

# ***Interactive comment on “Airborne measurement of peroxy radicals using chemical amplification coupled with cavity ring down spectroscopy: the PeRCEAS instrument” by Midhun George et al.***

**Midhun George et al.**

midhun@iup.physik.uni-bremen.de

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General comments:

(1) Comments from Referees: Overall the reviewer believes 23 figures is too many for an instrument development paper of this nature. An instrument schematic could replace the first three figures (photos of the instrument, inlet and inside of aircraft) similar to Horstjann et al 2014 figure 1.

(2) Response to RC2: The first three figures have been replaced by instrument schematics as suggested by the referee.

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(1) Comments from Referees: The authors referred to an improved inlet design (DUALER vs DUALER II) by modifying the pre-chamber design and reducing wall interaction in the inlet. This modification seems significant and likely affects the instrument performance more than discussed in this paper. A figure comparing the two inlet designs or the changes in inlet design would be useful.

(2) Response to RC2: A new figure (Figure 2) showing the changes to the pre-chamber and reactors in the DUALER has been included as suggested by the referee. In addition the text has been rewritten (Lines 143-151):

(3) Author's changes in manuscript: "In the DUALER, a stable pressure in the pre-chamber is achieved by a pressure regulator, which controls the flow through the bypass line. As noted the flow rate through the reactors is held constant during measurements. Consequently, when the outside air pressure changes, the bypass flow rate from the pre-chamber is changed. The outer dimensions, shape, form and weight of the DUALER are constrained by the inlet pylon in use with the research aircraft HALO. After the first version of the DUALER (from now on called DUALER I) was flown, the inner dimensions of the pre-chamber were further optimised to reduce the wall losses and turbulence in the pre-chamber. For this, in the DUALER II the volume of the pre-chamber was increased by extending its vertical extent, the length of the truncated cone on top of the reactors was reduced in 3 mm, and the volume of the reactors was increased to 130.5 ml from the 112 ml in DUALER I. These changes resulted in a higher eCL and improved pressure stability in DUALER II as compared to DUALER I. Figure 2 shows the upper part of both DUALER I and DUALER II."

(1) Comments from Referees: The general description of how the inlet operates (alternating measurement modes) is somewhat confusing and is evident in the Reviewer #1's comments. A time series figure of the operation of each channel would make this clearer (ie switching from amplification mode to background mode and showing how each channels mode switching is out of phase with each other).

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(2) Response to RC2: A new figure (Figure 4) has been added showing the ring down times of the two detector, the retrieved  $\Delta\text{NO}_2$  and  $\text{HO}_2$  for a laboratory calibration of  $\text{HO}_2$ . The text has been rewritten (Lines 127-142):

(3) Author's changes in manuscript: "Briefly, sampled air enters PeRCEAS through the DUALER pre-chamber, which is at a lower pressure than that outside of the HALO, through an orifice in a truncated cone, i.e. a nozzle. From this pre-chamber the air is pumped simultaneously through the two flow reactors and a bypass line. At the upper addition point a mixture of CO or N<sub>2</sub> and NO enters each reactor. At the lower addition point, a flow of N<sub>2</sub> or CO enters each reactor. This enables the CO and N<sub>2</sub> flows in the two reactors within the DUALER to be switched simultaneously but out of phase with one another from the upper to the lower addition point. At the addition points, the reagent gases enter the reactor through eight circular distributed 1 mm holes to facilitate the rapid mixing with the sampled air. During measurements, the pressure in the pre-chamber and both reactors is held constant. However, there is a small pressure fluctuation during the switching of flows between the upper and lower mixing point. The flow passing through each reactor enters a CRDS NO<sub>2</sub> detector. Afterwards, the sample flows together with the air from the bypass line are scrubbed for CO and NO<sub>x</sub> and, exhausted by the pump.

