Replies to **Anonymous Referee #1** ***(****acpd-14-C8024-2014****)***

The word "Sensitivity" probably should appear in the title

We have replaced the title with: '**Biomass burning related ozone damage on vegetation over the Amazon forest: A model sensitivity study.**'.

Other comments:

1. Has visible leaf damage to tropical trees ever been reported during/after the biomass burning season?

To our knowledge there are not published data of field experiments of ozone damage on plants for the Amazon forest.

2. Much of the paper is devoted to understanding the model's over prediction of surface ozone at 2 sites in the Amazon. The overprediction is a problem since the damage depends on the absolute magnitude of the ozone concentration. The authors' honesty is appreciated. Connected to this issue, that is not yet discussed in the paper but should be, how well does the HadGEM2 model simulate the meteorology over the Amazon? Please include discussion of this validation, what does the model surface temperature, precipitation etc. over Amazon look like compared with observations? Does the model ozone bias occur everywhere in the lower troposphere? Or does the model do a better job of ozone simulation in heavily polluted regions?

We have included the model evaluation for HadGEM2 meteorology and tropospheric ozone in the supplementary material.

3. Can you use satellite data of tropospheric ozone and NOx to evaluate the model's chemical performance over the Amazon further?

Unfortunately, we could not find reliable satellite date of tropospheric ozone and NOx for the Amazon region.

4. "The decade-mean CO2 atmospheric mixing ratio was 368 ppm". How sensitive are your results to this assumption i.e prescribed not dynamic CO2 levels? I imagine the atmospheric CO2 levels near the tropical leaves will be quite variable.

There are large variations on the diurnal cycle of CO_2 as well (respiration fluxes building up during the night, stable shallow boundary layer / night-time inversions). Further investigation will be needed, as current model simulations do not take into account of dynamic CO_2 levels. Indeed, all global vegetation models are run using annual global CO_2 concentration. Between 2000 and 2009 CO_2 concentrations increase by ca. 18ppm. Adopting a Beta factor approach, and assuming a beta factor of 0.60 from Free Air Carbon Enrichment experiments, Norby et al., 2005, this translates into an expected modest increase of ca. 2% in NPP over the decade.

5. The simulations aren't fully coupled such that the loss of forest leaves due the fires does not manifest as a change in the dry deposition of the ozone (and BVOC emission), correct? How does this lack of full coupling influence your results? Is it possible that the observed ozone cycles at the 2 sites might be related to the change in deposition (decreased ozone loss) over the season, rather than localized production from fire emissions?

As said in the Model Description (page 19961, line 5) and in the Discussion and Conclusions, the model does not include an interactive fire scheme. Leaf area is lost due to fires and, since stomatal conductance is a major sink for ozone, this may affect ozone deposition. However, the leaf area lost through fire is marginal in comparison to the total leaf area over the Amazon and should thus not affect the ozone concentration. Moreover, most fires occur in pasture areas, and not over forest areas. Second, ozone production in Amazonia is limited by NOx. In the dry season, NOx concentrations can rise by a factor of 5 in comparison to the wet season (e.g., Kirkman et al., 2002), and an increase of the same order is expected for the chemical production of ozone. It is true that the canopy resistance decreases in the dry season (Rummel et al., 2007), but not due to the loss of leaves by fire. It decreases mostly because specific humidity deficit increases in the dry season, resulting in closed stomata.

6. It is intriguing that the authors included domestic biofuel emissions into their analysis. Can they offer any reason why to do this? Isn't domestic biofuel a separate activity altogether? What are the emissions totals for each source in the region?

Domestic biofuel emissions include sources like fire wood burning, which is why we include domestic biofuel sources of biomass burning, please see page 19963 line 1.

At page 19963 line 2 we have added: 'The dominant fire types in South America are from

deforestation and degradation fires in an arc around Amazonia, with some regional hotspots of agricultural burning (see Figure 13 in Van der Werf et al., 2010). Between 2001 and 2009 the percentage contribution to annual fire emissions from fire types (deforestation and degradation, grassland and savanna, woodland, forest, agriculture) are (59%, 22%, 10%, 8%, 2%) over Southern Hemisphere South America (Figure 13 van der Werf et al., 2010), with minor differences between this dataset (GFedv3) and the earlier Gfedv2 in this region (see Fig. 16 in Van der Werf et al., 2010).'

