

We thank Dr. Andrés-Hernández for the comments and providing the opportunity to further discuss this important issue. Our responses are interspersed below (in non-italic font).

The manuscript entitled Peroxy Radical Measurements by Ethane - Nitric Oxide Chemical Amplification and Laser-Induced Fluorescence / Fluorescence Assay by Gas Expansion during the IRRONIC field campaign in a Forest in Indiana, by Shuvashish Kundu et al, quotes twice the ACP paper Andrés-Hernández et al., 2011 in a completely wrong context and with an erroneous interpretation of the conclusions of this work.

Kundu et al write in the introduction:

“Similarly, XO₂ measurements from two CO-based chemical amplifiers during the airborne African Monsoon 5 Multidisciplinary Analysis (AMMA) campaign differed by factors of 2-4 when the usual relative humidity-dependent calibration (Mihele and Hastie, 1998) was used for the chemical amplifier data (Andrés-Hernández et al., 2010).

As a result, the relative humidity dependence of the chemical amplification technique has been questioned (Andrés-Hernández et al., 2010;Sommariva et al., 2011) despite strong experimental evidence (Butkovskaya et al., 2007;Butkovskaya et al., 2005;Butkovskaya et al., 2009;Mihele et al., 1999;Mihele and Hastie, 1998).”

And again at the end of the discussion:

“As discussed earlier, the RH-dependence of the sensitivity of chemical amplifiers has recently been questioned (Andrés Hernández et al., 2010;Sommariva et al., 2011).”

This is certainly not true in the case of Andrés-Hernández et al., 2010. In this work it has never been questioned the relative humidity dependency of the amplification factor (chain length: CL) in the chemical amplification. In that context I also recommend the reading and quoting of a previous work of the same group: L. Reichert, M.D Andrés Hernández et al., JGR, 2003, discussing potential mechanisms for the humidity dependency discovered by Mihele and Hastie 1998, without any trace of this effect being questioned by the authors.

I would like to emphasise that in the section 2.1.1. on the Andrés-Hernández et al, 2010 publication is written:

The known dependency of the CL on the relative humidity (RH) of the air sampled (Mihele and Hastie, 1998; Mihele et al., 1999; Reichert et al., 2003) has a negligible effect under the AMMA measurement conditions.

A careful reading of the text helps to understand that this statement refers to the particular case of a developed PeRCA instrument for airborne measurements. During the mentioned AMMA campaign two different PeRCA instruments were used:

a) the DUALER from the University of Bremen deployed on the German Falcon, consisting of an inlet kept at constant pressure lower to the ambient. As explained in the text, this minimise humidity in the reactor and consequently its effect on the radical conversion.

b) The PERCA 4 of the University of Leicester deployed on the British FAAM-BAe-146. This instrument neither controlled the pressure during the flight or considered the RH in its calibration and had non solved instrumental issues during the intercomparison exercise. Overall the PERCA 4 measured unrealistic radical values by a factor of 4. This did not question the effect of water vapour on the chain length but the performance of this particular instrument. Therefore only the measurements of the RO₂ DUALER were used for the further comparison with the HO₂ measured by the FAGE instrument on board of FAAM.*

Concerning the quotation of Sommariva et al. 2011, there is in this publication the same kind of wrong interpretation of the results of Andrés Hernández et al., 2010. I came unfortunately across this paper after its publication. Though I contacted the first author Sommariva to clarify his wrong interpretation, the statements in that publication were never corrected.