The DUALER inlet comprises two PeRCA chemical reactors having alternating measurement modes, which are out of phase with one another. During the first part of the measurement cycle, the first reactor and detector are in amplification mode, while simultaneously the second reactor and detector are in background mode. In the second part of the cycle, the CO addition point in both reactors is switched. Consequently, the first reactor and detector are then in background mode while the second reactor and detector are in amplification mode. In the analysis of the measurements, the amplification and background signals from both detectors are combined appropriately. This improves accuracy and temporal resolution of the resultant RO<sub>2</sub>\* data set (see 3.1). "

(1) Comments from Referees: Furthermore, a detailed description of how the mixing

ratio of NO was decided on (30 ppmv) would be useful, as it differs significantly from the DUALER I (6ppmv) inlet and other groups PeRCA inlets (0.9 to 7.7 ppmv).

(2) Response to RC2: The objective of the present publication is to explain the dominant factors affecting the overall performance and accuracy of PeRCEAS for the determination of the hydroperoxy, HO<sub>2</sub>, and organic peroxy radicals, RO<sub>2</sub>, which react with NO to form NO<sub>2</sub>, when deployed on the HALO aircraft. The operating conditions of PeRCEAS are optimised for the specific sampling position used, cabin location of the instruments, safety requirements and the type of flight tracks and altitude profiles which were flown by HALO. Generally, these limitations are often different in different campaigns. For this reason, this manuscript does not aim at describing a unique universal set of PeRCEAS operating conditions.

(1) Comments from Referees: Generally speaking the flight data section of the paper should be focused on the improved performance of the instrument rather than flight tracks and mixing ratio figures. A comparison of DUALER I and DUALER II flight data is recommended. Considering how to show improvements between DUALER II deployments is recommended

(2) Response to RC2: The performance of DUALER I and DUALER II are now compared in section 5. In addition some key improvements of performance of DUALER II compared with DUALER I are highlighted. Lines 488-493:

(3) Author's changes in manuscript: "Two hours of measurements from the flight on the 19.03.2018 are shown in Figure 19 as an example of the third airborne deployment of PeRCEAS within the EMeRGe campaign in Asia. As can be seen in the figure, pressure fluctuations due to dynamic pressure changes have been reduced by up to 80 % in the improved PeRCEAS. Although the measured  $\Delta\text{NO}_2$  is affected by altitude changes, the value of the retrieved RO<sub>2</sub>\* does not change significantly except for the maximum climbing rate directly after take-off. Furthermore, the beam camera and the motorised mirror mounts enable the identification and immediate correction of

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small misalignments. This improves significantly the instrumental performance while simplifying maintenance.”

Specific comments:

(1) Comments from Referees: Page 4, line 120, “The optical cavity remains similar to that described in Horstjann et al...” It is useful to include mirror specifications (substrate, coating, reflectivity, diameter, etc) for a CRDS instrument, as they are critical part of theoretical instrument performance. Does the piezo optical alignment system run in a closed loop control with beam profile as a feedback parameter? If so describe this, as it seems novel.

(2) Response to RC2: The piezo optical alignment system was used in the previous PeRCEAS configuration using a single mode laser as reported by Horstjann et al., (2014). The actual PeRCEAS detector described here, has a multimode diode laser. The alignment is done manually using motorized mirror mounts while the beam camera confirms the TEM00 mode. The beam profile is checked manually in a regular basis but is not a feedback parameter for the alignment of the mirrors.

The text has been extended. Lines 153-155:

(3) Author's changes in manuscript: “The optical cavity remains similar to that described in Horstjann et al., (2014), i.e., a V-resonator of ca. 100 cm<sup>3</sup> volume formed between glued highly reflective mirrors (reflectivity, R = 99.995 %, diameter, d = 0.5”, radius of curvature, roc = 100 cm, AT Films, USA) on the side of a Teflon coated aluminium cuboid.”

