Supplement of

Aircraft Observations of Biomass Burning Pollutants In the Equatorial Lower Stratosphere over the Tropical Western Pacific During Boreal Winter

Jasna V. Pittman et al.

Correspondence to: Jasna V. Pittman (jasna@g.harvard.edu)

S1. HUPCRS Description

The Harvard University Picarro Cavity Ringdown Spectrometer (HUPCRS) consists of a G2401-*m* Picarro gas analyzer (Picarro Inc., Santa Clara, CA, USA) repackaged in a temperature-controlled pressure vessel, a separate calibration system with two multi-species gas standards, and an external pump and pressure control assembly designed to allow operation at a wide range of altitudes (see Fig. S1). The Picarro analyzer uses Wavelength-Scanned Cavity Ringdown Spectroscopy technology (Crosson, 2008; Rella et al., 2013; Chen et al., 2013).

Briefly, the analyzer uses three distributed feedback diode lasers in the spectral region of 1.55 – 1.65 micron. Monochromatic light is injected into a high-finesse optical cavity with a volume of 35 cc and a three highly reflective mirror (>99.995%) configuration. Internal control loops keep the cavity at 140 +/- 0.02 Torr and 45 +/- 0.0005^{o} C in order to stabilize the spectra. The injected light is blocked periodically and when blocked, the exponential decay rate of the light intensity is measured by a photodetector. The decay rate depends on loss mechanisms within the cavity such as mirror losses, light scattering, refraction, and absorption by a specific analyte. A sequence of specific wavelengths for each molecule is injected into the cavity in order to reconstruct the absorption spectra. A fit to the spectra is performed in real time and mixing ratios are derived based on peak height. High-altitude sampling (i.e., very low pressure and temperature) required transferring the core components of the Picarro analyzer to a sealed tubular pressure vessel, which is maintained at 35^{o} C and 760 Torr. The analyzer's components are isolated from the pressure vessel to provide vibration damping and decoupling from deformations in the pressure vessel caused by external pressure changes.

The sampling strategy for HUPCRS consists of bringing in air through a rear-facing inlet, filtered by a 2 μm Zefluor membrane, and dehydrating this air by flowing it through a multi-tube Nafion dryer followed by a dry-ice cooled trap prior to entering the Picarro analyzer. While the analyzer does measure H_2O, this trace gas is not reported given that it is removed from the sample. This removal serves multiple purposes: to avoid the spectral interference in the IR, to reduce dilution effects in the sample, and to eliminate dry/wet transitions in sample lines during in-flight calibrations. A choked upstream Teflon-lined diaphragm pump delivers ambient air to the analyzer at 400 Torr, regardless of aircraft altitude, via a flow bypass. A similar downstream pump, with an inlet pressure of 10 Torr, facilitates flow through the analyzer at high altitude and ensures adequate purging of the Nafion dryer. Measurement accuracy and stability during flight are monitored by performing periodic calibrations, which consist of replacing ambient air with air from two multi-tracer gas standards (low- and high-span) every 30 minutes. Each gas standard is sampled for two minutes. These standards are contained in 8.4 L carbon fiber wrapped aluminum cylinders and housed in a temperature-controlled enclosure. The total weight of the package is 170 lbs.

The nature of Global Hawk operation (e.g., remotely controlled, long hours and long range) required development of sophisticated software for communication between the aircraft and each instrument and between instruments and the ground. HUPCRS-specific software was developed to provide real-time data transfer to the aircraft and the ground (mixing ratio and house-keeping variables), instrument control for power on/off and capability of remote instrument access for optimizing core codes for optimal performance during flight.

HUPCRS is calibrated both during flight and on the ground. Ground calibrations of the flight instrument and the two flight standards are performed before and after each deployment. Each flight standard contains a dry mixture of either all-low or all-high CO_2, CH_4, and CO mixing ratios, which are carefully chosen to bracket the ambient mixing ratios encountered during flight. All standards are referenced to scales set at the Global Monitoring Laboratory at the National Oceanic and Atmospheric Administration, which serves as the World Meteorological Organization Central Calibration Laboratory (https://gml.noaa.gov/ccl/scales.html). For ATTREX, HUPCRS data are referenced to the WMO-CO_2-X2007 scale, with an accuracy of 0.1 ppmv, WMO-CH_4-X2004A scale with an accuracy of 2 ppbv, and WMO-CO-X2014A scale with an accuracy of 0.5 to 0.7 ppbv between 50 and 150 ppbv.

