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Supplementary Material for "Substantial increases in Eastern Amazon and Cerrado biomass burning-sourced ozone: Impacts on regional air quality"

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Supplementary Material (SM 1): Satellite Data

Anomalous *Fire Activity Years*

Precipitation data from the Tropical Rainfall Measuring Mission (TRMM) satellite, has suggested that 2005, 2007, 2010 and 2015 can be classed as extreme drought/anomalous fire (ED-AF) years where fire activity is enhanced across the western Amazon (Reddington et al., 2015; Aragäo et al., 2014). We undertook a similar approach to identify ED-AF years in the eastern Amazon (see defined region in **Figure SM1:** 40-60°W, 0-20°S), but did not find such a significant or distinct signal in this region. The correlation between precipitation and fire activity was also weaker in our study area. Therefore, as fire activity predominantly controls regional pollution, we used the GFED and GFAS datasets to identify ED-AF years. **Figure SM1** shows the ASO standardised anomalies for both fire products. ED-AF years where identified when the standardised anomalies of either product was greater than 1.0 standard deviations (top dashed blue line). This resulted in 2005, 2007, 2010 and 2012 being classified as ED-AF years and excluded from any trend analysis. We experimented with the size/shape of the domain to test whether 2015 should also be included as an ED-AF year, but at no point did either products' standardised anomaly reach 1.0 standard deviation.

Artificial Background NO_2 Trends

$TCNO_2$ from OMI has been subject to the OMI row anomaly (reduced quality of the radiance data at all wavelengths for a particular viewing angle; KNMI, 2012) for the latter years of the data record. This row anomaly, though partially filtered out using the product quality flags (Braak, 2010) provided, still yields "striping" issues with the data, especially in later years. This is when background $TCNO_2$ is artificially increased, which is evident in the biomass burning season (ASO) as seen in **Figure**

SM2a (2006), **b** (2009) and **c** (2014). Over the Amazon the artefact is more difficult to detect, but over the Pacific Ocean and north-western South America the data is becoming noisier with time and clear data "stripes" occur. When a linear least squares trend is calculated in the ASO mean 2005-2016 $TCNO_2$ time-series, there are positive (0.05-0.1 ×10^{15} molecules/cm^2/year, **Figure SM2d**) $TCNO_2$ trend regions with no or limited NO_x (nitrogen oxides, NO+NO_2) sources (i.e. over the ocean). This strongly suggests an artificial instrument space and time-dependent issue yielding false positive background $TCNO_2$ trends. To remove these artificial trends from the domain, the average background ASO 2005-2016 $TCNO_2$ percentage trend was calculated in each of the blue boxes (**Figure SM2d)** and then spatially interpolated across the entire domain. The top-left box is not directly in the corner of the domain as source regions exist there. The blue dashed contour lines represent the estimated size of the artificial background trend. This 2-D background trend field was then used to de-trend all OMI $TCNO_2$ time-series (i.e. one time series per grid box) in the domain yielding more robust trends shown in **Figure 2c** of the main manuscript. Background regions where the OMI row anomaly introduced excessively large artificial trends (i.e. grid boxes where $TCNO_2$ is less than 1.5 ×10^{15} molecules/cm^2 and has a positive trend greater than 5%) where removed from the analysis.

SM 2: TOMCAT Ozone (O_3) Evaluation

Surface Observations

Surface observations of O_3 (blue) are from Manaus (60.2°W, 2.6°S) in the Amazon and compared with the TOMCAT model (red) in **Figure SM3.** This site is representative of background Amazon conditions with data between 2010 and 2011 covering all months (**Figure SM3**). There is a clearly defined O_3 seasonal cycle with minimum (4-6 ppbv) concentrations from January to May and peak (13-15 ppbv) concentrations in August/September. The model reproduces this seasonal cycle, but is less well defined as it overestimates the observations by 7-8 ppbv between January and May. However, there is overlap between the model and observational variability (standard deviations). In the biomass burning season (ASO) the model is in good agreement peaking at 15 ppbv. From June-December, the model seasonal cycle sits within the observational variability and successfully reproduces the Manaus O_3 concentrations.

SAMBBA Aircraft Observations and Ozonesondes

NO_2 and O_3 aircraft (out of plume) data from The South AMerican Biomass Burning Analysis (SAMBBA; Darbyshire et al., 2019) campaign (September-October, 2012) have been averaged spatially to produce regional vertical profiles (**Figure SM4**). Here model output was co-located in time and space to the aircraft observations before both data sets were averaged into vertical profiles. In the lower troposphere, the model successfully reproduces the seasonal-regional aircraft O_3 profile (left panel) ranging from 30 ppbv near the surface to 50 ppbv at 2 km. At 2-3 km and above 4 km, TOMCAT underestimates (~10-15 ppbv) the SAMBBA O_3 profile. The model underestimation above 4 km is consistent with comparisons to ozonesondes at Natal for 2008 (**Figure SM5**). The nearest ozonesonde data, provided by the SHADOZ project, to the Amazon is from the Natal site and only available for 2007-2008. The model also underestimates O_3 (by 15-20 ppbv) at 600-400 hPa (approximately 4-6 km). The model chemical tropopause (i.e. altitude at which O_3 = 100 ppbv) is too low in the model (around 250 hPa) where the model overestimates the observations by 30-35 ppbv. However, in the boundary layer, the model and ozonesonde profiles have reasonable agreement.