(1) Comments from Referees: Page 5, line 146, “mode and modulation times...” it is not clear what mode and modulation times refer to, might be useful to define them discretely

(2) Response to RC2: The text has been extended for clarification at the beginning of 3.1. (Lines 181-190) and Figure 4 has been added:

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(3) Author's changes in manuscript: "The mode time is defined as the time selected for the measurement in either amplification or background mode. The modulation time is the time taken for a complete measurement cycle, which comprises the sum of one amplification and one background mode. The PeRCEAS measurement cycle is illustrated in Figure 4. The  $\Delta\text{NO}_2$  for each detector is calculated from the ring down time of two consecutive modes using Eq.(1). If the mode time is adequately selected, the  $\text{RO}_2^*$  retrieved per measurement cycle is identical in both measurement lines, as the two reactors are operated out of phase with one another. The final  $\text{RO}_2^*$  data is calculated as the mean of the  $\text{RO}_2^*$  determined from the  $\Delta\text{NO}_2$  and eCL of both detectors for a given measurement cycle. The time resolution of the  $\text{RO}_2^*$  measurement is then equal to the mode time. After switching modes, a small pressure pulse leads to an oscillation of the  $\text{NO}_2$  signal. Consequently, the first 20 s of each mode are not used in data analysis. The time lag arising from the time taken for the sample flow between the CRDS detector and the point of switching is typically less than 8 s (see Table 3)."

(1) Comments from Referees: Page 5, line 160, "...detector temperature. For this different detector temperature gradients,  $\Delta T$ , where applied to modulated signals generated by varying the sampled  $\text{NO}_2$  concentration..." it's not clear why the investigators modulated  $\text{NO}_2$  while applying a temperature gradient to the detector. Would it not be easier to interpret if a constant mixing ratio gas was sampled while applying a temperature gradient? It is not clear from the text where this temperature gradient is and how it was applied. It would be useful to readers that are not familiar with optics, on why a temperature gradient of 7 degC would cause detector instability. It is also not clear from the text, what was done to address this flaw in the detector design, as the authors state earlier detector stability is paramount in overall instrument performance.

(2) Response to RC2: A modulated signal was applied in order to study the effect on similar signals to those measured by PeRCEAS during operation i.e., a  $\Delta\text{NO}_2$  between amplification and background modes. The text has been extended for clarification. Lines 211-221:

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(3) Author's changes in manuscript: "Temperature changes of the detector affect: i) the diode laser emission, both its amplitude and wavelength, and ii) the mode matching between laser and detector, and consequently the  $\tau_0$ . The effect of the variations in  $\tau$ , resulting from changes in room or HALO cabin air temperatures, on the accuracy and precision of the  $\Delta\text{NO}_2$  determination was investigated by a series of laboratory experiments. For this, modulated concentrations of  $\text{NO}_2$  in the flow were generated. This was achieved by alternating between two selected  $\text{NO}_2$  concentrations once per minute. The temperature of the CRDS detector,  $T$ , and  $\tau$  were then measured. Detector temperature gradients over a time  $t$ , i.e.,  $\Delta T/\Delta t$ , determined by the temperature within the detector housing close to the photodiode, were induced by controlled changes in the room temperature.

Figure 6 shows the effect of introducing temperature perturbations in a modulated  $\text{NO}_2$  signal between 11.5 and 12.1 ppbv measured at 200 mbar and 23 °C. As can be seen in the figure, a temperature perturbation affects both precision and accuracy of the retrieved  $\Delta\text{NO}_2$ . For temperature gradients up to  $\Delta T/\Delta t \approx 7$  °C h-1 the experimental precision of the  $\Delta\text{NO}_2$  determination remains within ( $2\sigma$ ) 150 pptv (=  $7.3 \times 10^8$  molecules cm $^{-3}$  at 200 mbar and 23°C). "

Concerning T stability as states in 4.2, Lines 406-407:

"Generally, in-flight variations in the HALO cabin temperature affect minimally the accuracy of the  $\text{RO}_2^*$  determination. "

(1) Comments from Referees: Page 6, line187, "...of the sampled  $\text{O}_3$  by  $\text{NO}$  to form  $\text{NO}_2$  also depends on the concentration of  $\text{NO}$  added to the sample flow and the time for reaction before reaching the detector.". This would be a good place to discuss how 30 ppmv  $\text{NO}$  was decided on for a reagent mixing ratio and discuss flow rate choices for both  $\text{NO}$  and  $\text{CO}$ .

