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

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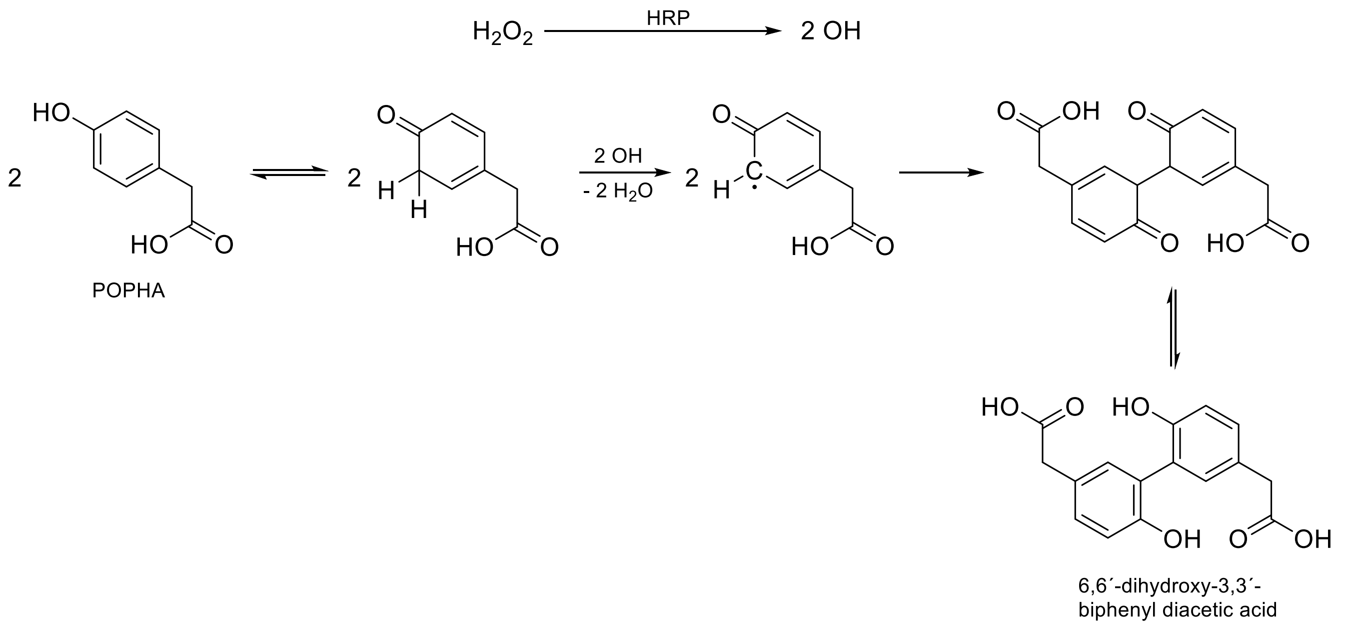
Table S1: Performance comparison of the most common hydroperoxide measurement techniques relative to the HYPHOP monitor (respective performance parameters are based on Kleindienst et al. 1988; Mackay et al. 1990; Staffelbach et al. 1996; Crounse et al. 2006; St Clair et al. 2010; Allen et al. 2022).

	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_2O_2: 20 pptv ROOH: 19 pptv	H_2O_2: 150 ppt$_v$ ROOH: 30 ppt$_v$	H_2O_2: 100 ppt$_v$	H_2O_2: 1–10 pptv MHP: 1–10 pptv
Precision	H_2O_2: 360 pptv ROOH: 210 pptv	H_2O_2: - ROOH: -	H_2O_2: -	H_2O_2: 50 ppt$_v$ MHP: 50 ppt$_v$
Accuracy	H_2O_2: 0.7% ROOH: 0.8%	H_2O_2: - ROOH: -	H_2O_2: 20%	H_2O_2: - MHP: 40%
Total measurement uncertainty (TMU)	H_2O_2: 12% ROOH: 40%	H_2O_2: 20% ROOH: 20%	H_2O_2: 20%	H_2O_2: 35% MHP: 40–80%
Artifacts	O_3 SO_2 Metal ions (NO)	Pollution Particles	none	H_2O $HOCH_2OH$

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
O_3	30 pptv H_2O_2/100 ppbv
NO	12 pptv H_2O_2/100 ppbv
PAN	X
NO_2	X
Glyoxal	X
Isobutane	X
Isobutylene	X
1-Butane	X
HCHO	X
Benzene	X
Toluene	X
MeOH	X
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

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



(SR1)

$$H_2O_2 + \text{catalase}_{red} \rightarrow H_2O + \text{catalase}_{ox} \quad \text{(SR2)}$$

$$H_2O_2 + \text{catalase}_{ox} \rightarrow H_2O + O_2 + \text{catalase}_{red} \quad \text{(SR3)}$$

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2 \quad \text{(SR4)}$$

$$H_2O_2 + 2\,H_2O \rightarrow O_2 + 2\,H_3O^+ + 2\,e^- \quad \text{(SR5)}$$

$$MnO_4^- + 8\,H_3O^+ + 5\,e^- \rightarrow Mn^{2+} + 12\,H_2O \quad \text{(SR6)}$$

