

**1 Biomass burning related ozone damage on vegetation over the Amazon forest: A model**  
**2 sensitivity study.**

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**17 Abstract**

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**19** The HadGEM2 Earth System climate model was used to assess the impact of biomass burning on  
**20** surface ozone concentrations over the Amazon forest and its impact on vegetation, under present-  
**21** day climate conditions. Here we consider biomass burning emissions from wildfires, deforestation  
**22** fires, agricultural forest burning, residential and commercial combustion. Simulated surface ozone  
**23** concentration is evaluated against observations taken at two sites in the Brazilian Amazon forest for  
**24** years 2010 to 2012. The model is able to reproduce the observed diurnal cycle of surface ozone  
**25** mixing ratio at the two sites, but overestimates the magnitude of the monthly averaged hourly  
**26** measurements by 5-15 ppb for each available month at one of the sites. We vary biomass burning  
**27** emissions over South America by +/-20, 40, 60, 80 and 100% to quantify the modelled impact of  
**28** biomass burning on surface ozone concentrations and ozone damage on vegetation productivity  
**29** over the Amazon forest. We used the ozone damage scheme in the “high” sensitivity mode to give  
**30** an upper limit for this effect. Decreasing South American biomass burning emissions by 100% (i.e.  
**31** to zero) reduces surface ozone concentrations (by about 15ppb during the biomass burning season)  
**32** and suggests a 15% increase in monthly mean net primary productivity averaged over the Amazon  
**33** forest, with local increases up to 60%. The simulated impact of ozone damage from present-day  
**34** biomass burning on vegetation productivity is about 230 TgC/yr. Taking into account that

**35** uncertainty in these estimates is substantial, this ozone damage impact over the Amazon forest is of  
**36** the same order of magnitude as the release of carbon dioxide due to fire in South America; in effect  
**37** to potentially double the impact of biomass burning on the carbon cycle.

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**Introduction**

Biomass burning is a global source of aerosol and trace gases, including ozone (O<sub>3</sub>) precursors, and can lead to local and regional O<sub>3</sub> pollution. Tropospheric O<sub>3</sub> is a greenhouse gas and, above background concentrations, an air pollutant: it is harmful to human health (e.g. Lippmann 1993; Burnett et al., 1997) and it damages plants (e.g. Rich et al., 1964; Fiscus et al., 2005; Felzer et al., 2007; Ainsworth et al., 2012). Tropospheric O<sub>3</sub> is a product of photochemical reactions whose main precursors are nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>) and volatile organic compounds (VOCs) (Seinfeld and Pandis, 1998). VOCs are particularly important in Amazonia because of the large natural biogenic and biomass burning emissions (Karl et al., 2007).

In the Amazon forest, biomass burning is mostly anthropogenic, and mainly occurs during the dry season (August to October). Biomass burning emissions drastically change the composition of the atmosphere, e.g. diurnal maximum mixing ratios of tropospheric O<sub>3</sub> varies from 12 parts per billion (ppb), during the wet season, to values as high as 100 ppb in the biomass burning affected dry season (Kirkman et al., 2002, Sigler et al., 2002, Artaxo et al., 2002, 2005, Rummel et al., 2007).

Surface O<sub>3</sub> mixing ratios over 40 ppb are known to produce visible leaf injury and damage to plants, reducing crop productivity and posing a threat to food security; nonetheless different climatic conditions (e.g. soil moisture and water stress) also play a role in determining leaf stomatal closure and hence there will be variable impacts of the same O<sub>3</sub> concentrations (Ashmore, 2005), e.g. tropical rainforest vegetation may be particularly sensitive to surface O<sub>3</sub>, even at concentrations below 40ppb (a threshold associated with extra-tropical vegetation), due to high stomatal conductances. Moreover, tropical vegetation evolved in low background O<sub>3</sub> concentrations and could be more sensitive to O<sub>3</sub>. In leaves, cellular damage caused by O<sub>3</sub> not only reduces photosynthetic rates but also requires increased resource allocation to detoxify and repair leaves (Ainsworth et al., 2012). Ozone damage to vegetation reduces plant productivity, decreasing the amount of carbon absorbed by plants, hence has an impact on climate via and indirect radiative forcing (Sitch et al., 2007).

Tropical rain forests play an important role in the global carbon budget, as they cover 12% of the Earth's land surface and contain around 40% of the terrestrial biosphere's carbon (Ometto et al., 2005, Taylor & Lloyd, 1992). It has been estimated that they may account for as much as 50% of

the global net primary productivity (Grace et al., 2001). Depending on age, land use and large scale meteorological conditions, tropical forest ecosystems can act as net carbon sources, sinks, or they can be in approximate balance (Lloyd et al., 2007, Gatti et al., 2013), but it is uncertain if global environmental changes are forcing these ecosystems outside their range of natural variation (Sierra et al., 2007). However, biomass burning may further reduce natural sinks in the neighbouring intact forest, via air pollution and O<sub>3</sub> damage on vegetation, and thus current estimates of the effects of biomass burning on the carbon cycle (Le Quéré et al., 2009) may be underestimated. Biomass burning is also an important aerosol source: regional levels of particulate matter are very high in the dry season in Amazonia (Artaxo et al., 2013), and the increase in diffuse radiation due to changes in aerosol loadings can increase net ecosystem exchange (NEE) quite significantly (Oliveira et al., 2007, Cirino et al., 2013). After a certain level of aerosol optical depth, the decrease in radiation fluxes can reduce significantly NEE over Amazonia (Cirino et al., 2013). This study does not consider the effects of the changes in diffuse radiation due to biomass burning on photosynthesis, or the impact of aerosols on O<sub>3</sub> chemistry via changing photolysis rate. That will be the focus of a separate study. Our specific aim is to estimate the effect of O<sub>3</sub>-induced changes on vegetation productivity due to biomass burning.

Importantly, Sitch et al. (2007) performed their assessment of the potential impact of O<sub>3</sub> on vegetation using an offline simulation where monthly mean O<sub>3</sub> concentrations derived with a global chemistry climate model were used in determining the impacts of O<sub>3</sub> damage. Here we use an online flux-gradient approach to quantify the impact of biomass burning on surface O<sub>3</sub> concentration and O<sub>3</sub> damage on vegetation over the Amazon forest (see model description). The HadGEM2 (Hadley Centre Global Environment Model 2; Collins et al., 2011; Martin et al., 2011) Earth System climate model is used to study these interactions. We show results of the evaluation of surface O<sub>3</sub> simulated with HadGEM2 against observations in the Amazon forest and model experiments quantifying the impact of biomass burning on plant productivity.

## Methods

We used HadGEM2 to simulate surface O<sub>3</sub> concentrations and O<sub>3</sub> damage on vegetation for present-day (2001-2009) climate conditions. Our version of HadGEM2 includes the O<sub>3</sub> damage scheme developed by Sitch et al. (2007). We evaluated simulated surface O<sub>3</sub> against observations taken at two sites in the Amazon forest: Porto Velho (Brazil; 8.69°S; 63.87°W), a site heavily impacted by

106 biomass burning emissions, and site ZF2 in the Cuieiras forest reserve in Central Amazonia (Brazil;  
107 2.59°S; 60.21°W). A description of the sites can be found in Artaxo et al. (2013). In a sensitivity  
108 study we varied biomass burning emissions over South America by +/-20, 40, 60, 80, 100% to  
109 quantify the potential impact of biomass burning on surface O<sub>3</sub> concentrations and O<sub>3</sub> damage over  
110 the Amazon forest.

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### 113 **Model description**

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115 HadGEM2 is a fully coupled Earth-system model (Collins et al., 2011). It is built around the  
116 HadGEM2 atmosphere-ocean general circulation model and includes a number of earth system  
117 components: the ocean biosphere model diat-HadOCC (Diatom-Hadley Centre Ocean Carbon  
118 Cycle, a development of the HadOCC model of Palmer and Totterdell, 2001), the Top-down  
119 Representation of Interactive Foliage and Flora Including Dynamics (TRIFFID) dynamic global  
120 vegetation model (Cox, 2001), the land-surface and carbon cycle model MOSES2 (Met Office  
121 Surface Exchange Scheme; Cox et al. 1998, 1999; Essery et al. 2003), the interactive Biogenic  
122 Volatile Organic Compounds (iBVOC) emission model (Pacifico et al., 2012), the United Kingdom  
123 Chemistry and Aerosol (UKCA) model (O'Connor et al., 2014) and an interactive scheme of O<sub>3</sub>  
124 damage on vegetation (Sitch et al., 2007; Clark et al., 2011).

