these fluctuations. We included this in the section on airborne performance:

"[...] We identified temperature fluctuations within ~ 0.3 K, pressure changes of up to ~ 200 hPa and relative humidity changes of up to 35 % in the instruments optical compartment during this flight. [...]"

10. **Pg9, Fig 9: specify the averaging time of the spectra.**

The averaging time of these spectra is $\tau = 0.5$ s. The values have been included in a revised version of the figure.

11. **Pg9, Fig 9: where is the CH₄ line in the C₂H₆ fit-window? What is causing the strong bias in the residual in the CH₄ fit-window?**

The bias in the residual of the CH₄ window is the remainder of the third-order polynomial used to model the spectral baseline. The relevant sentence on Pg. 10 has been changed to:

"A single adjacent CH₄ line, located at 2989.981 cm^{-1} has been included in order to obtain good C₂H₆ data even under these challenging conditions."

12. **Pg10, L7: a short clarification should be added why the authors chose this difficult spectral window? The range around 2224.5 cm⁻¹ would, e.g. contain all the species with significantly less spectral interference. The ambition of getting the CO₂ along with CO and N₂O introduces severe compromises in the achievable spectral sensitivity and selectivity. Adding the fact that the selected CO₂ line is not even the main isotopologue and seems to have large systematic bias, I seriously doubt whether this compromise is worthwhile.**

Thank you very much for hinting towards this spectral region. It seems to be a nice alternative. However, this region does neither include the primary CO₂ isotopologue and CO₂ absorption is smaller by approx. 30%. We do agree that CO seems to suffer less from spectral interference.

13. **Pg11, L9: indicate the precision and accuracy of the generated water vapor mixing ratios. What about hysteresis effects, i.e. humidifying vs. drying cycle?**

The relevant section might mistakenly give the impression that absolute water vapor concentrations are necessary to compute the water broadening coefficient. It is not. The water foreign broadening coefficient has been adjusted iteratively until reported dry-air mixing-ratios of the species of interest remained constant for the set of water vapor mixing ratios given the fixed concentrations in the calibration gas cylinder employed. We do not state how good our water vapor data actually is in terms of absolute values. Instead we just use the measured water vapor data to correct the species of interest. The cell has been flushed for a longer time with a given water vapor mixing ratio setpoint (on the order of minutes). From this we conclude, that the measurement cell was entirely flushed before every new setpoint. Hyteresis effects, i.e. humidifying vs. drying cycle should therefore have no influence.

14. **Pg12, L4: How well can the results obtained at 1 SLPM transferred to the 23 SLPM operation regim? What about simply using an empirical correction factor on the retrieved mixing ratios instead of introducing the broadening**

coefficient in the fitting procedure?

We think that the good agreement between the instruments presented in this work provides evidence enough, that the water broadening coefficients obtained at 1 SLPM can be transferred to the 23 SLPM regime. We further think that the water vapor correction approach used in this study reflects the relevant physical processes best. We did not try to use an empirical correction factor instead of the spectral approach, therefore we can't provide a statement on this.

15. **Pg12, Fig.7: it seems that the plot shows the deviation instead of variance. The Allan deviation plot indicates that the instrument drifts already after 30s even though operated under ground-based conditions. During flight, pressure and temperature variations, as well as mechanical vibrations tend to impair the performance of the instrument at even shorter time-scales. Considering the long-path of the optical cell, I wonder whether the authors did observe any correlated noise behavior when changing gas flow through the cell from 1 to 23 SLPM? As such, it would be useful to see the distribution diagram (or at least to give quantitative estimates of their spread) of the calibration gas measurements during flights.**

Thanks for pointing towards the wrong units in this figure. We did not observe a clearly correlated noise behavior when changing from low to high flow rates. The distribution diagram of the calibration gas measurements has been included in a supplement to the manuscript.

16. **Pg13, L9: what is meant by software based frequency lock mechanism?**

The way the frequency lock mechanism is implemented here is that the laser temperature is regulated to compensate for drifts using the spectral shift as the controller input and the current to the Peltiers as controller output. The controller itself is implemented in software on the data analysis computer.

We included this in the text:

"[...] Software based frequency lock refers to a controller regulating the laser temperature to compensate for drifts using the spectral shift as the controller input and the current to the Peltiers as controller output. The controller itself is implemented in software on the data analysis computer. [...]"

17. **Pg13, Fig8: what is the influence of the sudden frequency shift discontinuities on the retrieved mixing ratios?**

Using the spectral shift handling described within this work, the spectral shift discontinuities observed do not have a conspicuous effect.