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H_3O^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 14\,H_2O \quad \text{(SR7)}$$

$$[H_2O_2] = 5 \cdot \left(\frac{c(KMnO_4) \cdot V(KMnO_4)}{2 \cdot V(H_2O_2)_{STM}}\right);\ [mol \cdot L^{-1}] = \frac{[mol \cdot L^{-1}] \cdot [L]}{[L]} \quad \text{(S1)}$$

$$Q_{Air} = Q_{real} \cdot \frac{T_{std} \cdot p_{real}}{T_{real} \cdot p_{std}};\ [slm] = [L \cdot min^{-1}] \cdot \frac{[K] \cdot [hPa]}{[hPa] \cdot [K]} \quad \text{(S2)}$$

$$Q_{Stripping} = \frac{V_{Stripping}}{t};\ [L \cdot min^{-1}] \quad \text{(S3)}$$

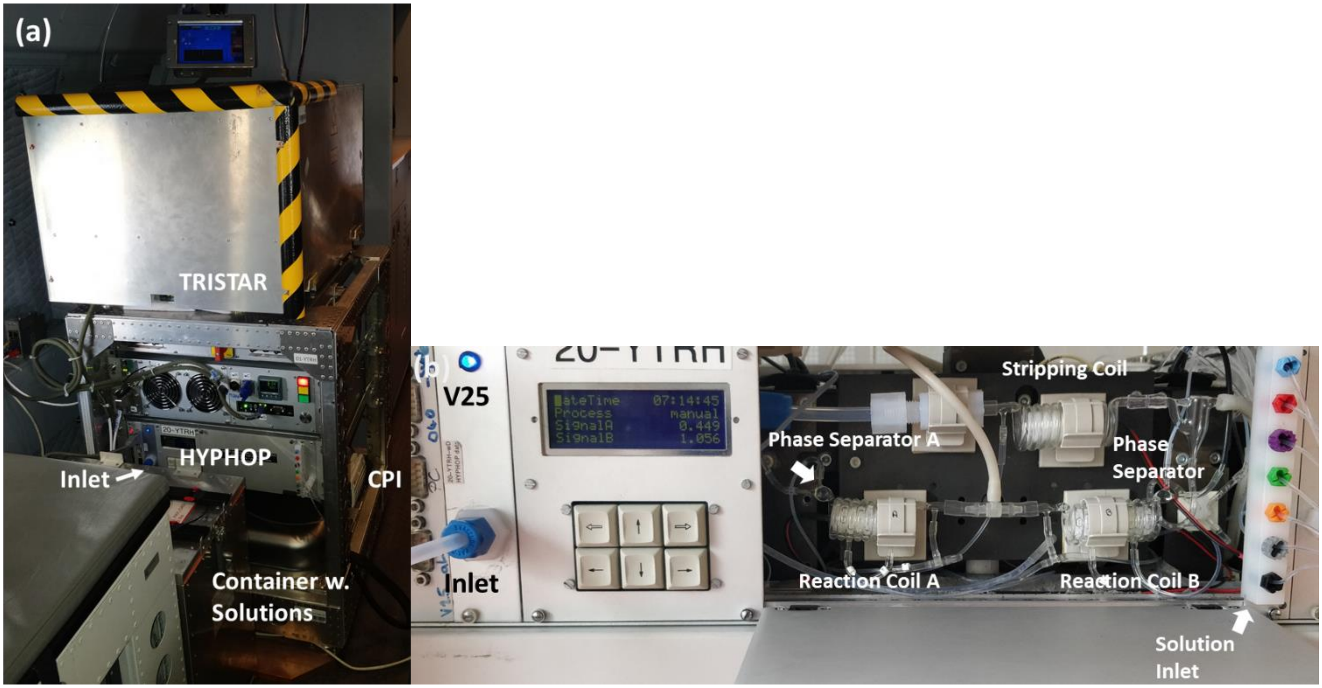


Figure S1: Front view of the measurement rack (a) and the HYPHOP monitor (b).