(2) Response to RC2: The purpose of this section is to present the effect of changing gas concentration and flows. A balance between different and competing effects, leads

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to a selection of the optimal operating conditions for a specific measurement campaign. 30 ppm NO has just been selected for some of the testing series in this work as an example for suitable reagent mixing ratio. The paper has been revised and additional measurement series have been included to illustrate some of the effects investigated.

(1) Comments from Referees: Page 6, line 192, “3.2.1 Effective Chain Length...”, This section seems to describe a well established method documented in literature. The reviewer recommends shorting the description of the method and explain better the difference in DUALER I and DUALER II eCL.

(2) Response to RC2: This part of the text has been modified taking into account the comments of both RC1 and RC2.

(1) Comments from Referees: Page 7, line 216, “The model was initialized with 9% CO, 3 ppb O<sub>3</sub>, 50 pptv HO<sub>2</sub>...” why was 3 ppb O<sub>3</sub> determined to be a representative mixing ratio for ozone? I may be misunderstanding the inlet chemistry, but it seems like missing 30 ppmv of NO would significantly affect the modeled CL. Assuming the box model initialization is correct, would it not be useful to vary the wall loss rate constants to match the eCL and determine if this wall loss is reasonable? It would also be useful to experimentally determine the wall loss of the inlet.

(2) Response to RC2: The model is initialised with 3 ppbv O<sub>3</sub> because this is the mixing ratio produced during the calibration. Sensitivity studies have shown no significant change in the simulated eCL up to 100 ppb O<sub>3</sub>. This is also confirmed by the experimental values shown in figure 17.

Following the recommendation of RC2, the simulations have been extended varying the wall losses in the pre-chamber to match the experimental values, as now explained in the text (Lines 280-306). PeRCEAS is operated at low pressures and the pressure regulation during operation prevents the direct experimental determination of the wall losses in the pre-chamber. However these are estimated by comparison with the model used.

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(1) Comments from Referees: Page 7, line 222, "figure 8 shows eCL vs CL", the authors should include error bars on these data.

(2) Response to RC2: The error bars on the experimental data are now included and the figure has been extended with more experimental and model data.

(1) Comments from Referees: Page 7, line 228, "Figure 9 depicts the O<sub>3</sub> decay simulated for 100 to 200 ppb..." these figures are somewhat confusing to the reviewer. One could take the 99% conversion time for each NO mixing ratio curve and plot all 4 conditions (ie pressure and O<sub>3</sub> mixing ratio) on 1 figure for varying NO mixing ratio. Additionally, adding an inlet residence time reference line would be useful for helping the reader visualize what time limit you have on this reaction.

(2) Response to RC2: The figures have been modified as suggested by the referee.

(1) Comments from Referees: Page 7, line 234, "PAN and PPN thermal decomposition", the reviewer believes that experimental work is justified to confirm 'this source of radicals is considered to be negligible'. The box modelling done for CL prediction was shown to not capture the actual inlet system, so it's not clear why it would do a better job with modelling PAN and PPN. Figure 11 shows up to 10 pptv interference, this does not seem negligible to the reviewer.

(2) Response to RC2: The discrepancies between measured eCL and simulated CL for the reactor are attributed to errors in the estimate of the wall losses in the inlet pre-chamber and not to the overall performance of the box model. The chemistry involved in the formation of CH<sub>3</sub>O<sub>2</sub> from the PAN decomposition has now been revised, and all the rates have been taken from the recommendations in JPL 15-10, with the equilibrium rate constant from Zhang et al (2011).

The results do not change for NO mixing ratios in reactor within 10 and 45 ppm.

During the flight the PeRCEAS reactors are located inside the pylon on the upper part of the HALO fuselage. As a consequence, the temperature in the reactors, which

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is measured, remains below 290K (Figure 20 and 21). Consequently the maximum interference expected for the transition times given in Table 3 will be below 2 pptv, which is within the measurement error. The figure (now Figure 11) has been updated and the text has been extended for clarification (Lines 324-339).