For a global model, TOMCAT performs reasonably well in capturing the observed NO_2 vertical profile. Global models typically struggle to reproduce NO_2 observations given the short NO_x lifetime and their coarse horizontal/vertical resolutions (Monks et al., 2017). Near the surface, the model underestimates by 0.05-0.07 ppbv but this is within the observational variability. In the lower troposphere (1-3 km), the model successfully captures the observational profile shape, but the model low bias (0.05 ppbv) is outside the observational variability range.

Overall, the TOMCAT model successfully captures the Amazon O_3 seasonality and absolute concentrations in the lower troposphere. This provides us with sufficient confidence in the model's O_3 simulations used in the main manuscript to investigate long-term changes in surface O_3 and the corresponding health impacts.

SM 3: TOMCAT O_3 Seasonality and Trends

Seasonality

Peak model-simulated surface O_3 occurs in ASO and reaches over 50 ppbv in the central Amazon (**Figure SM6**) during the biomass burning season. Minimum concentrations are in December-April over north-western South America. Throughout the year, O_3 production is simulated from the large Brazilian cities (e.g. Rio de Janeiro) ranging from ~30 ppbv in May to ~40 ppbv in September. Between November-April, there is clear outflow of O_3 from the central African fires entering the top-right of the domain (30-40 ppbv). However, between July and October, O_3 produced from southern African fire activity dominates concentrations over the South Atlantic (25-35 ppbv).

When South American fire emissions are switched off (TOMCAT "fire-off" simulation, **Figure SM7**) there is a small decrease in surface O_3 (several ppbv) between November-June. However, in July-October there is a large drop in O_3 concentrations over the Amazon with peak reductions (20-30 ppbv) in September. As no fire precursor gases are emitted there is no excess O_3 formation during the ASO season. In **Figure SM8**, Eastern Brazil (red) and Wider Amazon Region (blue) (see boxed area in **Figure 4d** of the main manuscript) seasonal cycles show enhanced domain-average surface O_3 (20-30 ppbv) in July-October (top panel). When fire emissions are switched off (middle panel), there is no seasonality with concentrations of 15-16 ppbv. The fire emission contributions to average surface O_3 (bottom) is approximately 0-1 ppbv from January to June in both domains. However, in August and September, fire emission contributions jump to 10-11 ppbv in the Amazon Region. Over Eastern Brazil, the peak O_3 contributions are 12-14 ppbv in ASO.

Surface Trends

Figure 4a & b of the main manuscript show significant (90% confidence level; 90%CL) trends in TOMCAT model ASO average surface NO_2 and O_3 concentrations between 2005 and 2016. To investigate whether pollutant trends were qualitatively similar to OMI $TCNO_2$ trends (**Figure 2c** of the main manuscript), average regional trends (black box region in **Figure 2a** of the main manuscript) were calculated over the Cerrado Region. Here, significant (90%CL) positive trends (**Figure SM9**) are found when the ED-AF years (2005, 2007, 2010 and 2012 – hollow circles) are removed from the analysis, supporting the satellite observed trends.

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Supplementary Figures:

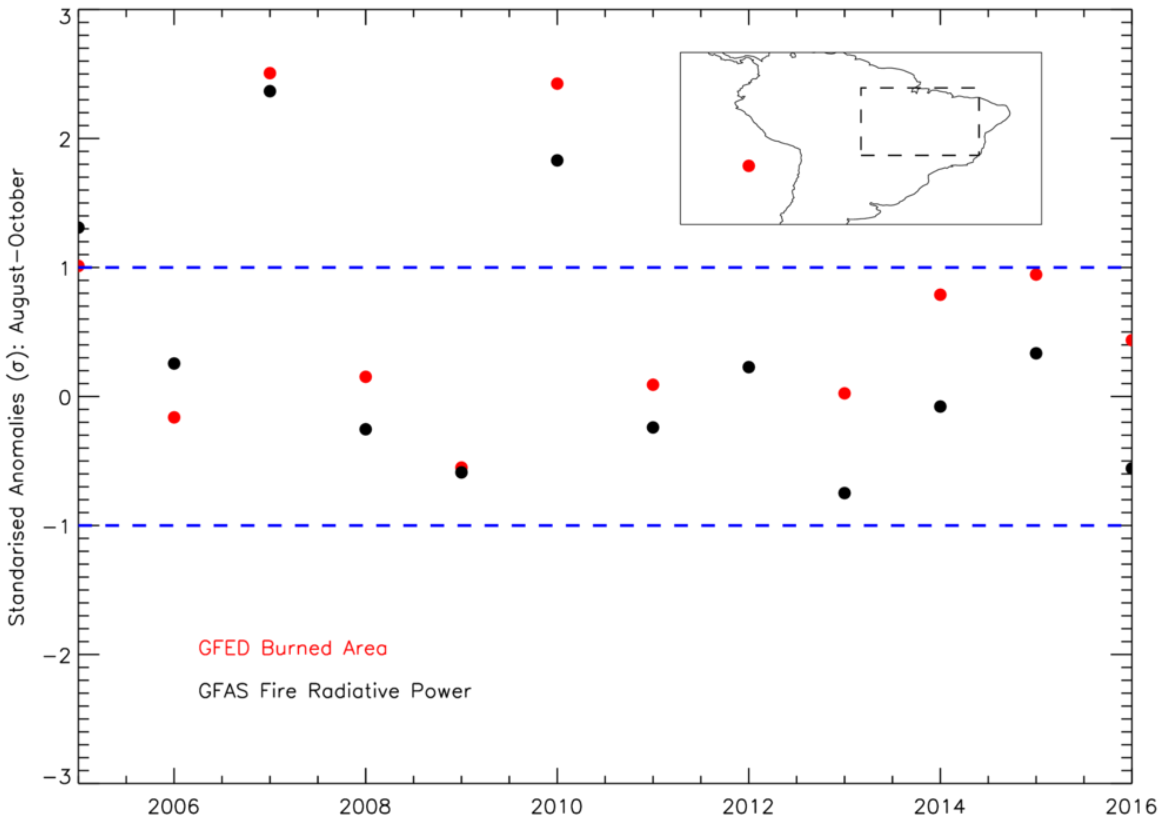

Figure SM1: Annual average standardised anomalies for GFED Fire-Burned-Area (FBA, red) and GFAS Fire Radiative Power (FRP, black) calculated over North-Eastern South America (black dashed region). Blue dashed lines show the ±1.0 standard deviations.

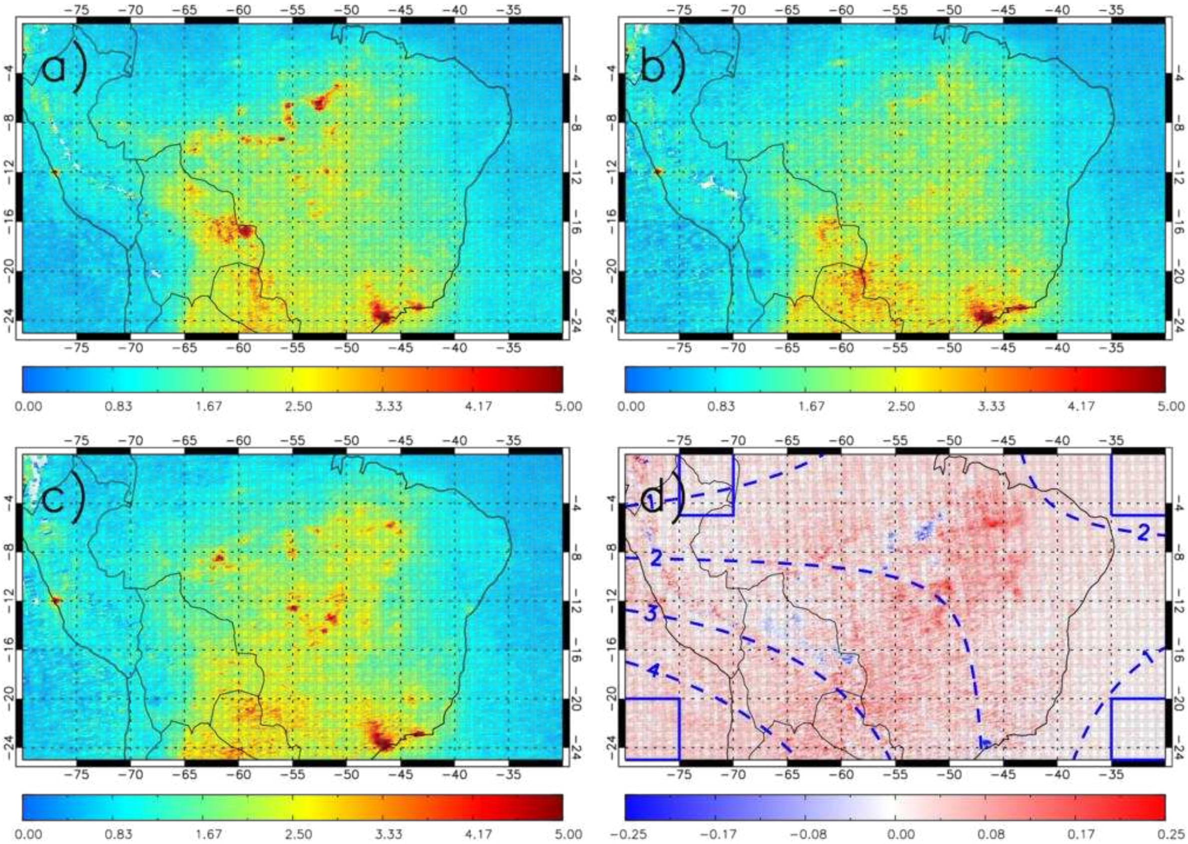

Figure SM2: Demonstration of deterioration of OMI $TCNO_2$ (10^{15} molecules/cm^2) retrieved over background regions (e.g. the ocean) for the ASO average in a) 2006, b) 2009 and c) 2014. The ASO trend (10^{15} molecules/cm^2/year) between 2005 and 2016 is shown in panel d). The blue boxes highlight the regions used to calculate the positive artificial background trends (%) mapped over the domain, used to de-trend the OMI $TCNO_2$ record.