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126 The configuration used here is a version of HadGEM2-UKCA with extended tropospheric  
127 chemistry (N96L38), the resolution is 1.25° latitude x 1.875° longitude (~200 x 140 km) at the  
128 equator with 38 vertical levels extending up to 39 km altitude. The land-based anthropogenic,  
129 biomass burning, and shipping emissions are taken from Lamarque et al. (2010), and represent a  
130 decadal (1997-2006) mean centered on the year 2000. The use of an emission pattern from 1997-  
131 2006 can lead to an overestimation of O<sub>3</sub> concentrations by the model, since the emissions vary on a  
132 year to year basis and are expected to be lower in recent years due to the reduction in Amazonian  
133 deforestation via burning, consequently reducing the amount of O<sub>3</sub> precursors. HadGEM2 runs at a  
134 30-minute time step with the exception of global radiation, which is updated every 3 hours and  
135 provides radiative fluxes between those time steps via interpolation. This configuration is described  
136 and evaluated in O'Connor et al. (2014) with the exception of the Extended Tropospheric  
137 Chemistry (ExtTC) that has been applied in this work. The ExtTC mechanism has been designed to  
138 represent the key species and reactions in the troposphere in as much detail as is necessary to  
139 simulate atmospheric composition-climate couplings and feedbacks while retaining the capability to

140 conduct decade-long climate simulations. UKCA-ExtTC simulates the spatial distribution and  
 141 evolution in time of 89 chemical species, 63 of which are model tracers. The model includes  
 142 emissions from anthropogenic, biogenic, soil, and wildfire sources for 17 species: nitrogen oxides  
 143 ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ),  $\text{CH}_4$ , carbon monoxide (CO), hydrogen ( $\text{H}_2$ ), methanol, formaldehyde,  
 144 acetaldehyde and higher aldehydes, acetone, methyl ethyl ketone, ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ),  
 145 butanes and higher alkanes, ethene ( $\text{C}_2\text{H}_4$ ), propene ( $\text{C}_3\text{H}_6$ ), isoprene, (mono)terpenes, and a lumped  
 146 species representing aromatics (toluene + xylene) from anthropogenic sources.  
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 148 Emissions of biogenic species (isoprene, terpenes, methanol, acetone) are computed by iBVOC and  
 149 provided to UKCA at every time step. The isoprene emission scheme is that of Pacifico et al.  
 150 (2011). Terpenes, methanol, and acetone emissions are simulated with the model described in  
 151 Guenther et al. (1995). Anthropogenic and wildfire emissions are prescribed from monthly mean  
 152 emission data sets prepared for CMIP5 using the historic scenario (Lamarque et al., 2010). Given  
 153 the difficulty in prescribing a diurnal cycle for fire emissions, these monthly mean emissions are  
 154 kept constant during the day. Wetland methane emissions are prescribed from data from Gedney et  
 155 al. (2004). Soil-biogenic  $\text{NO}_x$  emissions are prescribed using the monthly distributions provided by  
 156 the Global Emissions Inventory Activity (<http://www.geiacenter.org/inventories/present.html>),  
 157 which are based on the global empirical model of soil-biogenic  $\text{NO}_x$  emissions of Yienger and Levy  
 158 (1995).  $\text{NO}_x$  emissions from global lightning activity are parameterized based on the convective  
 159 cloud top height following Price and Rind (1992, 1994) and are thus sensitive to the model climate.  
 160 UKCA also includes a dry deposition scheme based on the resistance in-series approach as outlined  
 161 in Wesely (1989). Physical removal of soluble species is parameterized as a first-order loss process  
 162 based on convective and stratiform rainfall rates (Collins et al., 2011).  
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 164 The TRIFFID vegetation module of HadGEM2 simulates the dynamics of five plant functional  
 165 types (PFTs): broadleaf trees, needleleaf trees, shrubs, and  $\text{C}_3$  and  $\text{C}_4$  grass (i.e., grasses using the  
 166  $\text{C}_3$  and  $\text{C}_4$  photosynthetic pathway, respectively). Changes in the extent of croplands over time are  
 167 not simulated but are prescribed from land use maps prepared for the Coupled Model  
 168 Intercomparison Project 5 (CMIP5, Taylor et al., 2012). Here we use the historic (1850–2000; Hurtt  
 169 et al., 2009) data sets, as described in Jones et al. (2011). A further four surface types (urban, inland  
 170 water, bare soil, and ice) are used in the land-surface scheme for the calculation of water and energy  
 171 exchanges between the land and the atmosphere. Each model grid box can include varying  
 172 proportions of several vegetation and/or surface types. The model does not include interactive  
 173 deforestation due to fire.

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The parameterization of O<sub>3</sub> damage on vegetation is that of Sitch et al., (2007). This scheme uses a flux-gradient approach to model O<sub>3</sub> damage, rather than empirical approaches based on the accumulated O<sub>3</sub> exposure above 40 ppb (e.g. Felzer, et al. 2005). The Sitch et al. (2007) parameterization assumes a suppression of net leaf photosynthesis by O<sub>3</sub> that varies proportionally to the O<sub>3</sub> flux through stomata above a specified critical O<sub>3</sub> deposition flux. The critical deposition flux depends on O<sub>3</sub> concentration near the leaves, but also on stomatal conductance. This scheme also includes a relationship between stomatal conductance and photosynthesis, determining a reduction in stomatal conductance through O<sub>3</sub> deposition. As the O<sub>3</sub> flux itself depends on the stomatal conductance, which in turn depends upon the net rate of photosynthesis, the model requires a consistent solution for the net photosynthesis, stomatal conductance and the O<sub>3</sub> deposition flux. This approach to modelling O<sub>3</sub> effects on photosynthesis accounts for the complex interaction between CO<sub>2</sub> and O<sub>3</sub> effects, and can be used to study future climate impacts. This scheme includes a ‘high’ and ‘low’ parameterization for each PFT to represent species more sensitive and less sensitive to O<sub>3</sub> effects; in our analysis we use the ‘high’ sensitivity mode to establish the maximum response. The model was calibrated with data from temperate and boreal vegetation. Calibration data for other ecosystems, including tropical vegetation, are currently unavailable.

**Description of the model experiments**

All simulations use HadGEM2 in its atmosphere-only configuration, i.e., with all implemented couplings between atmosphere and land surface (including carbon cycle) active but without the atmosphere-ocean coupling. HadGEM2 was initialized with equilibrium concentrations of the major chemical components (O<sub>3</sub>, CO, H<sub>2</sub>, total reactive nitrogen (NO<sub>y</sub>), BVOCs) taken from the CMIP5 simulation (see description of the simulations in Jones et al., 2011). Methane mixing ratios were prescribed as specified by CMIP5, with values of 1750 ppb for present-day. The decade-mean CO<sub>2</sub> atmospheric mixing ratio was 368 ppm.

Monthly means of sea surface temperature and sea ice cover were prescribed using climatologies derived from the appropriate decade of the Hadley Centre CMIP5 transient climate run Jones et al., (2011). The vegetation distribution for each of our simulations was prescribed using the simulated vegetation averaged for the same decade from this transient climate run, on which we superimposed crop area as given in the CMIP5 historic and future land use maps (Hurtt et al., 2009; Riahi et al., 2007).