Replies to **Anonymous Referee #2 (**acpd-14-C6162-2014**)**

1) *The authors mention in the Introduction (page 19958, lines 1-5) that aerosols from biomass burning can impact the diffuse radiation and therefore, indirectly, NEE. Were these interactions included in the model simulations of this study? I would expect that some emissions from biomass burning (NOx, VOCs, CO) could impact ozone production in plumes, but that the aerosols could also impact this chemistry (by changing photolysis rates). Was this taken into account? Or any of the feedbacks to the meteorology? (e.g., boundary layer height, temperatures)? Along these lines, were the biogenic emissions changed with the different biomass burning scenarios, or were they kept constant?*

At page 19958, line 5 we have added: 'This study does not consider the effects of the changes in diffuse radiation due to biomass burning on photosynthesis, or the impact of aerosol on O_3 chemistry via changing photolysis rate. That will be the focus of a separate study. Our specific aim is to estimate the effect of ozone-induced changes on vegetation productivity due to biomass burning.'

The feedbacks of biomass burning emissions on meteorology (e.g., boundary layer height, temperatures) were not included. The idea was to focus on the biomass burning related O_3 damage on vegetation.

Biogenic emissions are calculated interactively (page 19960, lines 8-11), so they are not constant, but they are independent from the biomass burning scenario. At page 19970, line 5, we have added : ', and BVOCs emissions,'.

2) *I would appreciate a bit more information about the fire emissions used in this study. Although the authors state the references from which they got the estimates, it woul be helpful to include a bit more information about them here. For example, are they monthly emissions included constantly throughout a month, or is there a daily and/or hourly variation in these emissions? Wouldn't this make a difference in the modeled ozone production and results? Could this potentially also help explain the discrepancies between the model and the measurements?*

At page 19960 line 13, we have added: 'Given the difficulty in prescribing a diurnal cycle for fire

emissions, these monthly mean emissions are kept constant during the day.'

At page 19966 line 17, we have added: 'As stated earlier in the model description section, biomass burning emissions are prescribed as monthly mean and kept constant during the day, and this can have an impact on the hourly and day-to-day variation of surface O_3. For example, O_3 production will respond differently if biomass burning emissions occur during the day or at night, affecting simulated surface O_3 mixing ratios. These issues can be improved by modelling fire and biomass burning emissions interactively. The inclusion of an interactive fire model in HadGEM is currently under development.'

3) *The figures (particularly Figures 1, 2, 6) are very difficult to read. It would be very helpful to have them enlarged or simplified so that they are easier to see.*

We have improved Figures 1, 2 and 6.

Other comments:

Page 19958, line 8: "where" should be "were"

We have replaced 'where' with 'were' at page 19958 line 8

Page 19959, lines 18-21: Are biogenic emissions or anthropogenic emissions reduced due to deforestation, and why would this lead to an overestimation of ozone? This statement could include more details.

At page 19959, line 21 we have added: 'deforestation via burning, consequently reducing the amount of O_3 precursors'.

Page 19960, lines 12-14: How were monthly emissions temporally included in the model simulations?

At page 19960 line 13, we have added : 'Given the difficulty in prescribing a diurnal cycle for fire emissions, these monthly mean emissions are kept constant during the day.'

Page 19962, line 24: Use "that" instead of "which"

We have replaced 'which'with 'that' at page 19962 line 24

Figure 5: Label the graphs "a", "b", "c"

We have labelled the graphs in Figure 5: "a", "b", "c"

Replies to ***F. Dentener (Referee)*** *(acpd-14-C6433-2014)*

Detailed comments

p. 19956 l. 7 bias 5-15 ppb. The abstract should guide the reader to explain what that could mean for the calculated impacts.

At page 19956, line 7, we have added: '. The simulated impact of ozone damage from present-day biomass burning on vegetation productivity is about 230 TgC yr^{-1}. Taking into account that uncertainty in these estimates is substantial, this ozone damage impact over the Amazon forest is of the same order of magnitude as the release of carbon dioxide due to fire in South America; in effect to potentially double the impact of biomass burning on the carbon cycle.'

And we have removed: 'When biomass burning emissions are increased by 100%, our model simulates a maximum impact of 10% reduction in monthly mean net plant productivity averaged over the Amazon forest, with local peaks of 50-60% reduction for the months of intense fire activity.'

We have also replaced the title with: '**Biomass burning related ozone damage on vegetation over the Amazon forest: a model sensitivity study**'.

p. 19956 l. 12 reduces ozone by how much?

At page 19956, line 12 we have added : (by about 15ppb during the biomass burning season)

p. 19956 l. 10-17 Something needs to be said about the time period of evaluation, and what emissions are considered (there are issues).

At page 19956, line 3 we have added: ', under present-day climate conditions'.

At page 19956, line 5 we have added: 'for years 2010 to 2012'.