The HUPCRS dataset consists of CO_2 and CH_4 for ATTREX-2 and CO_2, CH_4, and CO for ATTREX-3. During extreme temperature testing for flight certification prior to ATTREX-2, unexpected backward flow from the pump caused contamination of the optical cavity, decreasing the precision for CO_2 and CH_4 and deeming the CO signal unrecoverable. After ATTREX-2, we replaced the entire optical cavity and achieved improved precisions during flight. Figures S2 and S3 show examples of instrument performance during selected ATTREX-2 and ATTREX-3 flights, respectively.

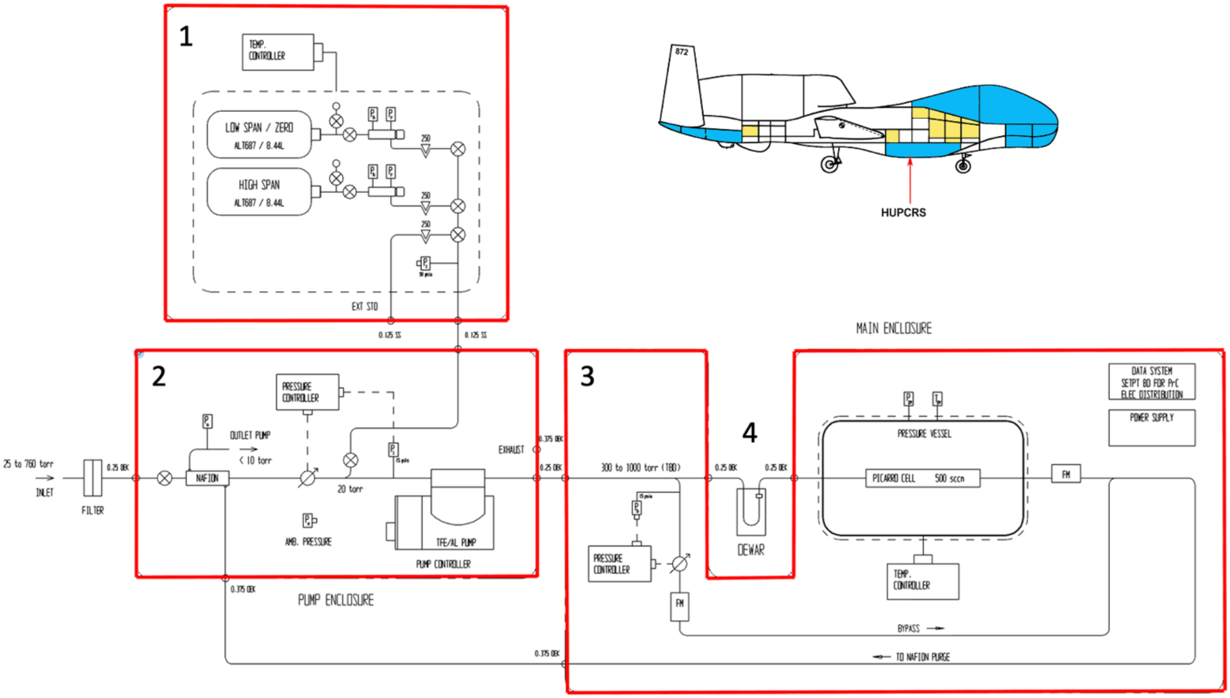

Figure S1: HUPCRS schematics and location on the Global Hawk. The instrument package consists of: 1- calibration system, 2- external pump and pressure-control assembly, 3- repackaged G2401-m Picarro analyzer in a temperature-controlled pressure vessel, and 4- dry ice cold trap.