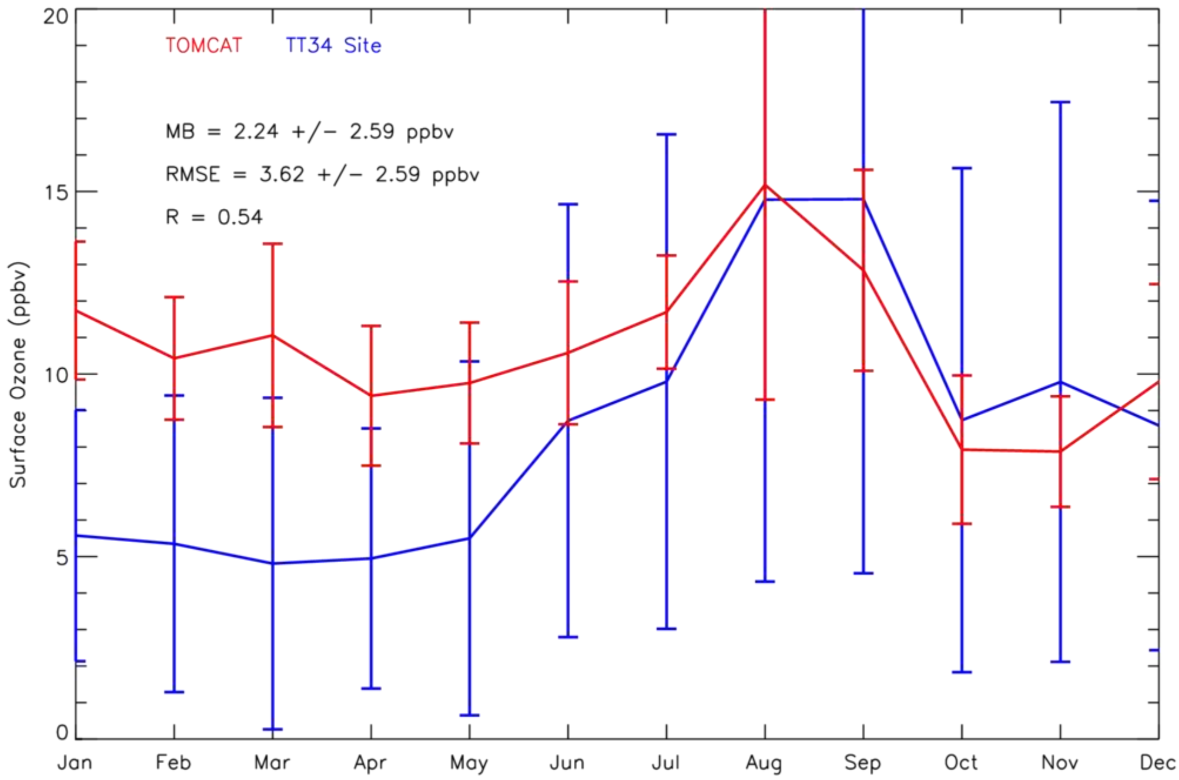

Figure SM3: Average surface O_3 (ppbv) seasonal cycle for 2010-2011 at Manaus (TT34), Brazil (60.2°W, 2.6°S). Observations and model seasonal cycles are shown in blue and red, respectively. Observational and model variability is represented by the monthly standard deviations.