208 We performed a 9-year (2001-2009) control simulation for present-day climate conditions  
 209 initialized from a centennial transient climate simulation with ocean couplings (Jones et al., 2011).  
 210 We analysed the last 8 years of the simulation, as the first year of simulation was used as spin-up. A  
 211 single year is considered sufficient for spin-up because one year is around five times longer than the  
 212 lifetime of the longest lived atmospheric species (with the exclusion of methane) involved in O<sub>3</sub>  
 213 chemistry. The control simulation was driven by anthropogenic and wildfire emissions of trace  
 214 gases and aerosols via historical scenarios (Global Fire Emissions Database GFEDv2; Lamarque et  
 215 al., 2010; Van der Werf et al., 2006) of anthropogenic and wildfire emissions.  
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 217 HadGEM2 is able to reproduce the main spatial distribution of surface temperature (Figure S1) and  
 218 precipitation (Figure S2). Surface temperature simulated with HadGEM2 exhibits a bias in the  
 219 region of up to 2°C colder than in the observations over the Amazon forest. Simulated precipitation  
 220 rate is in reasonable agreement with observations. The model is able to reproduce the main features  
 221 of the seasonal cycle of precipitation, but tends to simulate less precipitation in September and  
 222 November than the observations (Figure S03).  
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 224 Simulated HadGEM2 NPP is compared against a meta-analysis of field data from the Ecosystem  
 225 Model Data Model Intercomparison project (EMDI) (Olson et al., 2001). Measurements from the 81  
 226 ‘class A’ (‘well documented and intensively studied’) sites, representative of all major global  
 227 biomes, are compared against our simulations. Traditionally, global vegetation models  
 228 underestimate NPP in tropical ecosystems, and tend towards an asymptote of ~1000 g C m<sup>-2</sup>  
 229 (Prentice et al., 2007). HadGEM2 is able to reproduce the main geographical variations of NPP  
 230 globally (Figure S4), especially in the Northern Hemisphere, where more plentiful observations are  
 231 available. In addition HadGEM2 is able to better simulate higher tropical NPP.  
 232  
 233 Ozone concentration simulated with HadGEM2-UKCA-ExtTC agrees better with observations at  
 234 higher altitudes and higher latitudes (Figure S5). The model performs more poorly than the  
 235 ACCENT mean over tropical areas, especially closer to the surface. Comparison with a selection of  
 236 observed profiles of O<sub>3</sub> concentration shows the model overestimates O<sub>3</sub> for some locations but is in  
 237 extremely good agreement for others. Over the tropics the agreement is better in the few continental  
 238 profiles than the marine environment (Figure S6). Some differences may be expected given that the  
 239 observations are from campaigns with specific meteorological conditions, while the model  
 240 simulations represent a multi-year mean from the model. Comparison with a selection of surface O<sub>3</sub>



241 observations (Figure S7) confirms again how the model shows a better agreement with observations  
242 taken at higher latitudes.

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244 We also perform 10 experiments that differ from the control simulation in terms of assumed  
245 biomass burning emissions, i.e. biomass burning emissions over South America are either increased  
246 or decreased by +/-20, 40, 60, 80, 100%, while emissions over the rest of the world are kept  
247 unchanged. The vegetation distribution was not adjusted for loss of vegetation due to fire. We  
248 define biomass burning emissions as those from wildfires, deforestation fires, agricultural forest  
249 burning, residential and commercial combustion, including fuel wood burning, charcoal production  
250 and biofuel combustion for cooking and heating (Lamarque et al., 2010). The dominant fire types in  
251 South America are from deforestation and degradation fires in an arc around Amazonia, with some  
252 regional hotspots of agricultural burning (see Figure 13 in Van der Werf et al., 2010). Between  
253 2001 and 2009 the percentage contribution to annual fire emissions from fire types (deforestation  
254 and degradation, grassland and savanna, woodland, forest, agriculture) are (59%, 22%, 10%, 8%,  
255 2%) over Southern Hemisphere South America (Figure 13 van der Werf et al., 2010), with minor  
256 differences in this region between this dataset (Global Fire Emissions Database GFEDv3) and the  
257 earlier GFEDv2 used in this study (see Fig. 16 in Van der Werf et al., 2010). The residential and  
258 commercial combustion contribution accounts for 1 and 8% of the total annual biomass burning  
259 emissions of CO and NO<sub>x</sub> respectively.

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261 This set of experiments allows us to simulate the impact of biomass burning on surface O<sub>3</sub> and  
262 vegetation productivity. The control simulation was also used to evaluate surface O<sub>3</sub> mixing ratios  
263 against measurements over the Amazon forest.

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## 266 **Model site-level Evaluation**

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268 Over the data-sparse Amazonian region, comprehensive spatial data sets of surface O<sub>3</sub>  
269 concentration are extremely limited. We evaluated simulated surface O<sub>3</sub> against observations from  
270 two sites that have full annual analyses of O<sub>3</sub> concentration: Porto Velho (Brazil; 8.69°S;  
271 63.87°W) and site ZF2 in the Cuieiras forest reserve (Brazil; 2.59°S; 60.21°W). O<sub>3</sub> mixing ratios  
272 were measured with a UV absorption analyser (Thermo 49i, USA). Observations from both sites  
273 have an estimated 4% uncertainty, considering zero noise, zero and span drifts reported in the  
274 instrument manual, and the frequency of zero and span checks performed along the experiments.

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276 The Porto Velho sampling site is located in a forest reserve about 5 km NE (generally upwind) from  
277 the city of Porto Velho. Large land use change and regional biomass burning makes its atmospheric  
278 conditions characteristic of those of the Amazon forest with significant human interference (Brito et  
279 al., 2014). The whole region of Porto Velho has been subject to land use change since the 1980s. In  
280 Porto Velho, the dry season is from June to October and the wet season from November to May.  
281 Measurements of surface O<sub>3</sub> mixing ratios were taken from November 2011 to October 2012 in a  
282 forest clearance, at 5 m a.g.l..

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284 The Cuieiras forest reserve in Central Amazonia encloses 380 km<sup>2</sup> of pristine tropical rainforest  
285 forest. The reserve is located in the central Amazon Basin, 60 km NNW of downtown Manaus and  
286 40 km from the metropolis margins. This site is relatively undisturbed, as no biomass burning  
287 occurs in the forest reserve. Here rain showers are frequent with a short dry season from July to  
288 October. Measurements were taken at 39 m a.g.l. at the TT34 tower. The forest canopy height near  
289 the tower varied between 30 and 35 m, and the site is described in Martin et al. (2010), Rizzo et al.  
290 (2013) and Artaxo et al. (2013). Most of the time, the prevailing trade winds blow over 2000 km of  
291 the intact tropical forest before reaching the measurement tower. However, the site was also  
292 affected by regional transport of pollutants, either from biomass burning or urban sources (Rizzo et  
293 al., 2013). Measurements of surface O<sub>3</sub> mixing ratios were taken from April 2010 to June 2012,  
294 with the exclusion of a few months due to instrument maintenance.

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296 We compared simulated (averaged over 8 years of simulations) against observed average O<sub>3</sub> diurnal  
297 cycles at each site for each available month. The model overestimates observed monthly averaged  
298 hourly O<sub>3</sub> mixing ratios at the surface by about 5-15 ppb for all months at the Porto Velho site, but  
299 it reproduces the diurnal and seasonal cycle, including those months affected by biomass burning,  
300 i.e. August and September, at the Porto Velho site (Figure 1). The model is able to reproduce the  
301 diurnal cycle, including magnitude, at the ZF2 site for about 8 months out of 24. The model  
302 overestimates surface monthly averaged hourly O<sub>3</sub> mixing ratios by about 5-10 ppb for the rest of  
303 months, which are also the months with lower surface O<sub>3</sub> mixing ratios (Figure 2).