18. **Pg17, L4: what would be the required isotopic composition of such a CO₂?**

The required isotopic composition of such a CO₂ would be 98.447% primary isotopologue and 1.079% secondary isotopologue (¹³C¹⁶O₂)

"[...] In this study we used working standards of synthetic nature from *Air Liquide*. Usually these are produced with CO₂ from natural gas & oil combustion processes. We determined the CH₄ and CO₂ values of each working standard gas cylinder using a NOAA-anchored (Cert.-Nr. CB11361) Picarro G-1301m. This has the drawback that we do not know the isotopic composition of our working standards as its impact had been considered negligible, e.g. (Chen et al., 2010). We only found out during development of JFIT, that the instrument is using a ¹³C¹⁶O₂ line to derive ambient CO₂. We estimate the required isotopic composition of such a CO₂ to be 98.447% primary isotopologue and 1.079% secondary isotopologue or $\delta^{13}\text{C} = -19.6\text{‰}$ which seems reasonable according to B. Coplen et al. (2002). Since we are reporting retrieved mole fractions relative to the WMO scale, only the working standard reproducibility contributes to the total uncertainty of CH₄. Uncertainty on CO₂ is difficult to assess here because of the unknown isotopic composition in our working standards. [...]"

19. **Pg17, L8: give an estimate of the overall calibration gas consumption for the 18 flights and shortly discuss options for optimization.**

The overall calibration gas consumption for the 18 research flights amounts to $\sim 3.5\text{m}^3$. A reduction in necessary calibration gas as well as a significant increase in system response times could be achieved by reducing the physical sample cell volume. We included the overall calibration gas consumption estimate in the revised manuscript:

"[...] calibration strategy from Sect. 2.3. This required a total calibration gas amount of $\sim 3.5\text{m}^3$ (excluding zero air) for the 18 research flights. [...]"

20. **Pg19, L10:** as mentioned earlier, it would be useful in this context to show the distribution diagram of the calibration gas measurements performed at every 10 min interval and representing about 10% of the measurement time.

The distribution diagram of the calibration gas measurements has been included in a supplement to the manuscript.

- 5 21. **Pg19, L17:** it is somehow unclear what applies: in the previous section (pg18, L2) the authors claim that they were unable to reproduce the cabin pressure dependence, but in the conclusion is argued that the known cabin-pressure dependencies are effectively minimized by frequent two-point calibration.

The relevant part of Pg18 was misleading, we therefore rephrased to:

- 10 "[...] A severe cabin pressure dependence in excess of 0.3 ppb hPa^{-1} in CH_4 mixing ratio has been previously reported for airborne TILDAS instrumentation (Pitt et al., 2016). This instrumentation however physically differs from the one reported here. It is not possible to accurately compare the dependencies of one instrument relative to another since many factors/quantities involved are instrument-specific, e.g. the open-path length, the positioning and properties of optical elements, like windows and mirrors, the stiffness and thermal expansion coefficients of employed optical stands, etc.. We were nevertheless able to effectively minimize cabin pressure dependencies during operation of the QCLS instrument aboard the C130 using the calibration strategy from Sect. 2.3. [...]"
- 15

22. **Pg19, L24:** was the frequency lock mechanism active during flight operation only? Do the frequency-“jumps” correlate with laser heat-sink temperature changes?

The frequency lock mechanism is always turned on following an initial referencing after instrument startup. We do not see a correlation with laser operating temperature. We did further not directly measure the laser heat-sink temperature nor did we log the recirculating chillers temperature either. This however is a very interesting question with respect to the source of the observed discontinuities that we will try to address soon.

20

23. **Pg20, L2:** Having an uncertainty of 1 ppm and systematic bias of 10 ppm on the CO2 retrieval, projecting towards isotope ratio measurement is quite steep.

If you want to express that it will be quite a challenge to reach isotope ratio measurements than we fully agree.

25 **Technical corrections:**

1. **Pg1, L12:** “truly” is not a proper attribute for simultaneous. Remove it.

"truly" has been removed.

2. **Pg2, L15:** check reference, because Santoni et al. used QCLS instead of CRDS

Here, we are referring to established IR spectrometers in general. The wording has been changed accordingly to:

- 30 "[...] used for airborne research, e.g. established IR spectrometers [...]"

3. **Pg2, L20:** as above, Richter et al. used DFG instead of QCL

The sentence has been changed to:

"[...] reported on a custom-built difference frequency generation (DFG) absorption spectrometer [...]"

- 35 4. **Pg3, L16:** here and across the manuscript add space between value and unit. Also the chemical formula should be always printed in Roman (upright) type (see e.g. IUPAC Green Book).

This has been implemented in a revised version of the manuscript.

5. **Pg4, L3:** avoid using laser diode when referring to ICL/QCL devices.

This comment has been taken into account in the revised version of the manuscript.

6. **Pg8, L4:** replace “micro” by “fit” window.

40 Occurrences of "micro window" have been replaced with "fit window" in a revised version of the manuscript.

7. **Pg21, references:** check for typos and completeness, e.g. at L10, L13, L22, etc.

The reference pages have been checked for typos and completeness in a revised version of this manuscript.