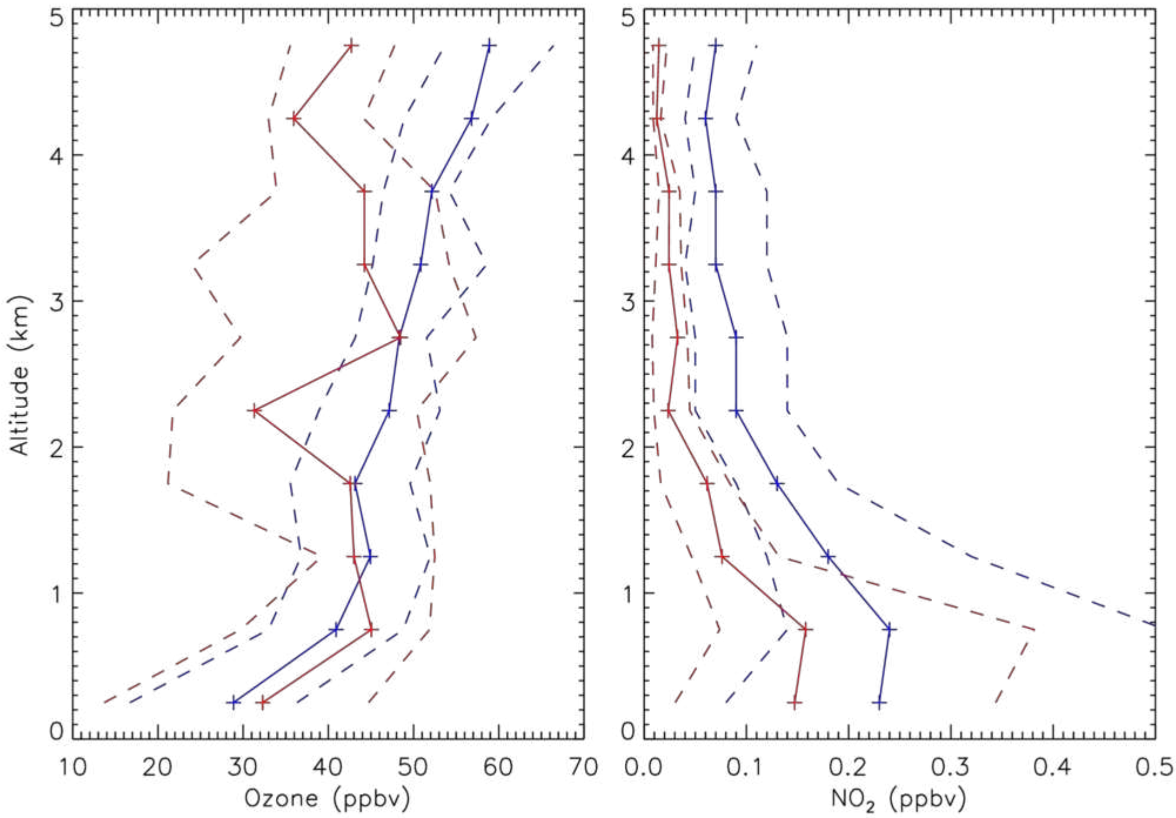

Figure SM4: Median aircraft (blue) and modelled (red) profiles from the SAMBBA campaign (September-October, 2012) of O_3 (left panel, ppbv) and NO_2 (right panel, ppbv) over the Amazon. Dashed lines represent the 25th and 75th percentiles in the model and aircraft data.