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306 **Results**

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308 Our analysis is focused on the region enclosed in the red rectangle in figure 3, this is a highly  
 309 vegetated region with homogeneous topography, and it includes the two sites used for the model  
 310 evaluation (Porto Velho and ZF2 in the Cuieiras forest reserve). This region of analysis is covered  
 311 by two PFTs in HadGEM2: broadleaf trees, which is the predominant, and C<sub>3</sub> grass (Figure 3).  
 312  
 313 Surface O<sub>3</sub> mixing ratios simulated with HadGEM2 are higher during the months of August,  
 314 September and October over the Amazon forest, and in particular over our region of analysis,  
 315 because of the higher biomass burning emissions in the model during these months. Monthly  
 316 average surface O<sub>3</sub> mixing ratios in our control simulation peaks at 55-60 ppb in this region (Figure  
 317 4), while the average over the region of analysis is peaked at about 30 ppb in August and  
 318 September, less in October (Figure 5a, black line).  
 319  
 320 Monthly total Net Primary Productivity (NPP) in our control simulation reaches its minimum  
 321 during the months of August and September (Figure 5b, black line), at about 300 TgC/month,  
 322 corresponding to the end of the dry season.  
 323  
 324 Decreasing biomass burning emissions over South America by -20%, -40%, -60%, -80%, -100%  
 325 decreases surface O<sub>3</sub> mixing ratios and increases net productivity. Vice versa, increasing biomass  
 326 burning emissions over South America by +20%, +40%, +60%, +80%, +100% increases surface O<sub>3</sub>  
 327 mixing ratios over the region of analysis and subsequently reduces net productivity because of O<sub>3</sub>  
 328 damage on vegetation (Figure 5c).  
 329 These sensitivity tests suggest that decreasing biomass burning emission by 100% over South  
 330 America brings monthly mean surface O<sub>3</sub> mixing ratios averaged over the region of analysis to  
 331 about the observed 15 ppb for each month (Figure 5a, dark blue line), even during the dry season,  
 332 with no values over 35 ppb for any grid-cell (Figure 6). Increasing biomass burning emissions by  
 333 100% suggests that monthly mean mixing ratios of surface O<sub>3</sub> averaged over the region of analysis  
 334 reach 40 ppb in August (Figure 5a), with peaks of about 65-70 ppb in some grid-cells (Figure 6a).  
 335 For both increases and decreases of between 20 and 80% in South American biomass burning the  
 336 model simulates almost linear changes in surface O<sub>3</sub> mixing ratios (Figure 6, the figure shows  
 337 increases and reductions by 40, 60 and 100%).  
 338  
 339 Suppressing biomass burning emissions (i.e. decreasing biomass burning emission by 100%) over  
 340 South America increases total NPP over the region of analysis by about 15%, to about 350-370  
 341 TgC/month, with peak increases of 60% for a few grid-cells, in August and September (Figure 6b):

342 this quantifies the impact of present-day biomass burning on vegetation productivity. When  
343 increasing biomass burning emissions over South America by 100%, monthly total NPP over the  
344 region of analysis is reduced by about 10%, i.e. to about 250 TgC/month, in August and September  
345 (Figure 5b), with peak values of 50-60% reductions for few grid-cells (Figure 6c). For reductions by  
346 20 to 80% in South American biomass burning the model varies NPP almost linearly (Figure 5c).  
347 However, the increase in South American biomass burning by 20 to 80% determine a very similar  
348 decrease in NPP, e.g. between 7 and 10% decrease in August (Figure 5c). Both increasing and  
349 reducing South American biomass burning from 20 to 80% increases the number of grid-cells  
350 where a significant variation of NPP takes place (Figure 6b). The percentages given above are  
351 significant against inter-annual variability in the control simulation, i.e. we only take into account of  
352 the variations above one standard deviation in the control simulation. We also exclude from our  
353 analysis the grid-cells with low productivity, i.e. where NPP in the control simulation is below 50  
354 gC/m<sup>2</sup>/month (i.e. we focus on high productivity regions, e.g. forests).

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## 357 Discussion and Conclusions

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359 The HadGEM2 model overestimates the magnitude of the O<sub>3</sub> diurnal cycle at the two sites used in  
360 the evaluation. Overestimation of simulated O<sub>3</sub> in the Amazonian boundary layer has been observed  
361 in other modelling studies, especially in clean air conditions (Bela et al., 2014). Nonetheless, our  
362 model reproduces the main features of the diurnal and seasonal cycle. In particular, the model is  
363 able to reproduce the increase in surface O<sub>3</sub> during the biomass burning season.

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365 As stated earlier in the model description section, biomass burning emissions are prescribed as  
366 monthly mean and kept constant during the day, and this can have an impact on the hourly and day-  
367 to-day variation of surface O<sub>3</sub>. For example, O<sub>3</sub> production will respond differently if biomass  
368 burning emissions occur during the day or at night, affecting simulated surface O<sub>3</sub> mixing ratios.  
369 These issues can be improved by modelling fire and biomass burning emissions interactively. The  
370 inclusion of an interactive fire model in HadGEM is currently under development.

371

372 The model overestimates surface O<sub>3</sub> mixing ratios by 5-15 ppb for several months at the ZF2 site in  
373 the Cuieiras forest reserve and for all available months at the Porto Velho site. The reasons for these  
374 systematic biases in surface O<sub>3</sub> mixing ratio are likely manifold. In a complex, highly coupled

375 system such as the HadGEM2 Earth System Model (ESM) it is not always easy to disentangle all  
376 processes and attribute model biases to specific components.

377 We attribute the systematic biases in the surface O<sub>3</sub> mixing ratio to the following, most likely  
378 reasons:

- 379 1. Model resolution in both the horizontal and the vertical dimension
- 380 2. Uncertainties in emissions, both magnitude, seasonality and location
- 381 3. Uncertainties in the O<sub>3</sub> dry deposition at the surface

382 Other factors such as uncertainties in the chemical mechanism, the photolysis rates, lightning NO<sub>x</sub>  
383 production over the area and transport of O<sub>3</sub> and precursors will certainly contribute. We will  
384 briefly discuss the three most important (in our opinion) factors that contribute to the systematic  
385 biases.

386

387 The relatively coarse resolution of a global ESM simulates mixing ratios of trace species (both trace  
388 gases and aerosols) that represent averages over large areas. This issue has been discussed  
389 previously in the literature, mostly in relation to air quality modelling (see, e.g., Valari and Menut,  
390 2008; Tie et al., 2010; Appel et al. 2011; Thompson and Selin, 2012). In our case one grid box  
391 equals approximately 30,000 km<sup>2</sup> (i.e., 200x150 km<sup>2</sup> in longitude and latitude). The implicit  
392 averaging pertains both to emission and concentration fields; the predominant consequence is a  
393 dilution in each grid-cell. Depending on the chemical regime, this can lead to reduced or enhanced  
394 net O<sub>3</sub> production. Additionally, HadGEM2-ES has a relatively coarse vertical resolution.  
395 HadGEM2-ES has a lowest model layer depth of 40m (global average) and the vertical profile of O<sub>3</sub>  
396 will undoubtedly show a gradient as the loss mechanism for O<sub>3</sub> is dominated by the surface (e.g.  
397 Colbeck and Harrison, 1967). The measurement level may explain part of the model overestimation,  
398 since it is well known that O<sub>3</sub> mixing ratios strongly decrease with height due to deposition within  
399 the canopy. The lowest layer of the model has a midpoint height 20 metres above the displacement  
400 height for the particular gridbox (generally approximated as 2/3 of the average height of the  
401 obstacle, in this case the canopy), while measurements were taken at 5 m and 39 m a.g.l.,  
402 respectively, at Porto Velho and ZF2 which are located either in or just above canopy level.  
403 Rummel et al. (2007) reports a 5-15 ppb O<sub>3</sub> decrease from 52 to 11 m a.g.l. in a forest site in  
404 Amazonia. This steep gradient near the surface is due to surface deposition but also due to in-  
405 canopy chemical processing (c.f., e.g., Stroud et al., 2005; Gordon et al., 2014). The latter is not  
406 represented in HadGEM2-ES.

407

408 The remote environment of the Amazon forest is dominated by relatively high concentrations of  
409 VOC, particularly of biogenic origin, and low concentrations of nitrogen oxides,  $\text{NO}_x$ . It is a  $\text{NO}_x$ -  
410 limited environment. In such an environment  $\text{O}_3$  is destroyed by reactions with BVOC (mainly  
411 isoprene and (mono-)terpenes). This destruction is more pronounced the higher the BVOC  
412 concentration becomes. Consequently, conditions in the global model are likely to differ from that  
413 of a measurement at a specific point such as those we compare to in Figures 1 and 2. It is a known  
414 problem in model evaluation.