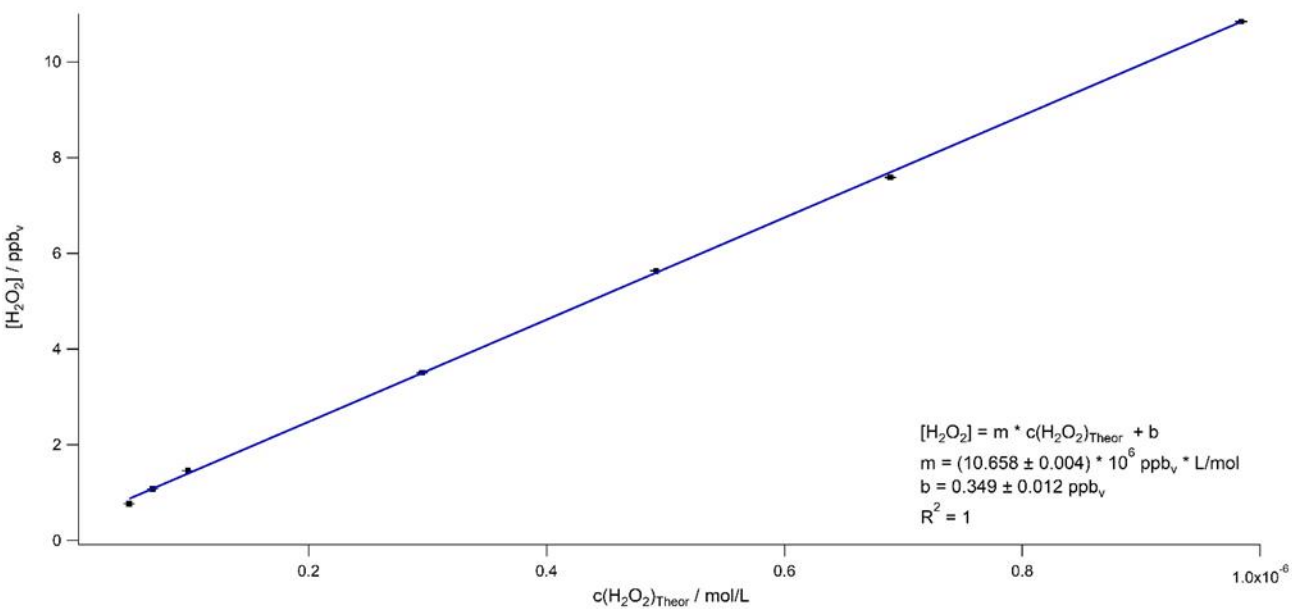


Figure S2: Hydrogen peroxide mixing ratios ([H2O2]) determined using HYPHOP plotted versus the theoretical hydrogen peroxide concentration ($c(H2O2)_{Theor}$) and the resulting linear regression (blue line).

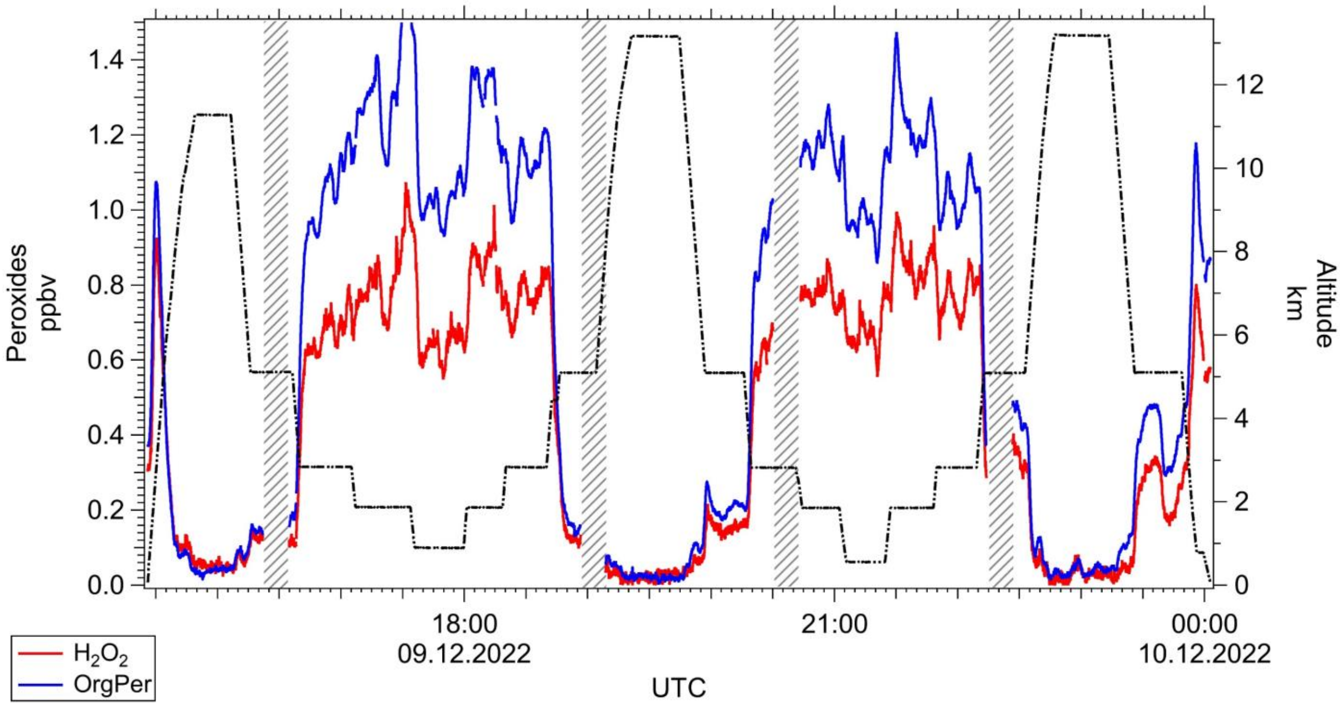


Figure S3: Temporal series of the measured hydroperoxides (H2O2: red; ROOH; dark blue; left plot) in correspondence with the altitude (black; right plot) during an exemplary flight of the CAFE-Brazil campaign performed on 9th December 2022. Dashed lines (black) represent performed background measurements.