At page 19956, line 3 we have added : Here we consider biomass burning emissions from wildfires, deforestation fires, agricultural forest burning, residential and commercial combustion. '.

p. 19956 l. 10-17 Something on the type of biomass burning deforestation fires.

Please see page 19962, line 27: 'We define biomass burning emissions as those from …'

We are not able to distinguish between anthropogenic and wildfire.

p. 19956 l. 10-17 More on implications in the abstract ('could be as large as the direct impact on the carbon cycle' but that is an upper limit). Would it be possible to present a more realistic range?

See above for modification of abstract text. In the absence of data on ozone damage to tropical forest species, it is not possible to present a more realistic range; therefore we purposely chose to study an upper limit to show whether ozone effects due to biomass burning could be important or not on the carbon cycle.

p. 19957 l. 9 40 ppb is kind of an arbitrary threshold- and it is not clear if it also holds for tropical vegetation- with different genotypes. It is picked up in the discussion, but could be alluded here.

At page 19957, line 13 we have added: ', e.g. tropical rainforest vegetation may be particularly sensitive to surface O_3, even at concentrations below 40ppb (a threshold associated with extra-tropical vegetation), due to high stomatal conductances.'

p. 19957 Is Le Quere reference for 'current' budgets or missing processes?

Le Queré is reference for current budgets. At page 19957, line 28 we have replaced: 'current estimates of the effects of biomass burning on the carbon cycle may be underestimated (Le Quéré et al., 2009).' With 'current estimates of the effects of biomass burning on the carbon cycle (Le Quéré et al., 2009) may be underestimated.'

p. 19958 l. 8 derived from ; where=>were

At page 19958, line 8 we have replaced 'where' with 'were'.

p. 19958 l. 19 describe shortly what this scheme is including (or refer to p. 19961).

At page 19958, line 9 we have added: 'flux-gradient'.

At page 19958, line 11 we have added: (see model description).

p. 19959 l. 20 Is the possible bias of these emission discussed later?

This is discussed at page 19967 starting from line 1.

p. 19960 Where is ExtTC scheme evaluated, was it part of an chemistry intercomparison for example ? Does it include state-of-the-art radical cycling and what does that mean for ozone?

The model used in this study does not include state-of-science OH recycling from BVOC chemistry. We use MIM (Mainz isoprene mechanism) for this study. OH recycling would increase oxidation capacity of the atmosphere to some extend and thus maybe increase ozone production. But that depends on other factors and would require further investigation.

p. 19960 l. 10 What are the uncertainties of the VOC emissions (see discussion)?

Please see page 19968 line 2.

p. 19961 l 19 The use of the 'high' sensitivity mode seems quite critical and should at least be mentioned in the abstract and conclusions.

This is mentioned in the conclusion, please see page 19969, line 27.

At page 19956, line 11 we have added: 'We used the ozone damage scheme in the "high" sensitivity mode to give an upper limit for this effect.'

p. 19961 l. 25 see earlier remark on 40 ppb as a threshold; indeed we know little about how ozone-vegetation interactions work in the tropics.

See response to earlier comment.

p. 19962 l. 27 Can you evaluate which fraction of the emissions are deforestation?

At page 19963 line 2 we have added: 'The dominant fire types in South America are from deforestation and degradation fires in an arc around Amazonia, with some regional hotspots of agricultural burning (see Figure 13 in Van der Werf et al., 2010). Between 2001 and 2009 the percentage contribution to annual fire emissions from fire types (deforestation and degradation, grassland and savanna, woodland, forest, agriculture) are (59%, 22%, 10%, 8%, 2%) over Southern Hemisphere South America (Figure 13 van der Werf et al., 2010), with minor differences between this dataset (GFedv3) and the earlier Gfedv2 in this region (see Fig. 16 in Van der Werf et al., 2010).'

p. 19962 To what extent was the landcover data adjusted to represent the recent conditions?

At page 19962 line 27 we have added: 'The vegetation distribution was not adjusted for loss of vegetation due to fire'.

p. 19962 I understand that the model evaluates 9 years of ecosystem response. Can something be said about response on longer-time scales?

In this study we focus on the short-term ecosystem-effects. Further study and longer simulations would be necessary to investigate to the longer-term effects, however prolonged reduced productivity will influence the carbon cycle for some years to come, and affect vegetation composition.

p. 19963 The availabity of ca. 1-2 years of ozone data is limiting the comparison. What is known about interannual variability? E.g. from Shadoz sonde networkhttp://croc.gsfc.nasa.gov/shadoz/Paramaribo.html

To our knowledge there are no longer surface ozone measurement records that are representative of the Amazon forest, apart those included in this study.

p. 19963 Figure 1/Figure 2 The figures are quite hard to read (font size of legenda, spaghetti of lines); if I understand it well the full dots are the monthly average measurements, and the individual lines are the single measurement days? It is not clear why the authors want to present these single days-since as expected the model standard deviation is much lower (monthly av. Emissions, coarse resolution). Perhaps the plots can be simplified and include an monthly average (or monthly daytime comparison of data in one additional panel, which would highlight the magnitude of seasonal bias.