We have carefully re-read Andrés-Hernandez et al. (2010) to investigate the apparent confusion over this issue. As described in the short comment, that paper describes the operation of two chemical amplifier (PERCA) instruments: the U. of Bremen DUALER instrument and the U. of Leicester PERCA4 instrument. The RH-dependence of the CL is described for both instruments:

1. For the U. Bremen DUALER instrument, in section 2.1.1 of that paper, the authors describe the U. of Bremen DUALER instrument and state “The known dependency of the CL on the relative humidity (RH) of the air sampled (Mihele and Hastie, 1998; Mihele et al., 1999; Reichert et al., 2003) has a negligible effect under the AMMA measurement conditions.” This conclusion is based on the fact that because the instrument reactor’s pressure was lower and temperature higher than ambient conditions, the RH is kept below 15%, a range in which the variability of the chain length is apparently smaller than the error in the CL determination: “The RH in the reactors remained below 15%. At 300 mbar this effect in the CL is expected to be within the error of the CL determination”. This last sentence is likely what initially confused us, since we would expect the effect to be experimentally quantified rather than use an “expected” effect. Furthermore, at atmospheric pressure the CL of the Bremen chemical amplifier is almost 40% lower at 15% RH compared to 0% RH (Reichert et al., 2003)! Even if the uncertainty in the CL determination is comparable or larger, this would probably be irrelevant since those uncertainties would cancel as they are correlated assuming they stem from the usual spectroscopic uncertainties (e.g., the absorption cross sections for O₂ and H₂O used for the water vapor photolysis calibration method). For example, if the CL at 0% RH is 100 ± 30% and the CL at 15% RH is 80 ± 30% (hypothetical numbers), that would still be a 20% decrease in sensitivity! Kartal et al. (2010), which describes the Bremen DUALER instrument in detail, does not show the RH dependence of the DUALER at 300 mbar.

We now recognize that the Bremen team did not question the RH dependence – rather they stated that it had a negligible effect as operated during those conditions. We remain confused how the change in CL between 0 and 15% RH can be considered negligible.

2. For the Leicester PERCA instrument, calibrations were only performed at ground level and not at altitude, which the authors recognize was not preferable. To correct for the effect of RH and the decreased pressure and temperature at aircraft altitudes, computational results were used.

When this computationally-based P, T, and RH-dependent chain length was applied to the data, however, very high concentrations results –more than four times higher than the DUALER peroxy radical measurements, higher than the LIF-FAGE HO₂ measurements, and higher than the modeled concentrations. Moreover, a trend in the modeled to measured peroxy radical concentration was observed when using the RH-corrected data, but not when using the uncorrected data. The authors conclude the following:

“To apply the humidity correction to this dataset may therefore be inappropriate and the intercomparison was made using the uncorrected data”

The authors hypothesize that the reason for this was condensation of water on their inlet, which would greatly decrease the RH inside their reaction chamber.

The 2nd paper we quoted – Sommariva et al (2011) – clearly rejected the RH-correction to their instrument:

“...the determination of CL during the experiment with the PAN source was carried out in ambient (humid) air. The agreement between the CL determined in ambient air with PAN and the CL determined in zero air with CH₃I demonstrates that the data collected during the TexAQS 2006 cruise did not require a correction for relative humidity. This was also the case for a similar PERCA instrument during another field campaign under similarly high ambient humidity and temperature conditions (Andres-Hernandez et al., 2010).”

Based on these two papers in aggregate, we reasonably concluded that the RH effect had been questioned. This is certainly the case for Sommariva et al. (2011). For Andres-Hernandez et al. (2010), we now see that we were incorrect to state that that paper questioned the RH dependence. We had interpreted their results - that the RH effect was expected to be negligible when their past results showed almost a 40% difference between 0 and 15% RH – to mean that the RH effect was in some way questioned. In the revision of our paper we will clarify that Sommariva et al. (2011) questioned the RH effect but Andres-Hernandez (2010) did. We will mention that the RH effect is addressed in a variety of ways, including that described by Andres-Hernandez et al. (2010) and Kartal et al. (2010), both of which stated that it is negligible for their airborne measurements.

The analysis of some of the instrumental results presented in the manuscript of Kundu et al., does seem not to fully take into consideration the long term experience and knowledge of the PERCA and LIF radical communities. As mentioned above it is too late now to get involved in the interactive discussion of the manuscript. But it should not be too late to prevent the use of a wrong interpretation of previous scientific work for supporting questionable results/instrumental characterisations.