$$SO_2 + 2\,H_2O \rightleftharpoons HSO_3^- + H_3O^+ \quad \text{(SR8)}$$

$$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O \quad \text{(SR9)}$$

$$HSO_4^- + H_3O^+ \rightarrow H_2SO_4 + H_2O \quad \text{(SR10)}$$

$$2HSO_3^- + 2CH_3OOH \rightarrow SO_4^{2-} + CH_3SO_4^- + H_2O + CH_3OH + H^+ \quad \text{(SR11)}$$

$$HSO_3^- + CH_3C(O)OOH \rightarrow SO_4^{2-} + CH_3C(O)OH + H^+ \quad \text{(SR12)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- \quad \text{(SR13)}$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad \text{(SR14)}$$

$$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2 \quad \text{(SR15)}$$

$$Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO + OH^- \quad \text{(SR16)}$$

$$SO_2 + 2H_2O \rightarrow HSO_3^- + H_3O^+ \quad \text{(SR17)}$$

$$HSO_3^- + HCHO \rightarrow HOCH_2SO_3^- \quad \text{(SR18)}$$

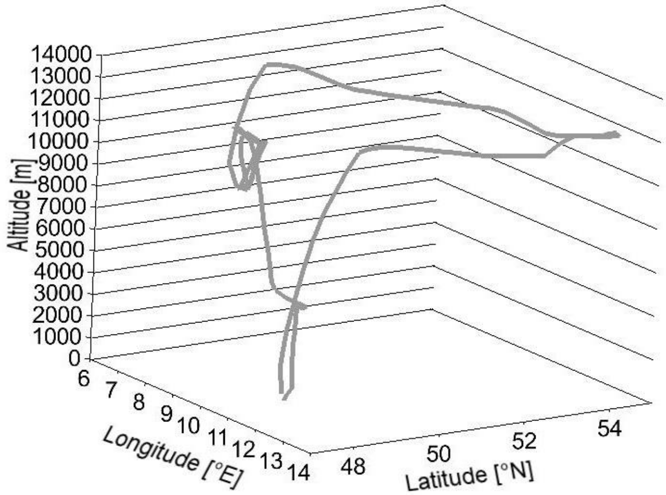


Figure S4: Flight pattern of the research aircraft HALO during the test flight on 22[nd] November 2022.

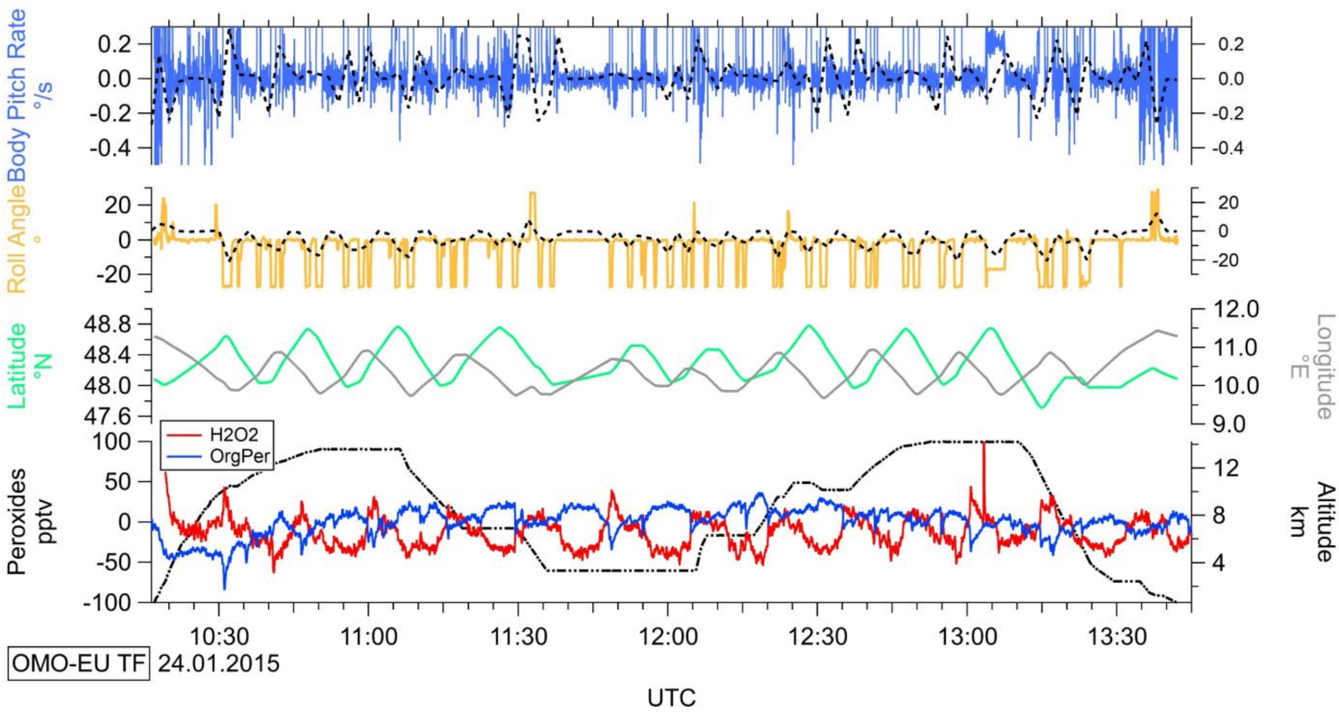


Figure S5: Temporal series of the measured signals in channel A (H_2O_2 + ROOH; red) and B (ROOH; dark blue; bottom plot) in correspondence with the altitude (black), latitude (green), longitude (grey), roll angle (yellow) and body pitch rate (blue; top plot) of the aircraft during an exemplary test flight of the OMO-EU campaign performed on 24[th] January 2015. Dashed lines (black) represent the temporal trends of the roll angle and the body pitch rate based on 2 min bins.