We have improved figure 1 and 2.

p. 19964 l. 23 higher than other months? Higher than measurements?

We have replaced the sentence at page 19964, line 23 with: 'Surface O_3 mixing ratios simulated with HadGEM2 are higher during the months of August, September and October over the Amazon forest, and in particular over our region of analysis, because of the higher biomass burning emissions in the model during these months.'

p. 19965 l.5 l. 22 I am missing an evaluation of NPP. It would be good to know if 'current' NPP is of the right order of magnitude. Is there any field evidence that vegetation was damaged by ozone in plumes?

We have added an evaluation of NPP in the supplementary material. To our knowledge there are no published data of field experiments of ozone damage on plants for the Amazon forest.

We added the following text in the supplementary material:

'Simulated HadGEM2 NPP are compared against a meta-analysis of field data from the Ecosystem Model Data Model Intercomparison project (EMDI). Measurements from the 81 'class A' ("well documented and intensively studied") sites, representative of all major global biomes, are compared against our simulations. Traditionally, global vegetation models underestimate NPP in tropical ecosystems, and tend towards an asymptote of ~1000 g C m^{-2} (Prentice et al., 2007). HadGEM2 is able to reproduce the main geographical variations of NPP globally (Figure 3), especially in the Northern Hemisphere, where more observations are available. In addition HadGEM2 is able to better simulate higher tropical NPP, although it appears to overestimate NPP over the Amazon region.'

p. 19966 l. 6 which variability is discussed? Interannual or daily variability?

At page 19966, line 6 we have added : 'inter-annual'.

p. 19666 l. 10 Why is this low productivity threshold chosen. Do the authors mean, i.e. the analysis focuses on high productivity regions?

At page 19666, line 10 we have replaced : '(i.e. forest, high productivity regions).' With '(i.e. we focus on high productivity regions, e.g. forests)'

p. 19666 l. 17 It would be good to include in Figure 1 and Figure 2 a panel that shows this increase more clearly; it is hard to read the numbers.

We have improved figure 1 and 2.

p. 19666 l. 23 : : :not impossible: : :=> redundant sentence.

At page 19666, line 23 we have removed 'however, it is not altogether impossible.'

p. 19967 resolutions=>resolution.

At page 19967 we have replaced ‘resolutions’ with ‘resolution’.

p. 19967 There has been no evaluation of the isoprene/terpenes/OVoc in this paper. What are tentatively the uncertainties (specifically for this region) and how could it contribute to the O3 overestimate.

For the evaluation of modelled isoprene emission we refer to Pacifico et al., (2011), please see page 19960 line 10.

For the evaluation of modelled terpenes, methanol, and acetone emission we refer to Guenther et al., (1995), please see page 19960 line 11.

p. 19969 A recurring science is issue the re-cycling of HOx. How was this included in the chemistry scheme and how could it influence ozone?

Our chemistry scheme does not include state-of-science OH recycling from BVOC chemistry. We use MIM (Mainz isoprene mechanism) for this study. OH recycling would increase oxidation capacity of the atmosphere to some extend and thus may increase ozone production. But that depends on many other factors and would require a separate study.

p. 19969 l. 10 this is an interesting perspective, and could already be alluded to in the introduction motivating this study.

At page 19957, line 13 we have added: ‘Moreover, tropical vegetation evolved in low background O_3 concentrations and could be more sensitive to O_3.’

p. 19969 l. 16 mention that this is for the ‘high’ sensitivity case, and for the Amazonian (whole or only the ‘box’?).

At page 19969, line 17 we have added: ‘over our area of analysis’.

At page 19969, line 18 we have added: ‘using the “high” sensitivity mode in the O_3 damage scheme’.

p. 19969 l. 27 It is not clear why the authors can use the +100 % case to estimate an ‘maximum’ effect, while earlier it was stated that even the ‘current’ emissions are probably overestimate since deforestation fires have declined. In my opinion these numbers, which also figure in the abstract are

somewhat handwaving, the authors have the means to do better; e.g. explore the low sensitivity case, a range between -50 and 50 % of emissions.