These last few comments we find puzzling. We recognize the concerns about the RH dependence as discussed above. Without explicit explanation of which aspects of our analysis comparing the ECHAMP and LIF results from July 2015 the commenter finds questionable, we are unable to respond to the criticism. The new ECHAMP instrument very much owes its existence to the prior work conducted by both the PERCA and LIF communities. ECHAMP’s predecessor instrument

(Wood and Charest, 2014) was a chemical amplifier that used the same CO and NO-based chemistry as all prior PERCA instruments (e.g., Cantrell and Stedman, 1982; Clemitshaw et al., 1997; Kartal et al., 2010), used the same anti-synchronized dual-channel design pioneered by the Leicester PERCA group (Green et al., 2006), and addressed the RH dependence first identified by Mihele and Hastie (1998) and studied in detail by others (Butkovskaya et al., 2007; Butkovskaya et al., 2005; Butkovskaya et al., 2009; Reichert et al., 2003). Its current version (Anderson et al., 2019) uses the O₃ chemical actinometry variation of the water vapor photolysis calibration method introduced by a chemical amplifier group (Schultz et al., 1995) and used by several PERCA and LIF groups (Bloss et al., 2004; Dusanter et al., 2008; Kartal et al., 2010). It also now uses a methyl iodide-based calibration source, similar to that described by other PERCA groups (Clemitshaw et al., 1997; Liu and Zhang, 2014). Furthermore, the Indiana University LIF-FAGE group plays a major role in this manuscript!

It cannot be given the wrong message to the community that the dependency of the chemical amplification on the water vapour is in any form questioned.

In our revision we will clarify that the RH dependence has not been questioned by the Bremen group, and only attribute that to Sommariva et al. (2011) who certainly did question the RH dependence, evident from the text quoted earlier. Sommariva et al. (2011) also appeared to ignore the large body of work on the homogeneous reaction between NO and the HO₂-H₂O adduct (Butkovskaya et al., 2007; Butkovskaya et al., 2005; Butkovskaya et al., 2009; Mihele and Hastie, 1998; Reichert et al., 2003) in their comment below as part of the open discussion of their paper:

“The mechanism of the humidity interference remains unclear, although it appears to be heterogeneous (i.e., wall loss) in origin.”

We hope that our revised paper, including this helpful discussion, clarifies that the RH-dependence must be addressed by all chemical amplifier instruments.

References

Anderson, D. C., Pavelec, J., Daube, C., Herndon, S. C., Knighton, W. B., Lerner, B. M., Roscioli, J. R., Yacovitch, T. I., and Wood, E. C.: Characterization of Ozone Production in San Antonio, Texas, Using Measurements of Total Peroxy Radicals, *Atmos. Chem. Phys.*, 19, 2845-2860, 10.5194/acp-19-2845-2019, 2019.

Andrés-Hernández, M. D., Stone, D., Brookes, D. M., Commane, R., Reeves, C. E., Huntrieser, H., Heard, D. E., Monks, P. S., Burrows, J. P., Schlager, H., Kartal, D., Evans, M. J., Floquet, C. F. A., Ingham, T., Methven, J., and Parker, A. E.: Peroxy radical partitioning during the AMMA radical intercomparison exercise, *Atmos. Chem. Phys.*, 10, 10621-10638, 10.5194/acp-10-10621-2010, 2010.

Bloss, W. J., Lee, J. D., Bloss, C., Heard, D. E., Pilling, M. J., Wirtz, K., Martin-Reviejo, M., and Siese, M.: Validation of the calibration of a laser-induced fluorescence instrument for the

measurement of OH radicals in the atmosphere, *Atmospheric Chemistry and Physics*, 4, 571-583, 2004.

Butkovskaya, N., Kukui, A., Pouvesle, N., and Le Bras, G.: Formation of nitric acid in the gas-phase $\text{HO}_2 + \text{NO}$ reaction: Effects of temperature and water vapor, *J. Phys. Chem. A*, 109, 6509-6520, 2005.