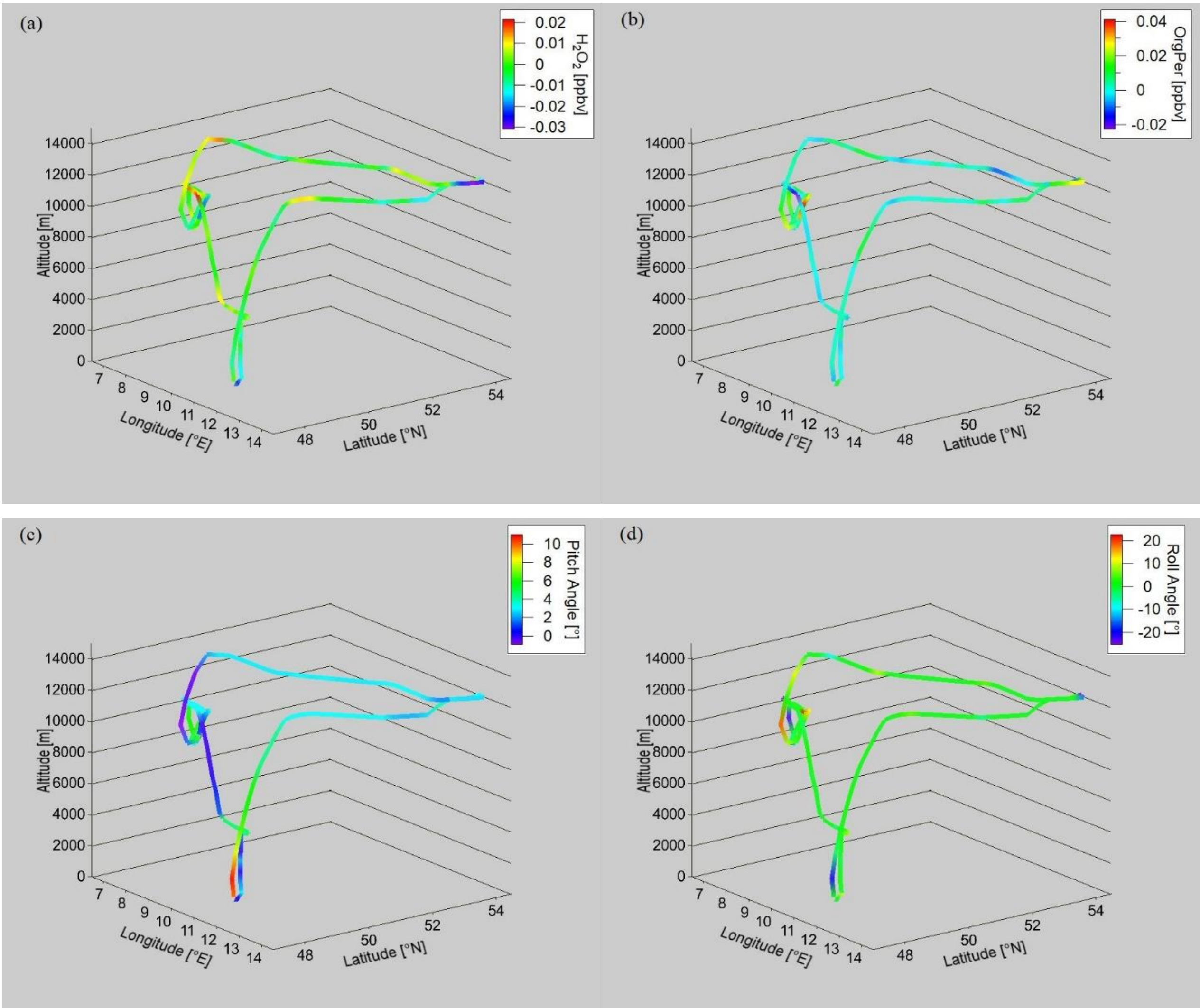


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Figure S6: GPS flight pattern of the research aircraft HALO during the test flight on 22nd November 2022 with respect to the observed background signals (channel A: H_2O_2 + ROOH; (a); channel B: ROOH; (b)), pitch angle (c) and roll angle (d) of the aircraft based on the instrumental time resolution of 2 min.