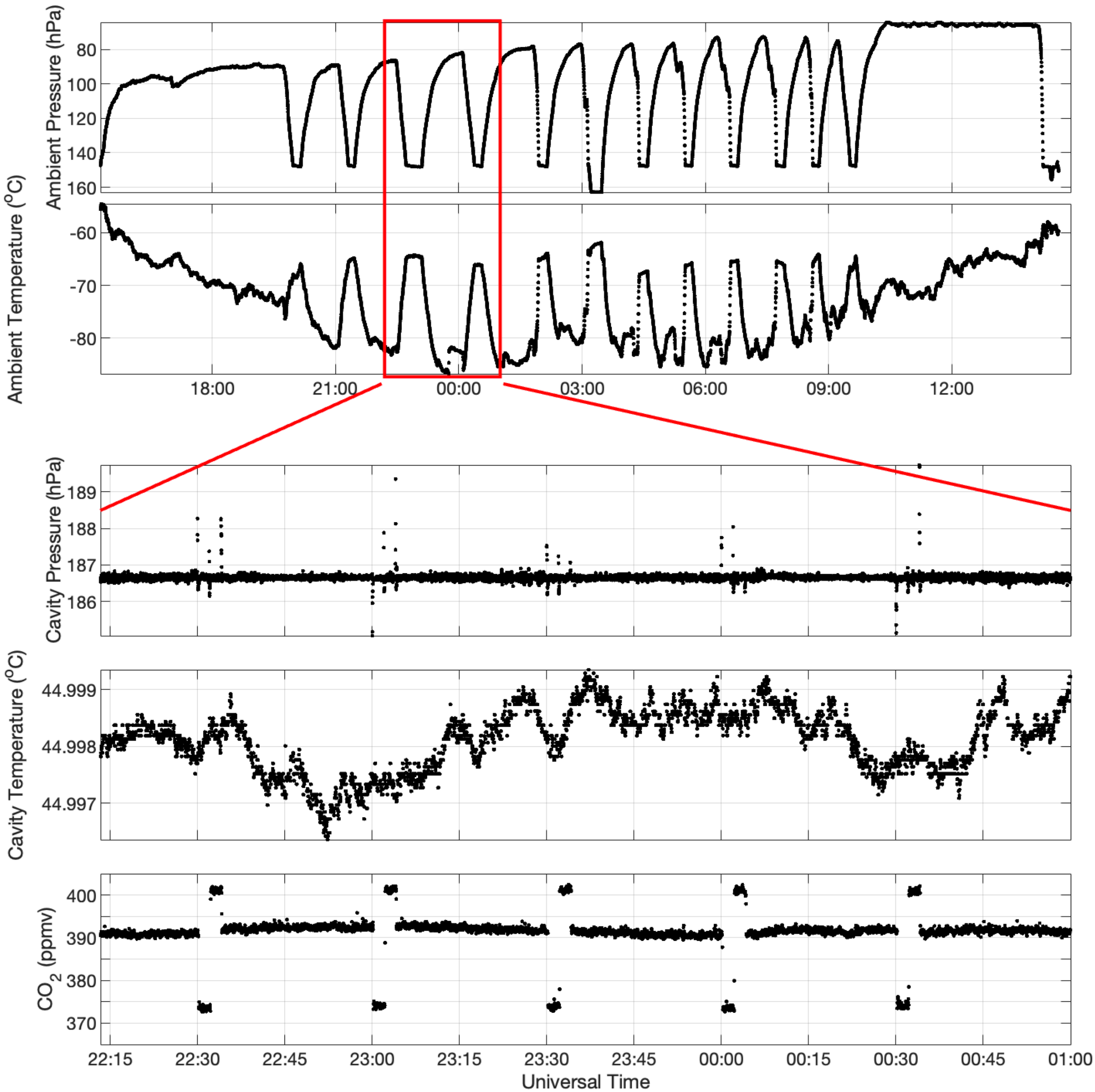

Figure S2. In-flight instrument performance during the 24.5-hour Southern Survey flight on 20130221 (ATTREX-2). Top two panels are ambient pressure and temperature. Bottom three panels are a 2.7-hr flight segment around the coldest ambient temperatures encountered during flight. Note the remarkable stability of the Picarro's cavity pressure and temperature and the 30-min cycling of calibration gases.