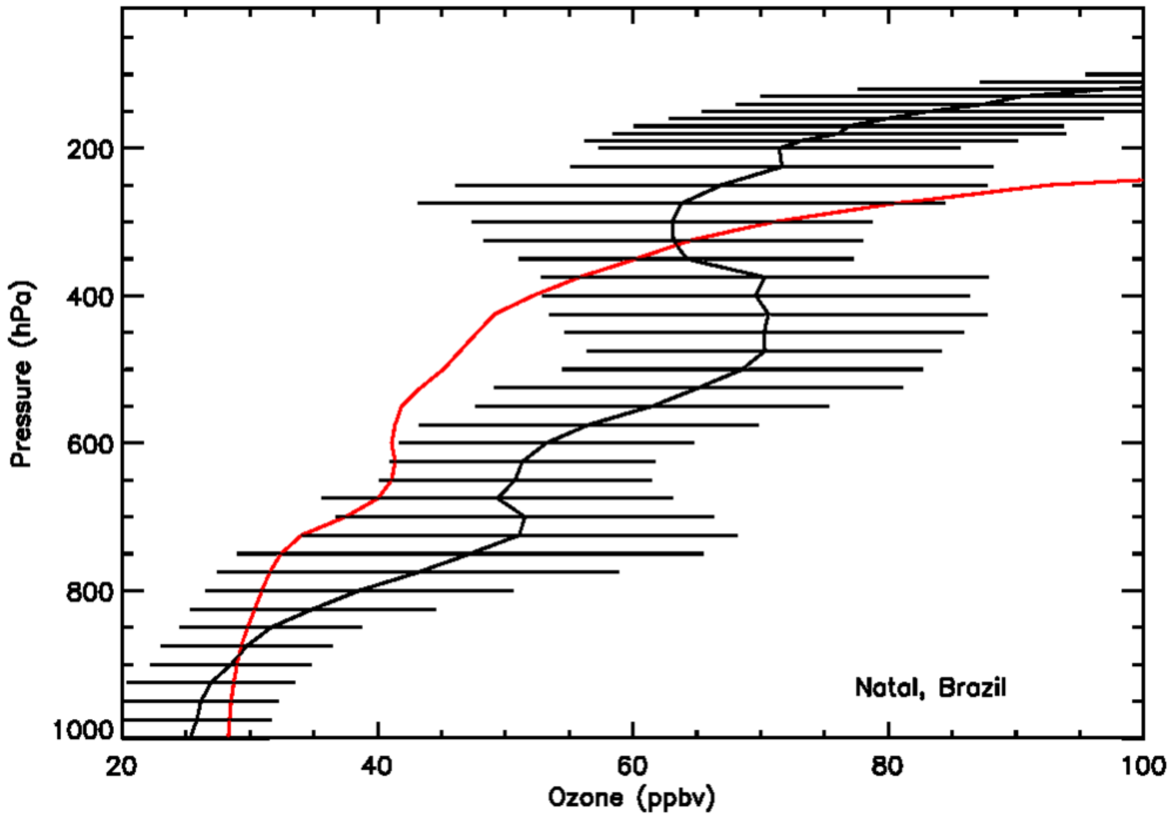

Figure SM5: Averaged ozonesonde (black) and model (red) vertical O_3 profiles (ppbv) for July-November (2007-2008) at Natal, Brazil. Black horizontal lines represent the observational variability (standard deviation).

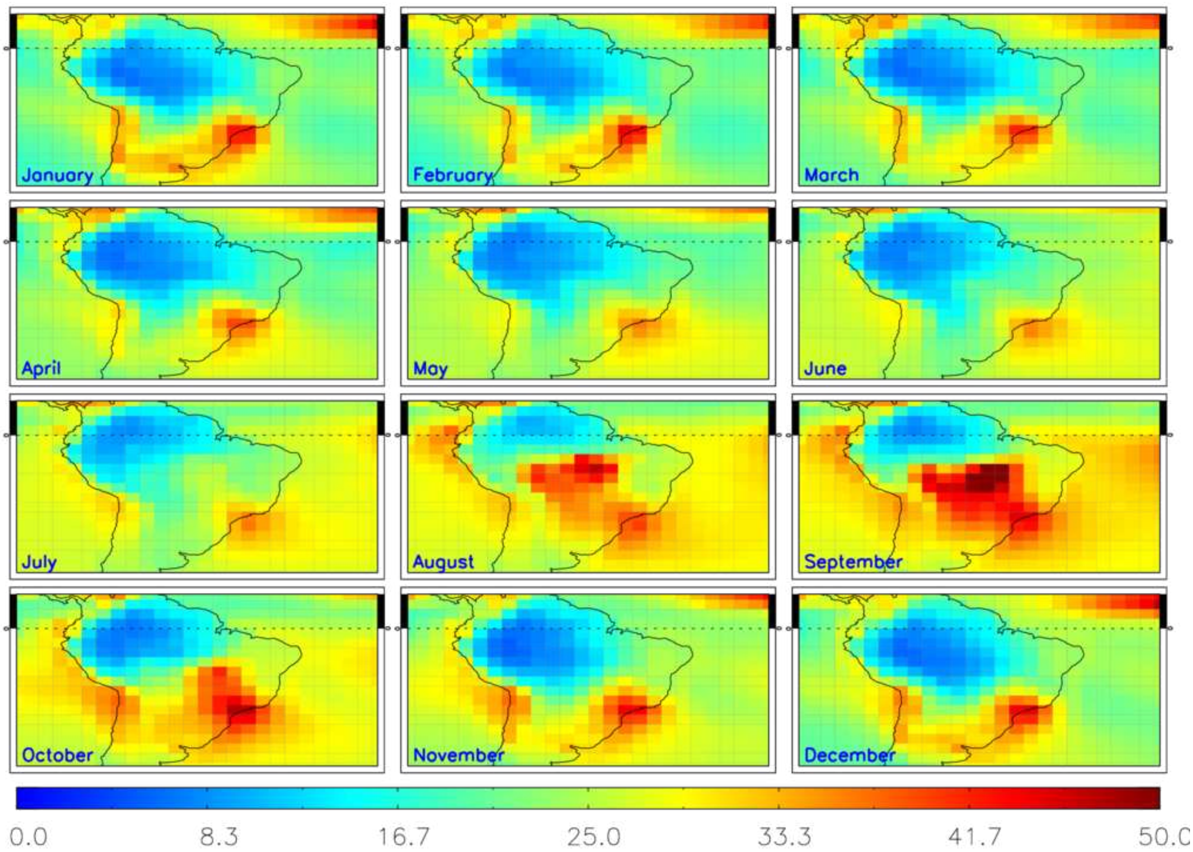

Figure SM6: Mean TOMCAT surface O_3 (ppbv) seasonal cycle (2005-2016 average) over South America from the simulation which includes fire emissions (fire-ctl).