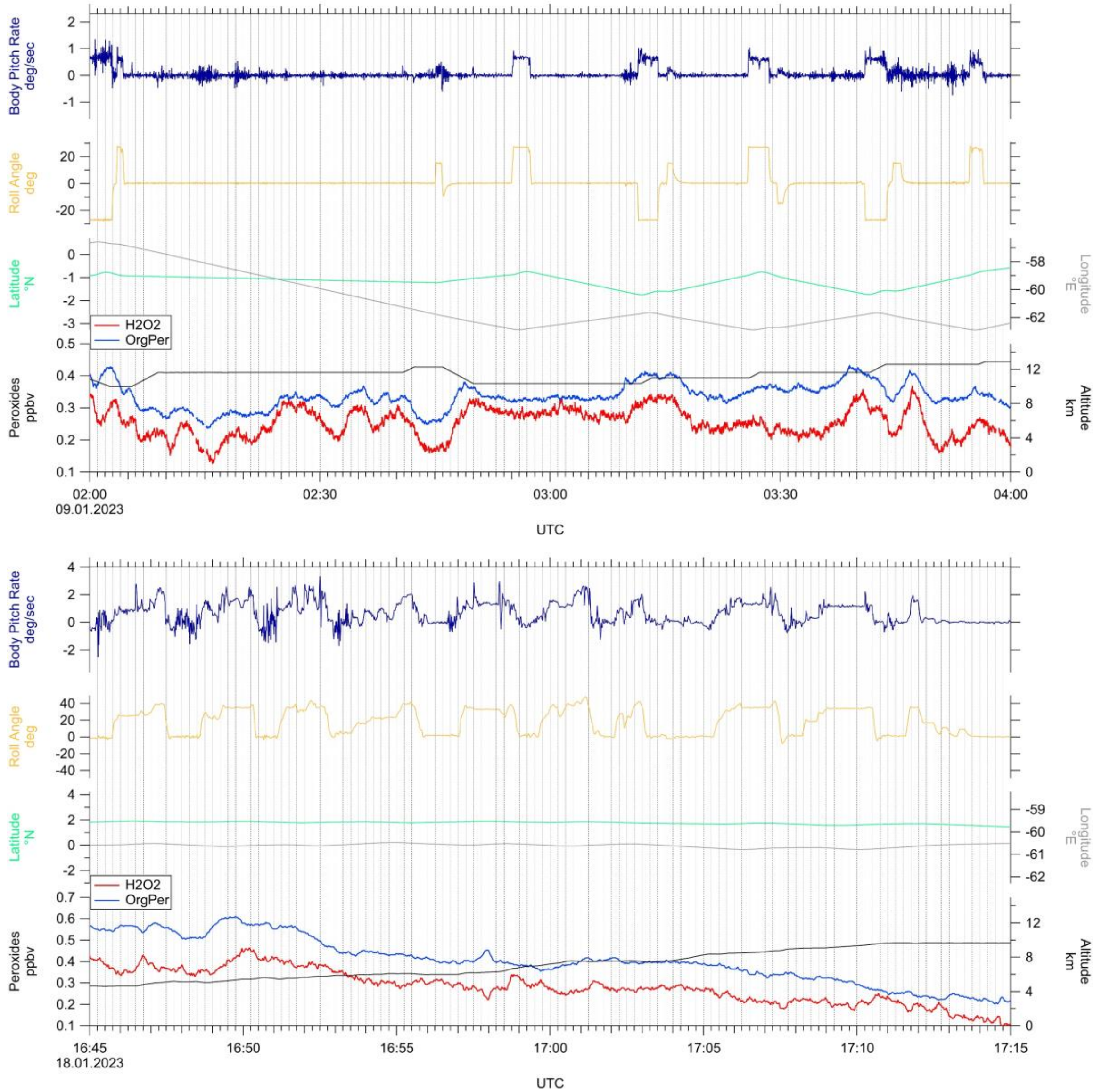

Figure S7: Temporal series of the measured hydrogen peroxide (red) and the sum of organic hydroperoxides (dark blue) in correspondence with the altitude (black), latitude (green), longitude (grey), roll angle (yellow) and body pitch rate (blue) of the aircraft during two exemplary measurement flights RF#13 (top panel) and RF#17 (bottom panel) performed on 9th and 18th January 2023 as a part of the CAFE-Brazil campaign.