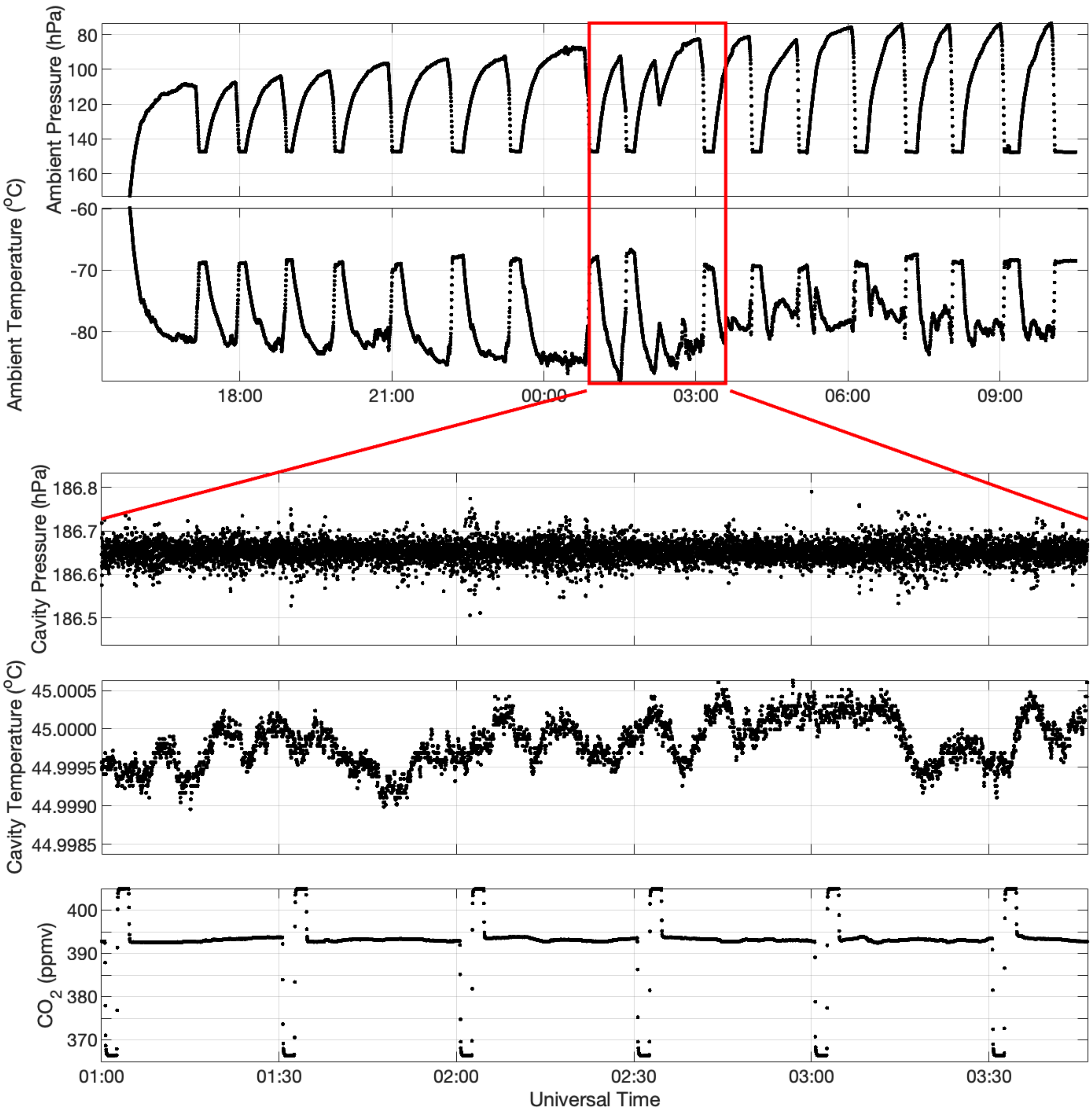

Figure S3. In-flight instrument performance during the 19.7-hour Southern Survey flight on 20140309 (ATTREX-3). Top two panels are ambient pressure and temperature. Bottom three panels are a 2.7-hr flight segment around the coldest ambient temperatures encountered during flight. Note improved Picarro cavity pressure and temperature stability as well as CO_2 precision compared to ATTREX-2 (Fig. S2).