(1) Comments from Referees: Page 8, line 252, "Figure 12 shows the variation of the eCL for 45 ppm NO within a pressure range...", The reviewer does not understand why this experiment was done with 45 ppm NO when the decided upon mixing ratio of NO addition seems to be 30 ppm NO for the rest of the paper. If this is a typo, it should be corrected, if not the experiment should be done at the actual mixing ratio the instrument is operated at.

(2) Response to RC2: The figure has been extended with similar measurements for 10 ppm NO. The results at 10 ppm NO confirm the recommendation of  $\bar{P} = 100$  mbar as the minimum operating pressure. The text (Lines 348-353) and the figure (now Figure 12) have been updated.

(1) Comments from Referees: Page 9, line 284, "Figure 15 depicts exemplary a comparison of spectra...", the reviewer does not believe including NO<sub>2</sub> absorption cross section and detector spectra is a useful figure for the main text of this paper. Remove or include in the SI.

(2) Response to RC2: The figure has now been included in the supplementary information. Line 387:

(3) Author's changes in manuscript: "A sample comparison of spectra obtained for the three PeRCEAS detectors is included in the supplementary information (Figure SI-1)."

(1) Comments from Referees: Page 9, line 289, "In addition, the effective  $\sigma$ NO<sub>2</sub> can be calculated by sampling known mixtures...", the reviewer does not believe including a time series of calibration gas addition to instrument is a useful figure for the main text of this paper. Remove or include in the SI.

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(2) Response to RC2: The figure has now been included in the supplementary information. Lines 392-396:

(3) Author's changes in manuscript: "The result of applying Eq. (5) to the PeRCEAS detectors is depicted in Figure 15. The detectors sampled known mixtures of NO<sub>2</sub> from commercial gas cylinders in synthetic air at 200 mbar as shown in the supplementary information (Figure SI-2)."

(1) Comments from Referees: Page 9, line 294, "The result of apply Eq. 4 to the PeRCEAS detectors at 200 mbar is depicted in Figure 17." It is more common to plot NO<sub>2</sub> number density [molecules/cm<sup>3</sup>] vs.  $\alpha$ , as the slope has the physical meaning of the absorption cross section of NO<sub>2</sub>.

(2) Response to RC2: In the case of CRDS  $\langle A \rangle$  is not measured but must be calculated by using Eq.1. In contrast, the variables plotted in the Figure 15 (originally Figure 17) are taken directly from the measurement and do not require a prior knowledge of  $\langle A \rangle_0$ . In addition the y intercept of the plot is the  $1/\tau_0$  for each detector.

(1) Comments from Referees: Page 9, line 302, "The main source of uncertainty..." the authors previously mention detector drift due to temperature changes (figure 5), is this not a significant source of uncertainty as well?

(2) Response to RC2: Temperature drifts can be minimised during laboratory measurements. Concerning in-flight measurements, it is mentioned in section 4.3 that the temperature in the HALO cabin remains reasonably constant and therefore is not a significant source of uncertainty during the airborne measurement. An example can be seen in Figures 18 and 19. A sentence has been added to clarify this point. Line 406:

(3) Author's changes in manuscript: "Generally, in-flight variations in the HALO cabin temperature affect minimally the accuracy of the RO<sub>2</sub>\* determination."

(1) Comments from Referees: Page 10, line 309, "Figure 18 shows the calculated eCL

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from 14 radical calibrations..." why were radical calibrations done with a NO mixing ratio of 45 ppm when the instrument is run at 30 ppm?

(2)Response to RC2: In this publication there is no intention to define one unique set of operating conditions for the PeRCEAS on HALO. Several concentrations and mixing ratios for NO were investigated. At 300 mbar the longest series of measurements was selected in the figure 18 to show the best statistics in the reproducibility and stability of eCL over time. These measurements were carried out to investigate the dependence of eCL on NO. Figure 18 (now Figure 16 in the revised version) is been replaced to show the data obtained at 300 mbar and 30 ppmv as suggested by the referee. The estimates of the corresponding eCL values for 10 ppm, 30 ppm and 45 ppm NO are now listed in Table 4.

