

Interactive comment on “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.

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After the conclusion of the open discussion phase of this paper, I received the following comment from Dr. Maria Dolores Andrés-Hernández. Please address the following comments regarding the representation of the water vapor correction for PERCA instruments in the current literature as part of the revised manuscript.

The manuscript entitled Peroxy Radical Measurements by Ethane - Nitric Oxide Chem-

ical 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 (AndrésHernández 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.

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.

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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. 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.

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