Butkovskaya, N., Kukui, A., and Le Bras, G.: HNO_3 Forming Channel of the $\text{HO}_2 + \text{NO}$ Reaction as a Function of Pressure and Temperature in the Ranges of 72-600 Torr and 223-323 K, *J. Phys. Chem. A*, 111, 9047-9053, 2007.

Butkovskaya, N., Rayez, M.-T., Rayez, J.-C., Kukui, A., and Le Bras, G.: Water vapor effect on the HNO_3 yield in the $\text{HO}_2 + \text{NO}$ reaction: experimental and theoretical evidence, *J. Phys. Chem. A*, 113, 11327-11342, 2009.

Cantrell, C., and Stedman, D.: A possible technique for the measurement of atmospheric peroxy radicals, *Geophys. Res. Lett.*, 9, 846-849, 1982.

Clemishaw, K. C., Carpenter, L. J., Penkett, S. A., and Jenkin, M. E.: A calibrated peroxy radical chemical amplifier for ground-based tropospheric measurements, *J. Geophys. Res.*, 102, 25405, 10.1029/97jd01902, 1997.

Dusanter, S., Vimal, D., and Stevens, P. S.: Technical note: Measuring tropospheric OH and HO_2 by laser-induced fluorescence at low pressure. A comparison of calibration techniques, *Atmos. Chem. Phys.*, 8, 321-340, 10.5194/acp-8-321-2008, 2008.

Green, T. J., Reeves, C. E., Fleming, Z. L., Brough, N., Rickard, A. R., Bandy, B. J., Monks, P. S., and Penkett, S. A.: An improved dual channel PERCA instrument for atmospheric measurements of peroxy radicals, *Journal of Environmental Monitoring*, 8, 530, 10.1039/b514630e, 2006.

Kartal, D., Andrés-Hernández, M. D., Reichert, L., Schlager, H., and Burrows, J. P.: Technical Note: Characterisation of a DUALER instrument for the airborne measurement of peroxy radicals during AMMA 2006, *Atmos. Chem. Phys.*, 10, 3047-3062, 2010.

Liu, Y., and Zhang, J.: Atmospheric Peroxy Radical Measurements using Dual-Channel Chemical Amplification Ravity Ringdown Spectroscopy, *Analytical Chemistry*, 86, 5391-5398, 2014.

Mihele, C. M., and Hastie, D. R.: The sensitivity of the radical amplifier to ambient water vapour, *Geophys. Res. Lett.*, 25, 1911-1913, 10.1029/98gl01432, 1998.

Reichert, L., Hernández, A., Stöbener, D., Burkert, J., and Burrows, J.: Investigation of the effect of water complexes in the determination of peroxy radical ambient concentrations: Implications for the atmosphere, *J. of Geophys. Res.*, 108, 2003.

Schultz, M., Heitlinger, M., Mihelcic, D., and Volz-Thomas, A.: Calibration source for peroxy radicals with built-in actinometry using H₂O and O₂ photolysis at 185 nm, *J. Geophys. Res.*, 100, 18811 - 18816, 1995.

Sommariva, R., Brown, S. S., Roberts, J. M., Brookes, D. M., Parker, A. E., Monks, P. S., Bates, T. S., Bon, D., de Gouw, J. A., Frost, G. J., Gilman, J. B., Goldan, P. D., Herndon, S. C., Kuster, W. C., Lerner, B. M., Osthoff, H. D., Tucker, S. C., Warneke, C., Williams, E. J., and Zahniser, M. S.: Ozone production in remote oceanic and industrial areas derived from ship based measurements of peroxy radicals during TexAQS 2006, *Atmos. Chem. Phys.*, 11, 2471-2485, 2011.

Wood, E. C., and Charest, J.: Chemical Amplification – Cavity Attenuated Phase Shift Spectrometer Measurements of Peroxy Radicals, *Anal. Chem.*, 86, 10266-10273, 2014.