415

416 Another issue related to model resolution, when comparing global models to point-like  
417 observations, is the uncertainty in global emission inventories, both with respect to magnitude and  
418 location. In particular the latter will result in discrepancies between modelled concentrations of  $\text{O}_3$   
419 and its precursors and point-like observations. But the uncertainties in emission magnitude are also  
420 substantial and can reach a factor of two or more in case of biogenic VOC (e.g., Guenther et al.,  
421 2006; Arneth et al., 2008, 2011; Pacifico et al., 2011, 2012).

422

423 Thirdly, and again related to model resolution, is the representation of  $\text{O}_3$  dry deposition at the  
424 surface. Its magnitude and diurnal cycle will depend on boundary layer turbulence, surface  
425 roughness, land surface type, vegetation type, soil moisture, photosynthetic activity, and more. In a  
426 recent sensitivity study by Folberth et. al (in preparation)  $\text{O}_3$  surface concentrations showed the  
427 largest sensitivity to perturbations in  $\text{O}_3$  surface dry deposition fluxes. Underestimating  $\text{O}_3$  surface  
428 dry deposition, in particular during the night preventing a complete flush of the PBL with respect to  
429  $\text{O}_3$ , will lead to systematic biases.

430

431 A comparison with Rummel et al. (2007) indicates that  $\text{O}_3$  dry deposition velocities on average  
432 compare favourably with observations. Rummel et al. (2007) reported day-time velocities of up to  
433 2.25 cm/s and night-time velocities of typically around 0.5 cm/s during the wet season; during the  
434 dry season reported day-time velocities are between 0.25 cm/s and 1.0 cm/s, and night-time  
435 velocities between 0.2 cm/s and 1.6 cm/s for one site in the Amazon region. HadGEM2-ES predicts  
436 annual mean  $\text{O}_3$  deposition velocities of 0.5 to 0.6 cm/s (see Figure S8) in fair agreement with the  
437 observations. Furthermore, the model is able to capture well the variability between the wet season  
438 and the dry season. However, more data are needed to conduct a robust evaluation, but, this  
439 admittedly crude comparison is sufficient to demonstrate a basic capability of HadGEM2-ES to  
440 reproduce observed ozone deposition velocities in the Amazon region to a reasonable degree.

441

442 Interestingly, however, the latter process may also represent a redeeming feature of the model.  
443 According to our model of O<sub>3</sub> plant damage it is the total O<sub>3</sub> flux into the plant that determines the  
444 amount of damage caused to the photosynthetic activity and, hence, carbon assimilation. However,  
445 the total O<sub>3</sub> flux (or dose) is a function of both O<sub>3</sub> surface concentrations and dry deposition, i.e. for  
446 plants there is a compensation effect when concentrations are overestimated while deposition  
447 velocities are underestimated. Underestimating the O<sub>3</sub> dry deposition flux implies reduced O<sub>3</sub> plant  
448 uptake, and consequently an underestimation of the plant damage and productivity losses. However,  
449 it also leads to higher O<sub>3</sub> concentrations, which subsequently act to increase plant O<sub>3</sub> uptake and  
450 damage, compensating for the initial effects on productivity. Still, a detailed assessment and  
451 quantification of this interdependence of O<sub>3</sub> concentration and dry deposition fluxes is beyond the  
452 scope of this study and must be referred to future research.

453

454 August, September and October are the months when biomass burning and surface O<sub>3</sub>  
455 concentrations are higher over the Amazon forest, but also the months when plant productivity is at  
456 its lowest which will tend to suppress the impact of O<sub>3</sub> damage on plant productivity. This is  
457 because stomatal conductance is reduced due to water limitations (also accounted for in the model)  
458 during the dry season, thus reducing the flux of both carbon dioxide and O<sub>3</sub> into the leaves, and  
459 consequently reducing O<sub>3</sub> plant damage.

460

461 Ashmore (2005) noted how O<sub>3</sub> exposure is poorly correlated with flux into leaves and also the  
462 potential for damagingly high O<sub>3</sub> fluxes in leaves at concentrations significantly below 40 ppb at  
463 maximum stomatal conductance. Consequently, global vegetation models as used in this study have  
464 adopted flux-based parameterizations to represent O<sub>3</sub> impacts on vegetation, moving away from  
465 application of the earlier exposure based metrics, e.g. accumulated O<sub>3</sub> exposure above a threshold  
466 of 40 ppb, AOT40.

467

468 The parameterization of O<sub>3</sub> damage used in this study is calibrated for high-latitude vegetation.  
469 Unfortunately data for calibrating this O<sub>3</sub> damage scheme for tropical vegetation are currently not  
470 available and observations of O<sub>3</sub> damage in the Amazon forest are very limited. Observations of O<sub>3</sub>  
471 damage on tropical forests are urgently needed, including observations at moderate (e.g. 20-30 ppb)  
472 and high surface O<sub>3</sub> mixing ratios.

473

474 The simulated impact of present-day biomass burning on vegetation productivity over our area of  
475 analysis is about 230 TgC/yr (i.e. the difference between the dark blue line and the black line in Fig.

476 5b) using the “high” sensitivity mode in the O<sub>3</sub> damage scheme. Taking into account that the  
477 uncertainty in these estimates is substantial, this O<sub>3</sub> damage impact over the Amazon forest is of the  
478 same order of magnitude as the release of CO<sub>2</sub> due to land fire in South America, as quantified in  
479 van der Werf et al., (2010; 293 TgC/yr from table 7 of that paper); in effect to potentially double the  
480 impact of biomass burning on the CO<sub>2</sub> fluxes. This highlights the urgent need for more tropical data  
481 on plant O<sub>3</sub> damage to better constrain estimates.

482  
483 Despite overestimating surface O<sub>3</sub> mixing ratios our model simulates only a moderate reduction in  
484 NPP associated with elevated O<sub>3</sub> due to biomass burning emissions. Given that our model  
485 systematically overestimates O<sub>3</sub> mixing ratio, assuming accurate dry deposition, and that we use our  
486 model in the high sensitivity mode, our simulations where we increase biomass burning emissions  
487 by 100% suggest a maximum 10% average reduction in monthly plant productivity, and peak  
488 reductions of 50-60% reductions in few grid-cells. This is because, despite the increase in biomass  
489 burning, monthly average surface O<sub>3</sub> mixing ratios do not exceed a moderate 40 ppb. Moreover, our  
490 model does not include deforestation due to fire, which would reduce vegetation cover when  
491 increasing biomass burning emissions in our sensitivity experiments, reducing NPP, and BVOC  
492 emissions, further. However, local and daily/hourly impact of O<sub>3</sub> damage on plant productivity can  
493 be higher.

494  
495 Estimates of the magnitude of the reduction in plant productivity due to O<sub>3</sub> damage can be  
496 improved with additional field studies and improving the representation of tropospheric O<sub>3</sub> in ESMs  
497 (sources, chemistry and sinks). Nevertheless, considering these processes in a coupled system can  
498 provide an improvement in robustness of conclusions, as e.g. it can treat processes with a specific  
499 diurnal cycle, like photosynthesis and surface O<sub>3</sub>, interactively on a short time scale (e.g. half an  
500 hour in our model).