S2. Aircraft and satellite comparisons

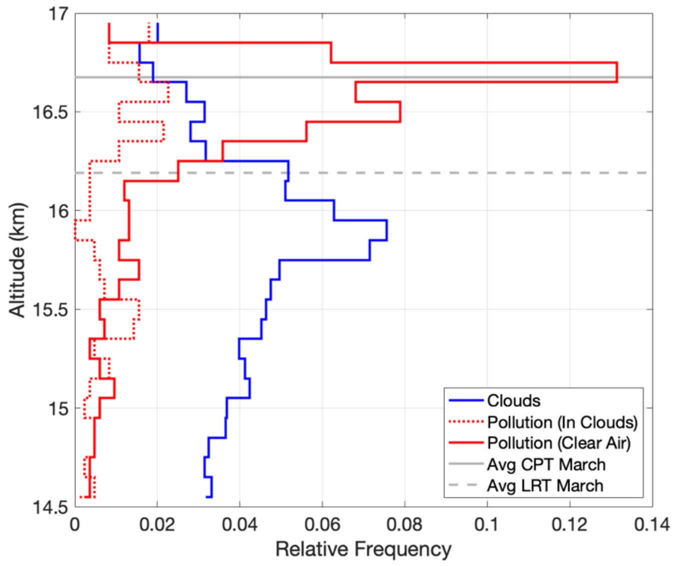

Figure S4. Histograms of observed pollution plumes and clouds in the tropical UT/LS in the deep tropics (12° S–15° N) over the tropical western Pacific in March 2014. Clouds are defined as ice water content greater than 5 ppmv. Pollution plumes are defined as CO greater than the 80th percentile within each latitude bin (see text for bin definitions).

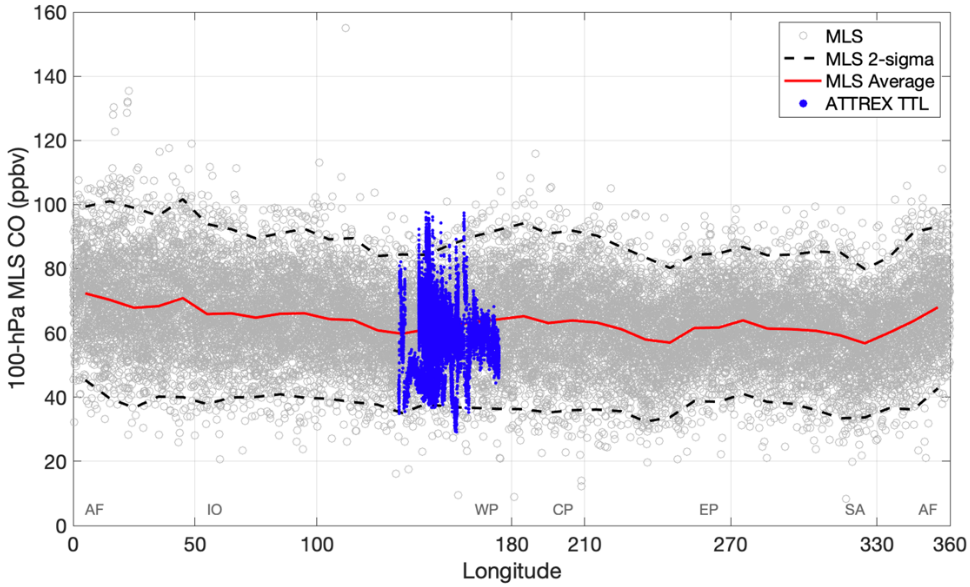

Figure S5. Aircraft (blue) and 100-hPa satellite observations from MLS (gray) of CO across the deep tropics (15º S–15º N) in February-March 2014. The aircraft data shown are between 80 and 140 hPa, the layer equivalent to the vertical resolution of the 100-hPa MLS CO retrieval. Longitudes are grouped by geographical areas: AF (Africa, 0-50º E, 345-360º E), IO (Indian Ocean, 50-100º E), WP (Western Pacific, 100-180º E), CP (Central Pacific, 180-210º E), EP (Eastern Pacific, 210-270º E), and SA (South America, 270-330º E).