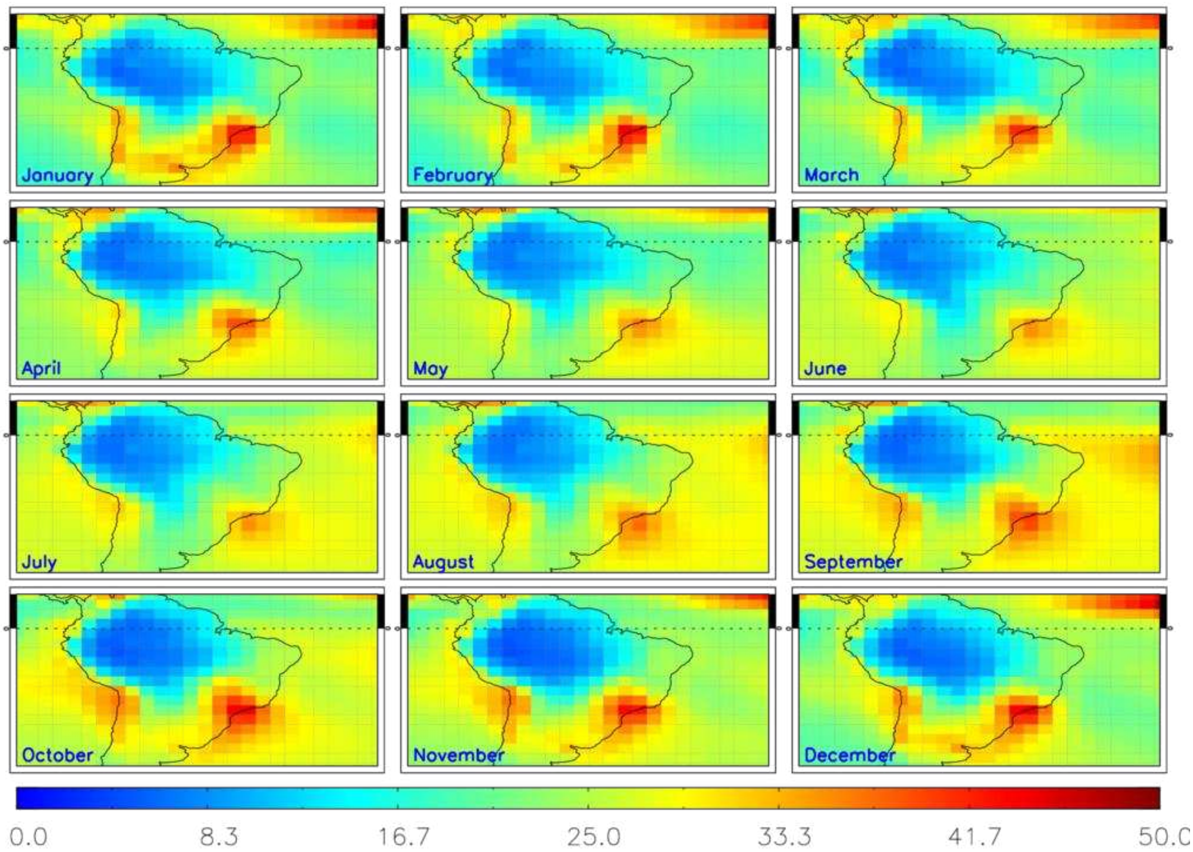

Figure SM7: Mean TOMCAT surface O_3 (ppbv) seasonal cycle (2005-2016 average) over South America from the simulation without fire emissions (fire-off).