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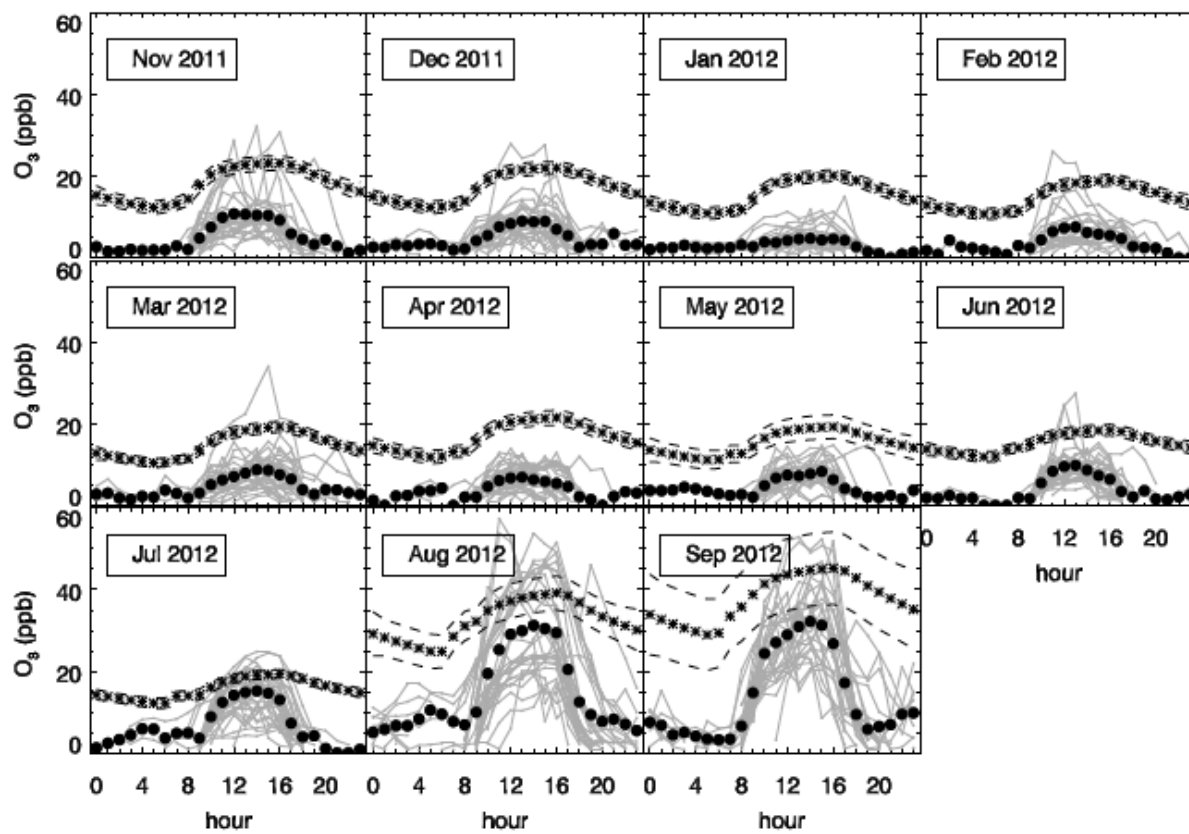
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Figures

1. Comparison of measured (dots) and simulated (stars) monthly averaged diurnal cycle of surface O<sub>3</sub> mixing ratios at the Porto Velho site, including measured day-to-day variability (grey lines) and standard deviation (dashed lines) for the model results. The measurements have an uncertainty of 4%.
2. Comparison of measured (dots) and simulated (stars) monthly averaged diurnal cycle of surface O<sub>3</sub> mixing ratios at the ZF2 site in the Cuieiras forest reserve, including measured day-to-day variability (grey lines) and standard deviation (dashed lines) for the model results. The measurements have an uncertainty of 4%. We show one of the two available years of observations. Legend as in Figure 1.
3. Vegetation cover in HadGEM2 for the month of September. The red rectangle is our region of analysis. The two sites used in the model evaluation (the sites of Porto Velho and ZF2 site in the Cuieiras forest reserve) are also marked.
4. Monthly average surface O<sub>3</sub> mixing ratio simulated with HadGEM2 for the month of September (average over 8 years of simulations).
5. Clockwise from the top-left: (a) Simulated monthly surface O<sub>3</sub> mixing ratios; (b) Simulated monthly total NPP; (c) Simulated monthly variation in total NPP. The plots show the results for the control simulation (i.e. using the decadal mean biomass burning emissions from Lamarque et al. (2010) centered on year 2000; 2000 BB emissions) and the various experiments with increased (+) or decreased (-) biomass burning emissions over South America by 20, 40, 60, 80 and 100%. All data are averaged over the region of analysis for 8 years of simulations.
6. From the left: simulated variation in surface O<sub>3</sub> mixing ratios and NPP over the region of analysis for the months of August, September and October.
7. Probability density function (histogram) of the variation in NPP for the same months. The plots show the variation between the experiments with South American biomass burning increased/decreased by 40, 60 and 100% and the control simulation.



Porto Velho (8.69°S, 63.87°W)



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833 Figure 1

ZF2 Cuieras forest (2.59°S, 60.21°W)

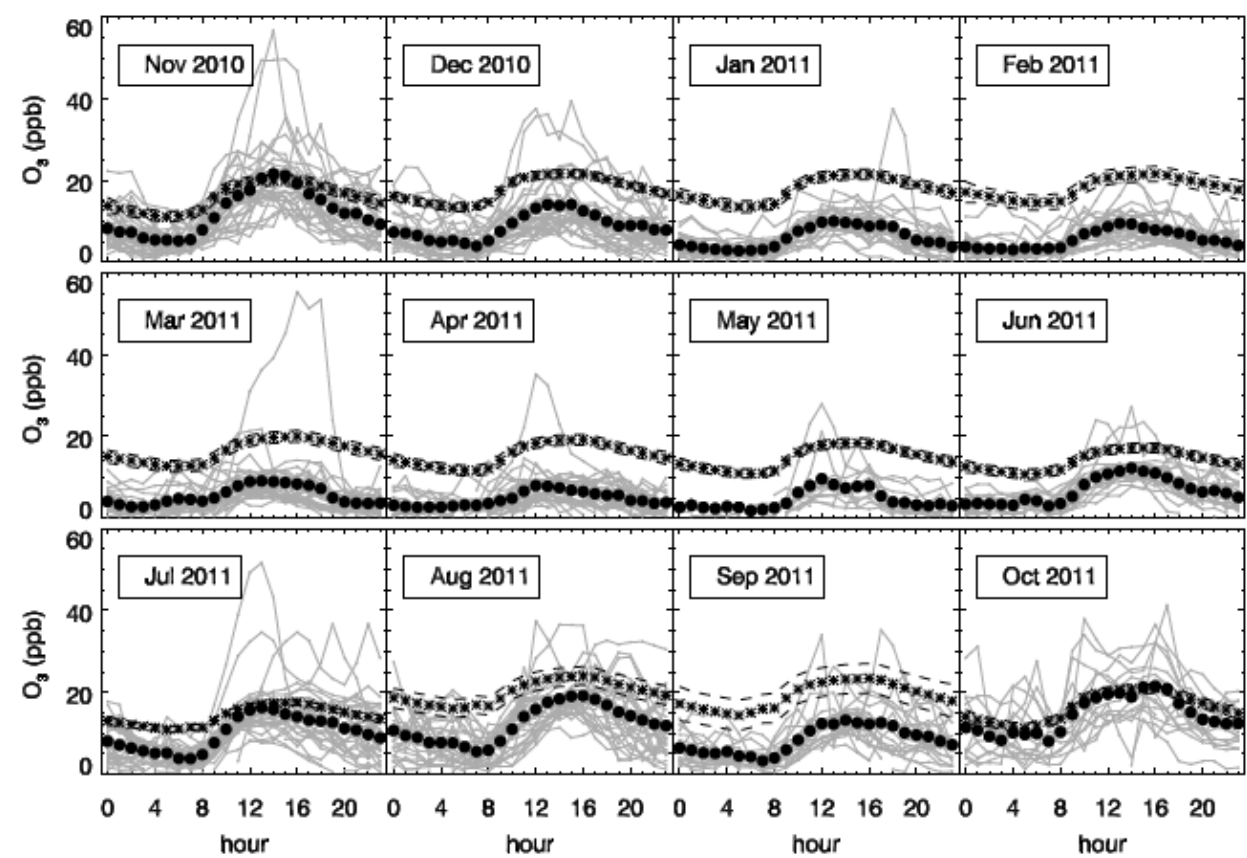
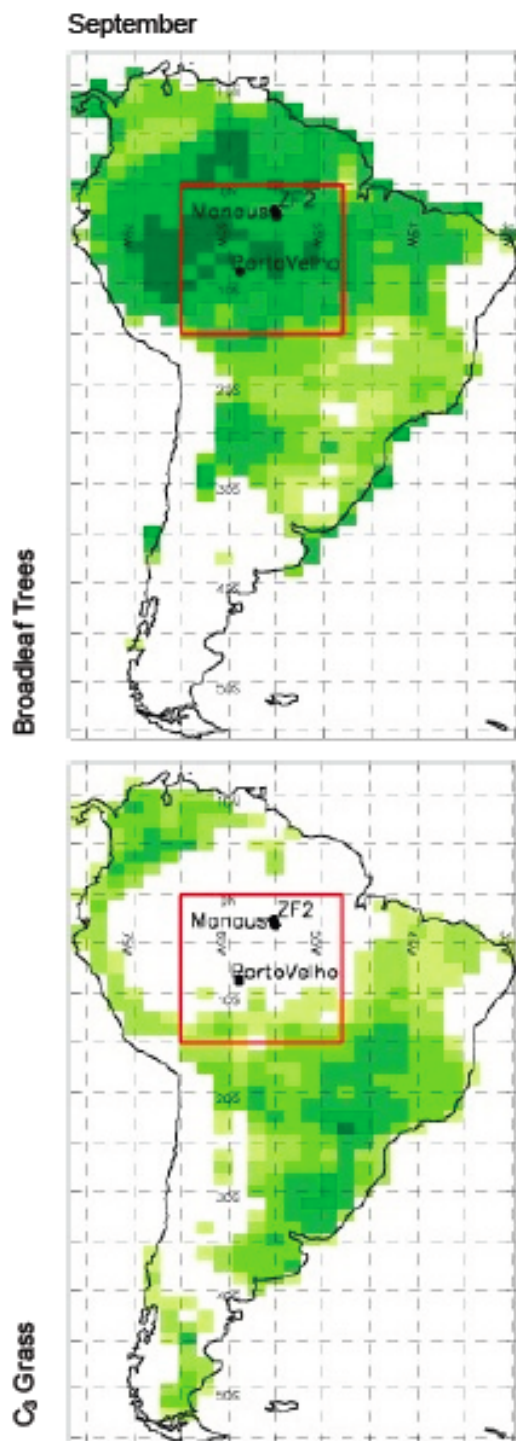