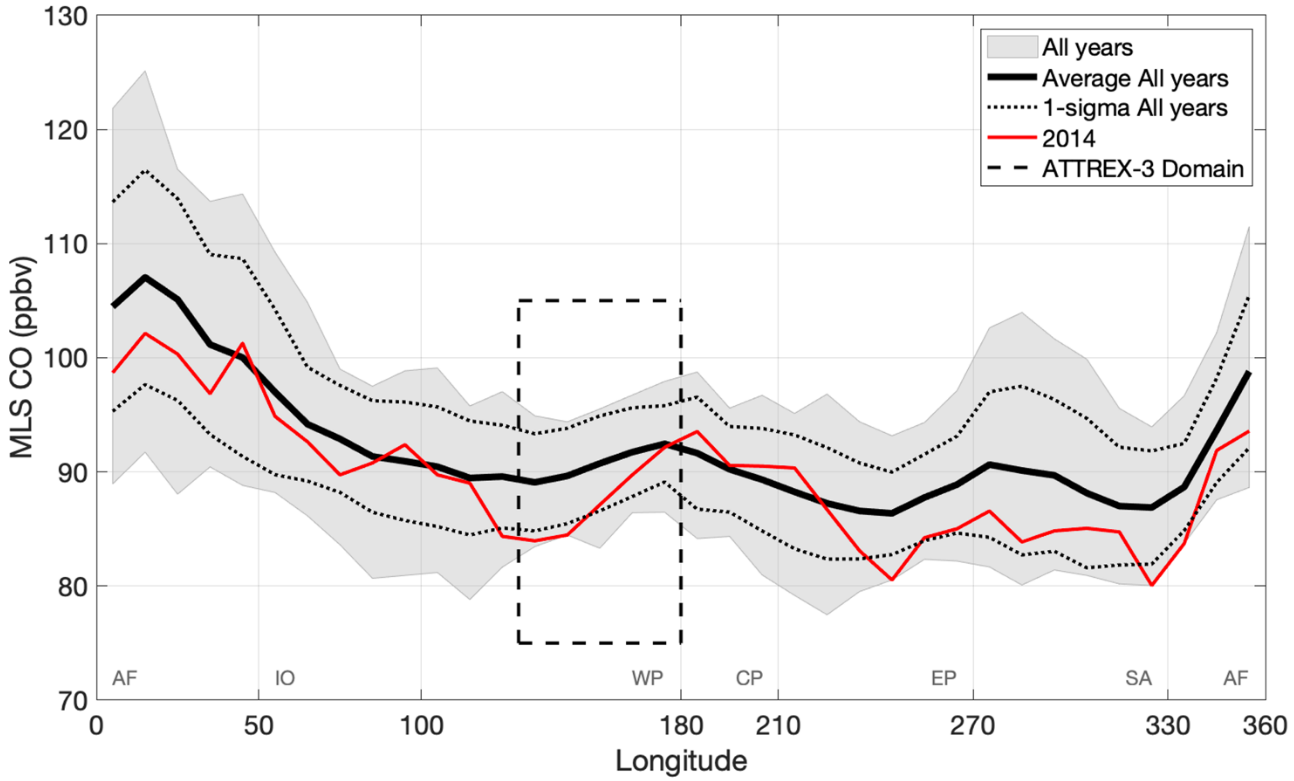

Figure S6. Ten-year record for extreme MLS CO at 100 hPa between 2010 and 2020, across the deep tropics (15^{o} S–15^{o} N), in February-March (Julian Days = 40-70). Extreme CO is defined as CO + 2 standard deviations. The red line corresponds to 2014, the year of the ATTREX-3 campaign. The maximum CO at 100 hPa is consistently found over Africa. Longitudes are grouped by geographical areas: AF (Africa, 0-50^{o} E, 345-360^{o} E), IO (Indian Ocean, 50-100^{o} E), WP (Western Pacific, 100-180^{o} E), CP (Central Pacific, 180-210^{o} E), EP (Eastern Pacific, 210-270^{o} E), and SA (South America, 270-330^{o} E).