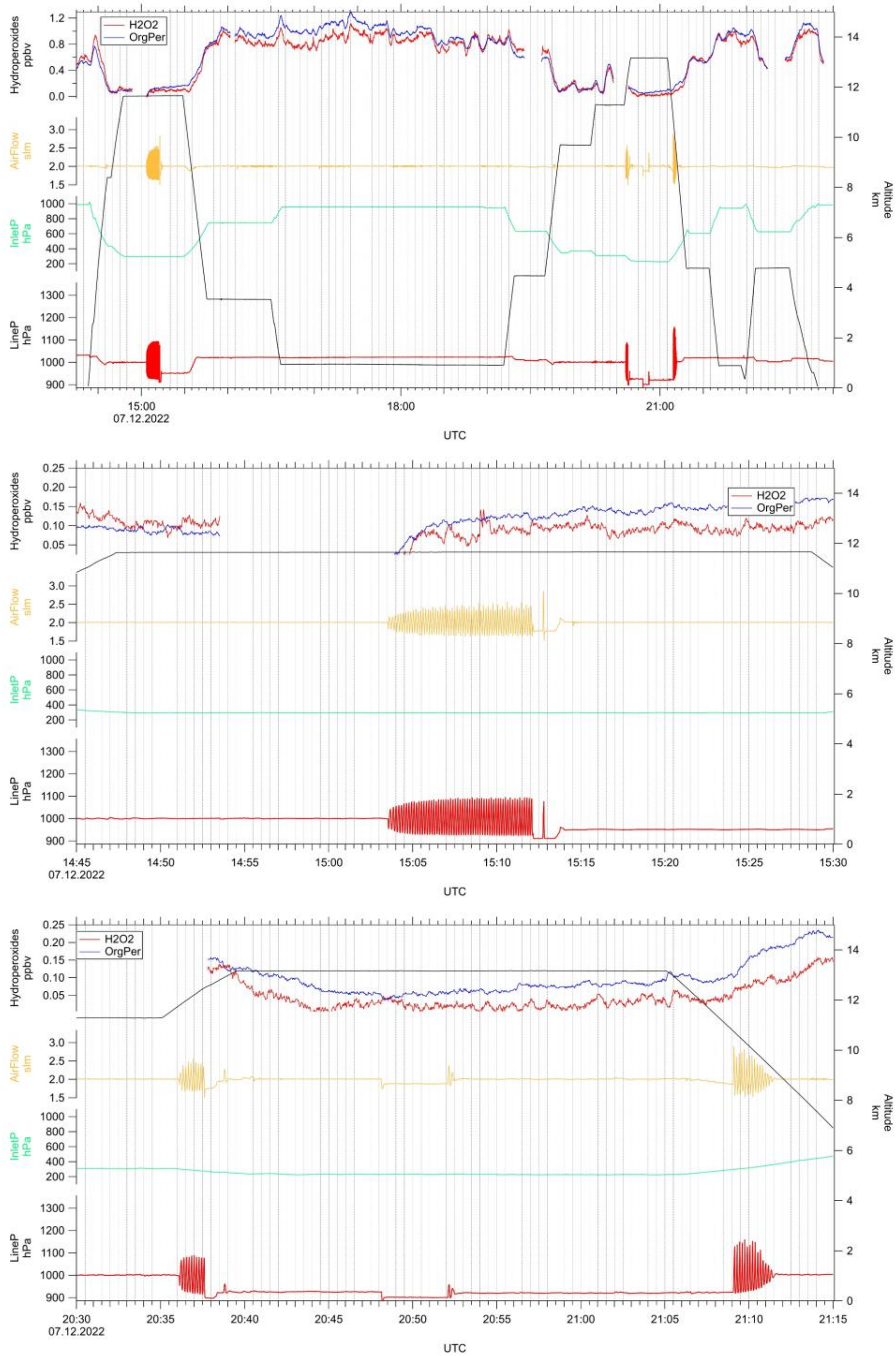

Figure S8: Temporal series of the tracked line pressure (red) complimented by the GPS flight altitude (black), measured inlet pressure (green), the air mass flow (yellow), and hydroperoxide levels (H2O2:red and ROOH: blue) of the aircraft during an exemplary measurement flight of the CAFE-Brazil campaign performed on 12th December 2022 with 1 sec temporal resolution (overview: top panel; detailed insight during high legs: middle and bottom panels).

Table S3: Mean (±1σ) of the estimated time resolution in sec based on the signal rise and fall from 10% to 90% and vice versa assumed to be the lowest temporal limit and the pump time of the flow-through cuvettes assumed as the highest temporal limit of the monitor.

Mean (±1σ) /sec	Calibrations		Background		Convection peaks		Varying LqStd		Cuvettes
Channels	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	
Signal rise	120 (±7.12)	135 (±10.8)	86.3 (±14.4)	88.8 (±16.3)	120 (±61.6)	124 (±59.6)	111 (±23.9)	134 (±21.2)	-
Signal fall	114 (±7.17)	107 (±30.9)	98.3 (±16.2)	99.7 (±16.1)	129 (±56.8)	132 (±53.1)	110 (±7.25)	114 (±8.58)	-
Pump-through	-	-	-	-	-	-	-	-	52.5 (±2.32)
Measurement density	15		70		22		14		4

110 **Table S4: Instrumental precision, limit of detection, temporal resolution and total measurement uncertainty (TMU) of HYPHOP during the airborne campaigns OMO 2015 (Hottmann et al. 2020), CAFE-Africa (Hamryszczak et al. 2022a), BLUESKY 2020 (Hamryszczak et al. 2022b) and CAFE-Brazil 2022/23.**

	OMO 2015	**CAFE-Africa 2018**	**BLUESKY 2020**	**CAFE-Brazil 2022/23**
Precision H_2O_2	0.2% (5.2 ppbv) – 1.3% (5.9 ppbv)	1.3% (5.5 ppbv)	0.3 % (5.1 ppbv)	6.4% (5.7 ppbv)
Precision ROOH	0.3% (5.0 ppbv) – 2.1% (6.0 ppbv)	0.8% (5.6 ppbv)	0.2 % (5.4 ppbv)	3.6% (5.8 ppbv)
LOD H_2O_2	8 – 53 pptv	15 pptv	35 pptv	20 pptv
LOD ROOH	9 – 52 pptv	6 pptv	13 pptv	19 pptv
Time resolution	120 sec	122 sec	120 sec	52.5 – 114 sec
TMU H_2O_2	**25%**	**9%**	**28%**	**12%**
TMU ROOH	**40%**	**41%**	**40%**	**40%**