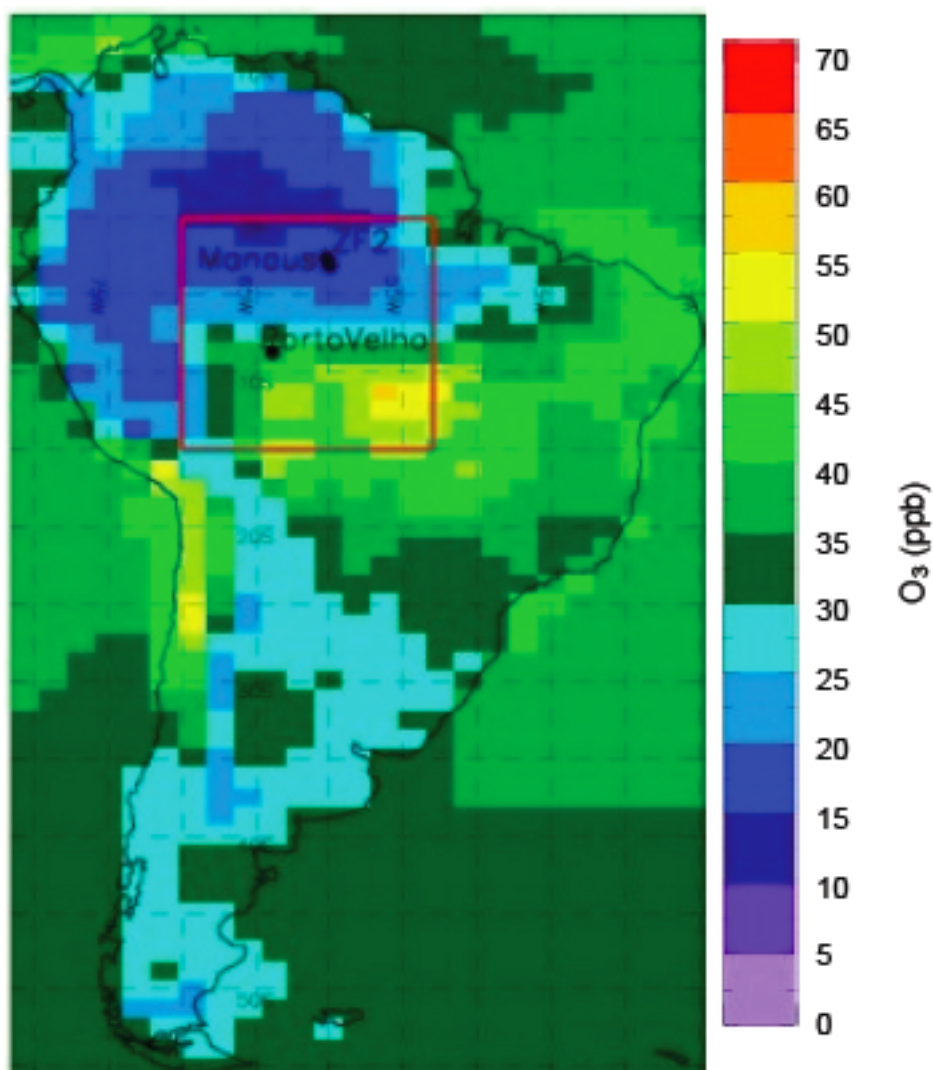
Figure 2



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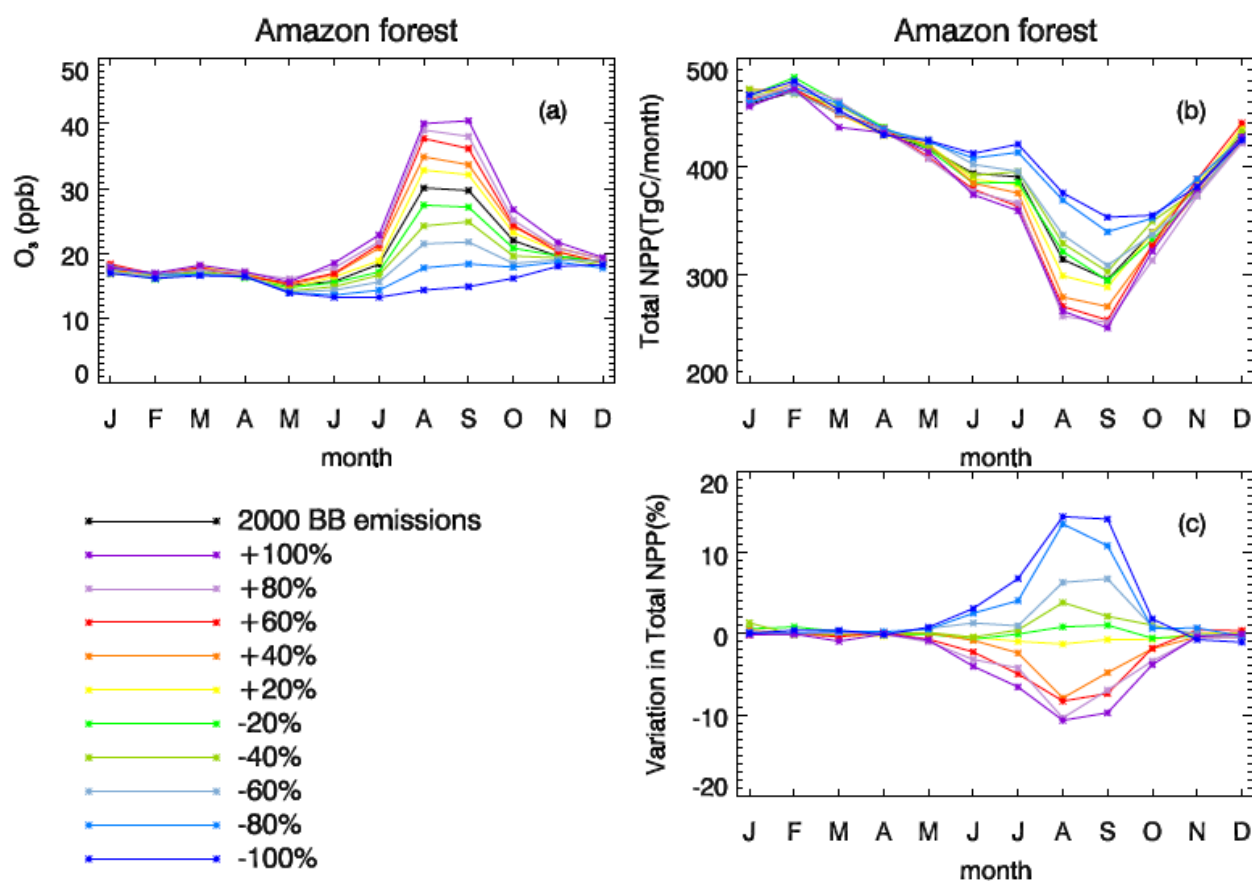
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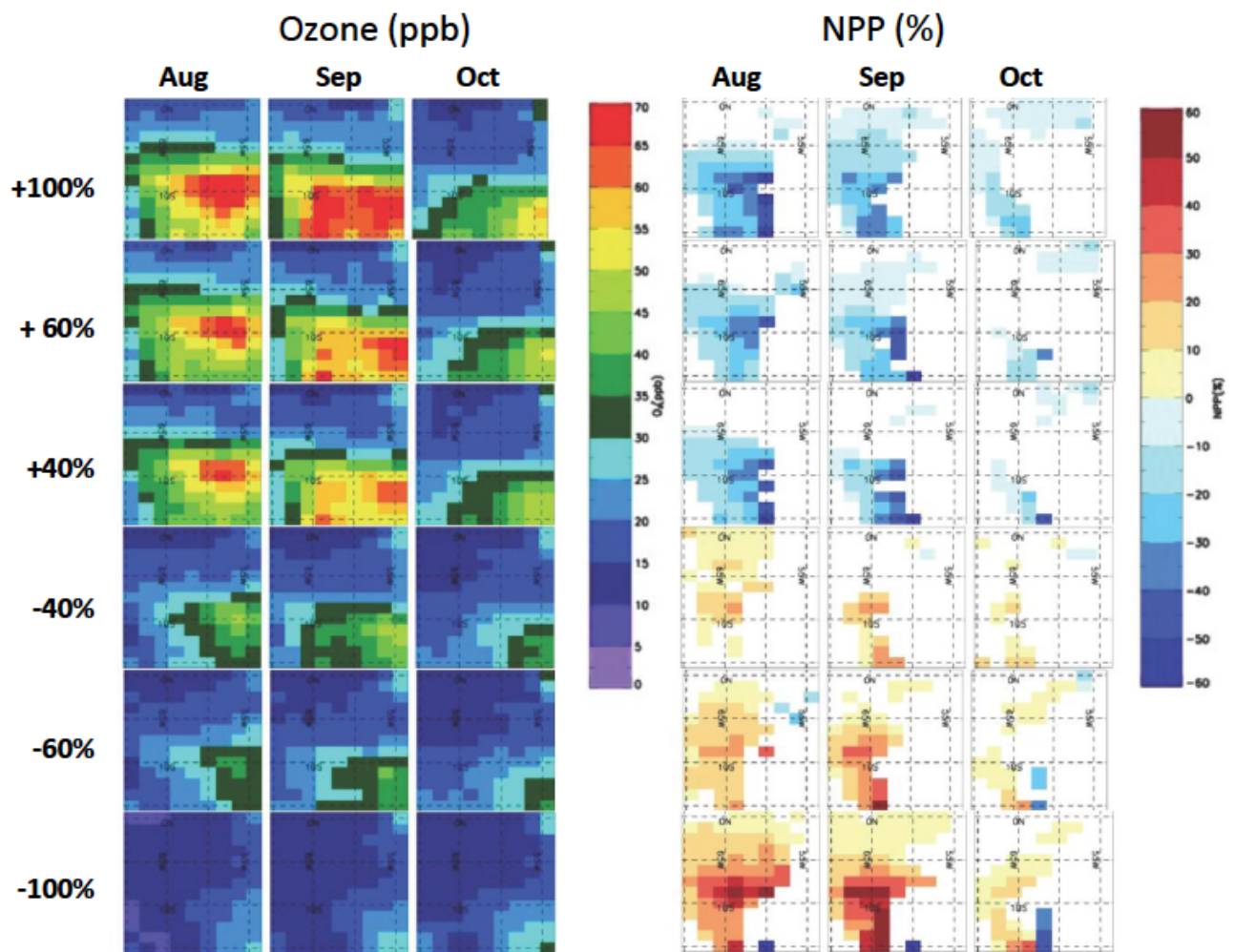