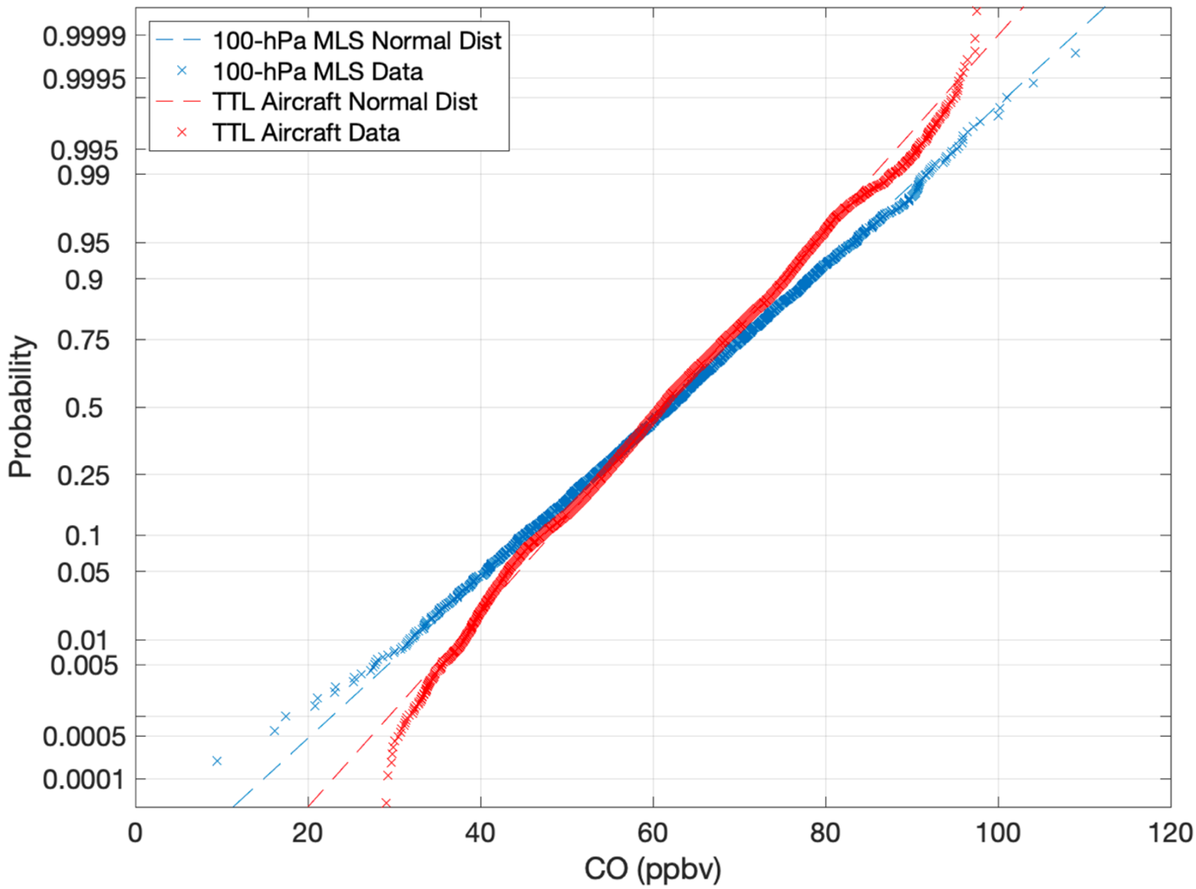

Figure S7. Normal probability plot comparing data and theoretical normal distributions for aircraft measurements from ATTREX-3 (red) and satellite observations from MLS (blue) over the TWP (130–180° E) in middle February – middle March 2014. At extreme values (CO>85 ppbv), the Kolmogorov-Smirnov test at the 95 % C.I. reveals that satellite observations are not statistically different from a normal distribution, while aircraft data depart from a normal distribution. These results indicate that the extreme high values are considered noise in the satellite data, but signal in the aircraft data.