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

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$$H_2O_2 + 2 H_2O \rightarrow O_2 + 2 H_3O^+ + 2 e^-$$
 (SR5)

$$MnO_{4}^{-} + 8 H_{3}O^{+} + 5 e^{-} \rightarrow Mn^{2+} + 12 H_{2}O$$
(SR6)

$$2 \operatorname{MnO}_{4}^{-} + 5 \operatorname{H}_{2}\operatorname{O}_{2}^{-} + 6 \operatorname{H}_{3}\operatorname{O}^{+} \to 2 \operatorname{Mn}^{2+} + 5 \operatorname{O}_{2}^{-} + 14 \operatorname{H}_{2}\operatorname{O}^{-}$$
(SR7)

 $c(H_2O) = 5 \cdot \left(\frac{c(KMnO_4) \cdot V(KMnO_4)}{2 \cdot V(H_2O_{2)}_{STM}}\right)$ (S1)

$$Q_{Air} = Q_{real} \cdot \frac{T_{std} \cdot p_{real}}{T_{real} \cdot p_{std}}$$
(S2)

$$Q_{\text{Stripping}} = \frac{V_{\text{Stripping}}}{t}$$
(S3)



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

	$SO_2 + 2 H_2 O \rightleftharpoons HSO_3^- + H_3 O^+$	(SR8)
	$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O$	(SR9)
50	$\mathrm{HSO}_{4}^{-} + \mathrm{H}_{3}\mathrm{O}^{+} \rightarrow \mathrm{H}_{2}\mathrm{SO}_{4} + \mathrm{H}_{2}\mathrm{O}$	(SR10)
	$HSO_3^- + CH_3OOH \rightarrow SO_4^{2-} + CH_3SO_4^- + H_2O + CH_3OH + H^+$	(SR11)
	$HSO_3^- + CH_3C(0)OOH \rightarrow SO_4^{2-} + CH_3C(0)OH + H^+$	(SR12)

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

(0D14)

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$$OH + H_2O_2 \rightarrow H_2O + HO_2$$
 (SR14)  
 $HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$  (SR15)

$$F_{0}^{2+} + POOH \rightarrow F_{0}^{3+} + PO + OH^{-}$$
(SP16)

$$SO_2 + 2H_2O \rightarrow HSO_3^- + H_3O^+$$
 (SR17)

$$60 \quad \text{HSO}_3^- + \text{HCHO} \rightarrow \text{HOCH}_2\text{SO}_3^- \tag{SR18}$$



Figure S2: Flight pattern of the research aircraft HALO during the test flight on 22<sup>nd</sup> November 2022.



65 Figure S3: Temporal series of the measured signals in channel A (H<sub>2</sub>O<sub>2</sub> + 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<sup>th</sup> January 2015. Dashed lines (black) represent the temporal trends of the roll angle and the body pitch rate based on 2 min bins.



Figure S4: GPS flight pattern of the research aircraft HALO during the test flight on 22<sup>nd</sup> November 2022 with respect to the observed background signals (channel A: H<sub>2</sub>O<sub>2</sub> + 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 S5: 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 9<sup>th</sup> and 18<sup>th</sup> January 2023 as a part of the CAFE-Brazil campaign.



Figure S6: 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 12<sup>th</sup> December 2022 with 1 sec temporal resolution (overview: top panel; detailed insight during high legs: middle and bottom panels).

Table S1: Mean  $(\pm 1\sigma)$  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	Α	В	Α	В	A	В	Α	В	
Signal rise	120	135	86.3	88.8	120	124	111	134	
	(±7.12)	(±10.8)	(±14.4)	(±16.3)	(±61.6)	(±59.6)	(±23.9)	(±21.2)	-
Signal fall	114	107	98.3	99.7	129	132	110	114	
	(±7.17)	(±30.9)	(±16.2)	(±16.1)	(±56.8)	(±53.1)	(±7.25)	(±8.58)	-
Pump-through									52.5
	-	-	-	-	-	-	-	-	(±2.32)
Measurement	15		70		22		14		4
density									+

Table S2: 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.

	ОМО 2015	CAFE-Africa 2018	BLUESKY 2020	CAFE-Brazil 2022/23	
Precision H <sub>2</sub> O <sub>2</sub>	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 <sub>2</sub> O <sub>2</sub>	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 <sub>2</sub> O <sub>2</sub>	25%	9%	28%	12%	
TMU ROOH	40%	41%	40%	40%	

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Figure S7: 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.<sup>1</sup>

	Table S3: Mean $(\pm 1\sigma)$ , median and maximum hydroperoxide mixing ratios (ppbv) over the entire tropospheric column (left column)
105	and subdivided into the approximate main tropospheric regions (right).

	Total		0 < 2 km		2 < 8 km		≥8 km	
	H <sub>2</sub> O <sub>2</sub>	ROOH	H <sub>2</sub> O <sub>2</sub>	ROOH	H <sub>2</sub> O <sub>2</sub>	ROOH	H <sub>2</sub> O <sub>2</sub>	ROOH
Mean	0.30	0.43	0.74	0.99	0.45	0.62	0.12	0.22
(±1σ)	(±0.30)	(± <b>0.36</b> )	(±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

<sup>&</sup>lt;sup>1</sup> WaveMetrics, Inc. 10200 SW Nimbus, G-7 Portland, OR 97223.

https://www.wavemetrics.net/Downloads/IgorGIS/GISData/ <last access: 09.06.23023>