839 Figure 4





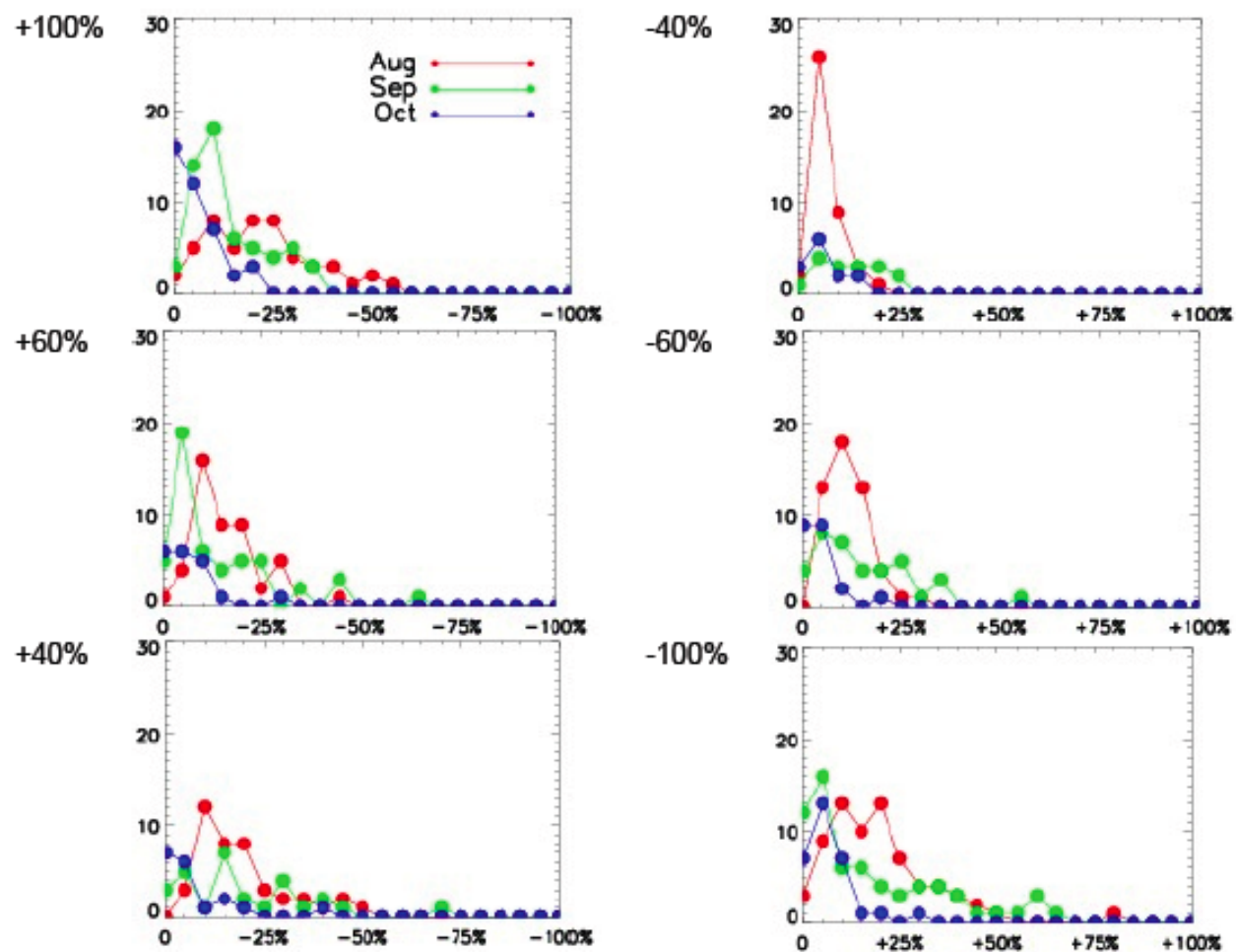
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841 Figure 5



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843 Figure 6



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