

Answer to: Comment on “HYPHOP: a tool for high-altitude, long-range monitoring of hydrogen peroxide and higher organic peroxides in the atmosphere” by Hamryszczak et al.

Anonymous referee #1

Please note the used color code

(black: Referee Comments, red: Author Comments, blue: manuscript changes according to Referee’s recommendations and comments)

Review comments for: HYPHOP: a tool for high-altitude, long-range monitoring of hydrogen peroxide and higher organic peroxides in the atmosphere

Hamryszczak et al. detail the performance of the HYPHOP instrument for airborne hydroperoxide measurements. The instrument has already been used in a number of field experiments and a full description in the literature is warranted. This manuscript is a thorough description of the instrument and its performance. Multiple sources of measurement uncertainty are characterized including chemical interference, dynamic flight patterns, cabin temperature, and line pressure changes. I recommend publication after attention to the following minor comments.

We thank the referee for his/her valuable comments and recommendations. Following the referee’s recommendation, the manuscript was changed as described in detail below.

Comments:

The introduction/manuscript is lacking information about the performance of other airborne hydroperoxide measurement techniques. How does HYPHOP performance compare to the best available alternatives?

The following table gives a general overview regarding the measurement performance of the most common hydroperoxide measurement techniques with their corresponding references. The table was added to the supplementary information of the manuscript (Table S1 of the Supplement). Corresponding brief reference was added in L56.

Table S1: Performance comparison of the most common hydroperoxide measurement techniques relative to the HYPHOP monitor (respective performance parameters are based on Kleindienst et al. 1988; Mackay et al. 1990; Staffelbach et al. 1996; Crouse et al. 2006; St Clair et al. 2010; Allen et al. 2022).

	HYPHOP	HPLC	TDLAS	CIT-CIMS
Sampling interval	continuous	45 min	60 sec	continuous
Data point frequency	1 Hz	$0.28 \cdot 10^{-3}$ Hz	$0.56 \cdot 10^{-3}$ Hz	> 1 Hz
Instrumental detection limit (IDL)	H ₂ O ₂ : 20 pptv ROOH: 19 pptv	H ₂ O ₂ : 150 pptv ROOH: 30 pptv	H ₂ O ₂ : 100 pptv	H ₂ O ₂ : 1–10 pptv MHP: 1–10 pptv
Precision	H ₂ O ₂ : 360 pptv ROOH: 210 pptv	H ₂ O ₂ : - ROOH: -	H ₂ O ₂ : -	H ₂ O ₂ : 50 pptv MHP: 50 pptv
Accuracy	H ₂ O ₂ : 0.7% ROOH: 0.8%	H ₂ O ₂ : - ROOH: -	H ₂ O ₂ : 20%	H ₂ O ₂ : - MHP: 40%
Total measurement uncertainty (TMU)	H ₂ O ₂ : 12% ROOH: 40%	H ₂ O ₂ : 20% ROOH: 20%	H ₂ O ₂ : 20%	H ₂ O ₂ : 35% MHP: 40–80%
Artifacts	O ₃ SO ₂ Metal ions (NO)	Pollution Particles	none	H ₂ O HOCH ₂ OH

L56 was changed to:

An overview of the measurement performance of the airborne measurement techniques discussed above relative to the instrument presented in the scope of this work is shown in the Supplement of this work (Tab. S1).

The HYPHOP background measurements are important for the calibration, but there is no mention of how often these measurements are taken during a typical flight (other than "frequent measurements") or how the background is interpolated.

We thank the referee for pointing out the missing information. L199–209 (former L190–193) was changed according to the referee's comment.

L199–209 (former L190–193) was changed to:

Due to the characteristics of the wet chemical measurement method, corrections regarding background signal variations (15–33 pptv between two consecutive background measurements and approximately 50–70 pptv over the duration of a typical measurement flight) and time modification due to the delay caused by liquid transport within the instrument (approximately 300 sec) have to be performed. Additionally, signal corrections regarding hydroperoxide transmission efficiencies due to potential wall losses at the inner surface of the sampling inlet (up to 300 pptv at 1.5 ppbv H₂O₂ and up to 100 pptv at 1.5 ppbv PAA, respectively), and sampling efficiencies have to be initially performed to obtain absolute hydroperoxide mixing ratios.

In order to account for potential measurement divergencies and background signal alterations initiated by pressure, and temperature instabilities during the measurement flights, the frequently measured background (typically at least 3–4 times per flight) signal is interpolated according to the background measurement signals ($U_{A,0}$; $U_{B,0}$) obtained during the four-point calibration procedure. A typical background sampling frequency and duration are presented based on an exemplary measurement flight during the most recent research campaign, CAFE-Brazil in the Supplement of this work (Fig. S3).

The performance of this instrument is evaluated in pristine air – a statement on any projected interfering variables in unclean air (ex. urban air, wildfires) would be beneficial.

The following table gives an overview of potential chemical interferences related to polluted air masses and biomass burning¹. The overview was incorporated into the Supplement of the manuscript (Tab. S2). L85 (former L83) was extended by information referring to the presented table.

Table S2: Overview of potential chemical interferences affecting the measurement performance of the HYPHOP monitor. The overview is based on the information provided by the commercial distributor of the instrument, on which the HYPHOP set up is based (Aero-Laser, Garmisch-Partenkirchen, Germany)¹.

Tropospheric trace gas	Max. expected interference
O₃	30pptv H ₂ O ₂ /100 ppbv
NO	12 pptv H ₂ O ₂ /100 ppbv
PAN	X
NO₂	X
Glyoxal	X
Isobutane	X
Isobutylene	X
1-Butane	X
HCHO	X
Benzene	X
Toluene	X
MeOH	X

¹ <https://www.aero-laser.de/gas-analyzers/h2o2-al2021.html> (last access: 27.07.23)

Acetone	X
Methylamine	X
Dimethylamine	X
n-Butane	X
Cis-2-Butene	X
Trans-2-Butene	X
Iodide	X
Chloride	X
Nitrate	X
Bromide	X
Phosphate	X
Benzoate	X

L85 (former L83) was changed to:

Further chemically driven interferences potentially affecting the instrumental measurement performance are not considered based on the information on the commercially available hydroperoxide monitor AL2021 (Aero-Laser, Garmisch-Partenkirchen, Germany), on which the HYPHOP monitor is based (Tab. S2).

References

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