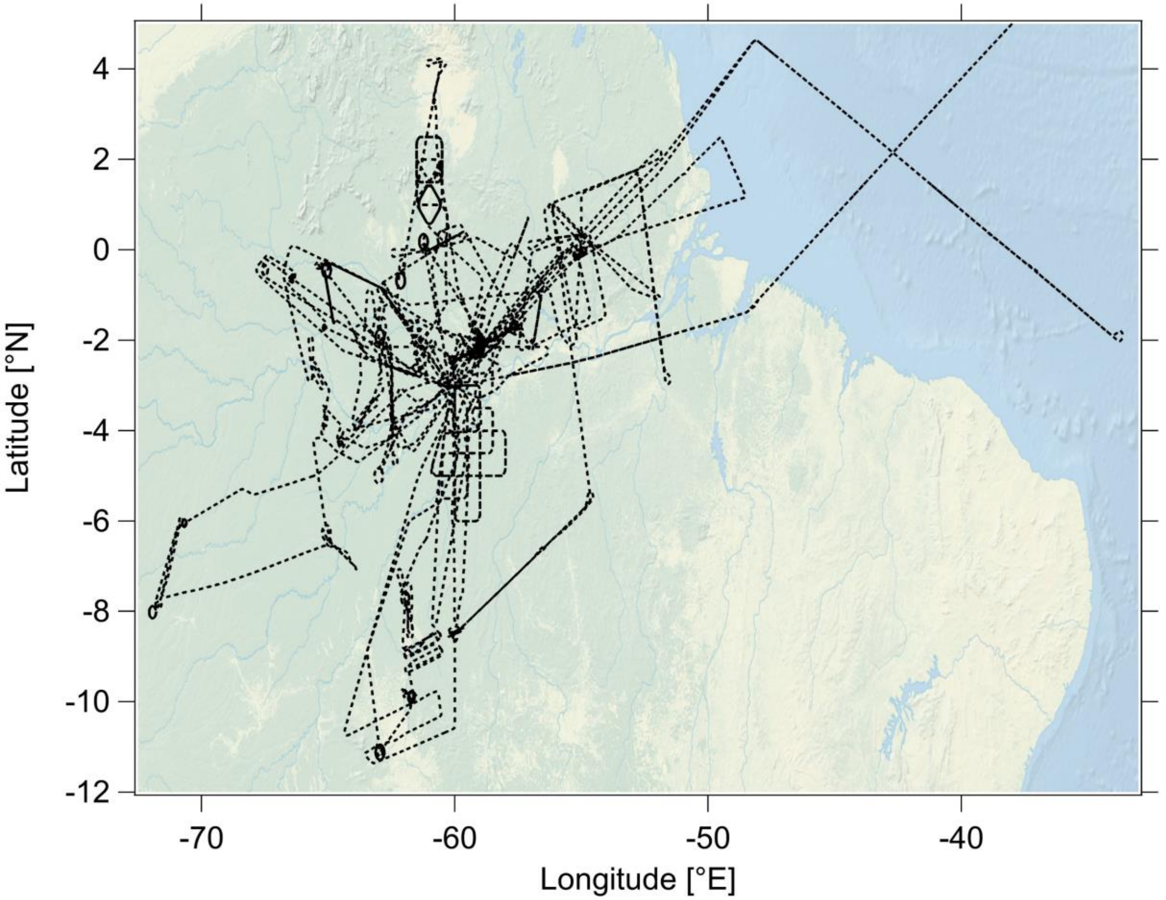

Figure S9: Spatial resolution of the flight tracks during CAFE-Brazil campaign performed in December 2022 and January 2023. Global topography relief raster is based on data set available from WaveMetrics. [2]

Table S5: Mean (±1σ), median and maximum hydroperoxide mixing ratios (ppbv) over the entire tropospheric column (left column) and subdivided into the approximate main tropospheric regions (right).

	Total		**0 < 2 km**		**2 < 8 km**		**≥ 8 km**	
	H_2O_2	**ROOH**	**H_2O_2**	**ROOH**	**H_2O_2**	**ROOH**	**H_2O_2**	**ROOH**
Mean	**0.30**	**0.43**	0.74	0.99	0.45	0.62	0.12	0.22
(±1σ)	**(±0.30)**	**(±0.36)**	(±0.25)	(±0.31)	(±0.26)	(±0.34)	(±0.09)	(±0.12)
Median	**0.17**	**0.28**	0.76	1.00	0.43	0.59	0.10	0.22
Maximum	**1.94**	**1.73**	1.76	1.73	1.94	1.51	0.85	0.85

[2] WaveMetrics, Inc. 10200 SW Nimbus, G-7 Portland , OR 97223.
https://www.wavemetrics.net/Downloads/IgorGIS/GISData/ <last access: 09.06.23023>