(1) Comments from Referees: Page 10, line 330, "As can be seen in Figure 19...", it would be useful to plot actual O<sub>3</sub> mixing ratio rather than set point in the top panel of this figure. It would also be useful to plot chamber pressure or channel pressure, as it seems like when the O<sub>3</sub> mixing ratio is changed the NO<sub>2</sub> signal displays a large amount of noise (50 ppb). It is also unclear what D1, D2, SG and BG stand for in this figure.

(2)Response to RC2: The original figure 19 is now Figure 17. The O<sub>3</sub> mixing ratio is set at the calibrated O<sub>3</sub> generator and cannot be measured during the PeRCEAS measurement, as it is converted in NO<sub>2</sub>.

The variation observed in the  $\ddot{\lambda}$ NO<sub>2</sub> (the NO<sub>2</sub> signal is not plotted) is not related to any change in the pressure but to the change in the O<sub>3</sub> concentration in the sample, which takes approximately 1 minute to stabilise after changing the set point in the ozone generator.

The meaning of D1, D2, AP and BG are now explained in the figure caption. SG has been replaced by AP for clarification.

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(1) Comments from Referees: Page 11, line 364, "The pressure regulation in PeRCA based airborne instruments results in lower eCL than ground based ones." This statement should be substantiated. The reviewer sees a range of eCL for aircraft instruments from 45 to 322 and ground based instruments a range of 91 to 1010. A description of why lower pressure or pressure regulation in general affects eCL would be useful.

(2) Response to RC2: As now described in section 2 the pressure in the inlet in PeRCEAS is controlled in the pre-chamber during the flight. This pre-chamber prior to the reactors causes radical losses which do not have the ground based instruments without pressure chamber and pressure regulation. The sentence has been extended for clarification. Lines 469-470:

(3) Author's changes in manuscript: "The pressure regulation in PeRCA based airborne instruments results in lower eCL than ground based ones. This is attributed to radical losses in the pre-chamber prior to the addition of reagent gases for the radical chemical amplification."

(1) Comments from Referees: Page 11, line 367, "the detection limit and uncertainty of PeRCA based instruments are strongly depending on the variation of O<sub>3</sub> and NO<sub>2</sub> in the sampled air mass..." The reviewer believes this statement should be substantiated with uncertainty and/or detection limit analysis to show the reader the magnitude of this affect. If the changes in O<sub>3</sub> and NO<sub>2</sub> are measured (as often are in aircraft field campaigns) can a correction method not be proposed and evaluated?

(2) Response to RC2: The effect of O<sub>3</sub> changes in the RO<sub>2</sub>\* determination has been shown and quantified in figure 17. Simultaneous measurements of O<sub>3</sub> and NO<sub>2</sub> on-board can be used as a reference for the correction of the background variations in individual cases, but a method that relies on other measurements to correct the background will have to deal with different instrumental resolutions and sources of errors of the instruments involved.

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(1) Comments from Referees: Page 12, line 379, "As can be seen in figure 20..." this reviewer believes it would be useful to add the detector temperature (or  $\Delta T$  used earlier) to this figure, as this was determined to be a large effect on  $\Delta NO_2$  earlier in the manuscript. If  $NO_2$  and  $O_3$  mixing ratio data is available from the flight, this would be useful to include as well. (2) Response to RC2: The figure 20 (now figure 18) has been modified to include the inlet and detector temperatures as suggested by the referee.

(1) Comments from Referees: Page 12, line 383, "Figure 22..." the reviewer does not believe this or figure 21 add considerable value to this paper. Recommend removing or moving to SI.

(2) Response to RC2: This figure has been removed as suggested by the referee.

(1) Comments from Referees: Page 12, line 387, "...illustrate the improvement in the dynamical stability achieved in successive airborne deployments..." the reviewer finds it difficult to see the improvements made in the measurement by looking at time series data. Suggest thinking of a different way of presenting this conclusion. It would also be very useful to add a comparison to the previous generation of instrument somewhere in the paper.

(2) Response to RC2: The figures 18 and 19 have been modified to make clearer the improvement made as suggested by the referee.

Please also note the supplement to this comment:

<https://www.atmos-meas-tech-discuss.net/amt-2019-359/amt-2019-359-AC3-supplement.pdf>

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