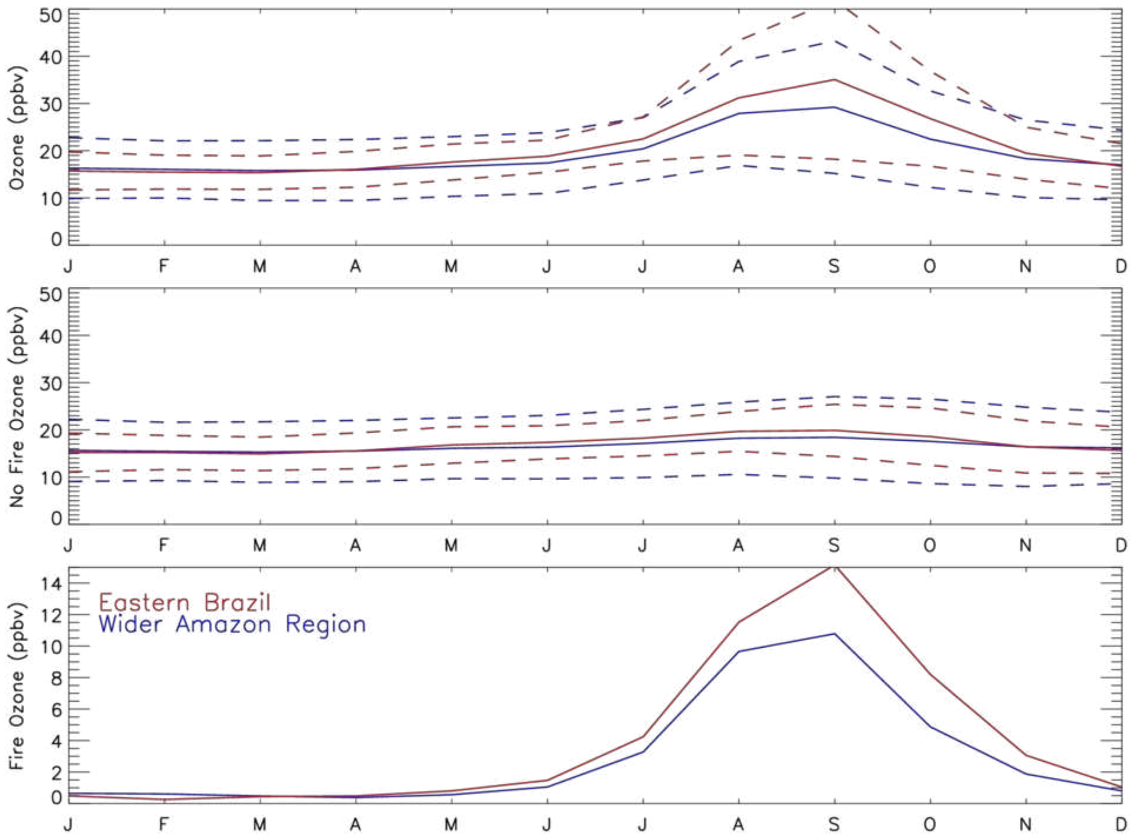

Figure SM8: TOMCAT surface O_3 (ppbv) seasonal cycle (2005-2016 average) for the Wider Amazon Region (blue) and Eastern Brazil (red; see **Figure 4** of the main manuscript). Surface O_3 from the TOMCAT "fire-ctl" simulation, "fire-off" simulation and "fire-ctl" - "fire-off" difference are shown in the top, middle and bottom panels, respectively. Dashed lines represent the monthly standard deviations.

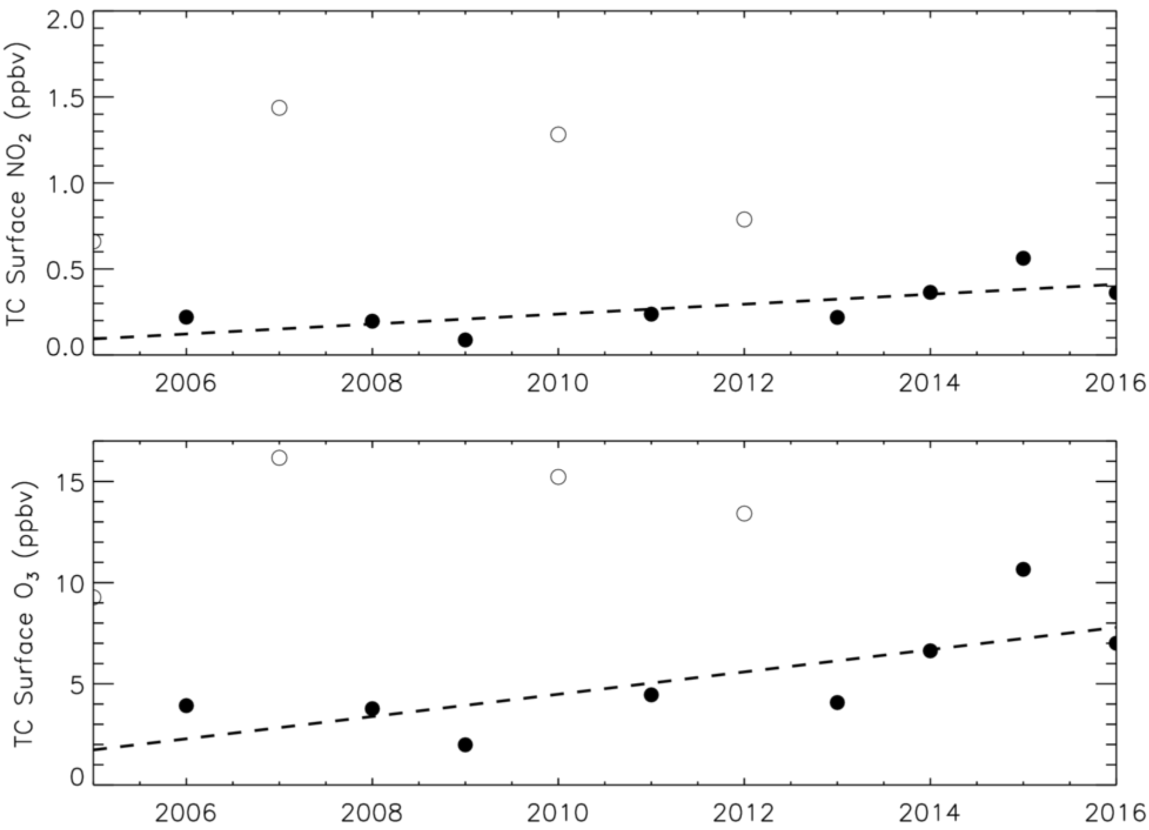

Figure SM9: TOMCAT surface NO_2 (ppbv, top panel) and O_3 (ppbv, bottom panel) averaged over the black box in Figure 2a (main manuscript) for August-September-October (ASO) between 2005 and 2016. Hollow circles represent extreme drought – anomalous fire (ED-AF) years. Black dashed lines show significant trends (90%CL).