We think that the high-sensitivity -100% (i.e. no biomass burning) compared with the present-day biomass burning case establishes an upper limit for the expected effect. Referring to smaller perturbation scenarios (e.g. +/-50%) for the low-sensitivity ozone damage scheme would give a lower-perturbation response and is thus already included in our range. Sensitivity is only one factor, chemistry, and above all process understanding is at least as important. We are establishing a first assessment not a final definitive answer. It is more a qualitative than quantitative assessment and just points out that more research is needed. We also explored both increases and decreases in biomass burning to investigate possible non-linearities in response.

Replies to ***M. O. Andreae (Editor)*** *(acpd-14-C8192-2014)*

I would like to raise some questions/comments regarding the ozone measurements that are being compared with the model output. The measurement height at the TT34 site is being reported as 54 m. According to Artaxo et al. (2013), the inlet height for ozone is 39 m. Based on our experience at the ATTO site, which is very similar to TT34, this can make a difference of almost a factor of two. Please verify which inlet height is the correct one.

We double-checked the information. Trace gas measurements at TT34 were made at 39 m a.g.l., while aerosol measurements at the same site were made at 54 m a.g.l. We have corrected the manuscript at page 19963 line 27.

An advantage of the TT34 site is that the tower is located in essentially undisturbed forest, so that strong horizontal gradients are not to be expected. This makes it a relatively good candidate for comparison with a low-resolution model. But pronounced vertical gradients exist in the height range from 0 to 100 above ground (see Rummel et al. 2007 and unpublished data from the ATTO site), which may seriously affect model/observation comparisons. The Porto Velho site is even more complex. To my knowledge, the measurements were made from a shelter located in a cleared area with adjacent forest. The air intake was not very high above the ground (5 m). This needs to be specified in some detail in the paper, since it can possibly explain a part of the model/observation discrepancies. Small-scale circulations between forest and clearing can bring significant amounts of sub-canopy forest air into the clearing, which can reduce O3 levels to near-zero, especially at low levels. This introduces considerable uncertainty into what type of air and what effective height is actually sampled at such a site.

We agree that the height at which ozone is measured have a crucial impact over the comparison between measurements and model. More information about the height of detection for each site was added to the 'Model site-level Evaluation' section (page 19963). The following sentence was added to the 'Discussion and Conclusions' section (page 19967 line 17):

"The measurement level may explain part of the model overestimation, since it is well known that O_3 mixing ratios strongly decrease with height due to deposition within the canopy. The lowest layer of the model is 48 m (which corresponds to canopy top over vegetated grid-cells), while measurements were taken at 5 m and 39 m a.g.l. respectively at Porto Velho and ZF2. Rummel et al.

(2007) reports a 5-15 ppb O_3 decrease from 52 to 11 m a.g.l. in a forest site in Amazonia."

These considerations point to a more general issue, which is the difficulty of comparing model results with observations for a species with strong near-surface gradients. The paper points out that the lowest model layer depth is 48 m. It needs to be stated whether this is 48 m from the ground surface or from the canopy top.

Please see the comment above.

In the Amazon forest, the mean concentration in the 0-50 m layer would be typically about 1/3 or ¼ of that in the 30-80 m layer (heights relative to the ground); for example in the dry season at ATTO, 3 ppb vs 10 ppb. A corollary of this is that for model/observation comparisons of ozone over vegetated surfaces, measurements at a single level may not be very useful. Instead, one needs to measure a profile and then extrapolate to a height (maybe 100 m over forest, 50 m over grass) where concentration gradients become small.

The results in this paper highlight the general difficulty models have in accurately predicting ozone over vegetated surfaces, especially in clean regions. I suspect this is dominated by underestimation of surface deposition to vegetation, but incorrect treatment of vertical mixing and problems with clean-air oxidant chemistry may also play a role. In your paper you correctly point out that for plants there is a compensation effect, when concentrations are overestimated while deposition velocities are underestimated. (Actually, I think there is an error in the text: "Underestimating the O3 dry deposition flux not only leads to a positive bias in the O3 concentration, and consequently an underestimation of the damage caused by O3,: : :" – shouldn't it be "overestimation" here?).

To clarify this concept we have added, at page 19968 line 16:

'However, the total O_3 flux (or dose) is a function of both O_3 surface concentrations and dry deposition, i.e. for plants there is a compensation effect when concentrations are overestimated while deposition velocities are underestimated. Underestimating the O_3 dry deposition flux implies reduced O_3 plant uptake, and consequently an underestimation of the plant damage and productivity losses. However, it also leads to higher O_3 concentrations, which subsequently act to increase plant O_3 uptake and damage, compensating for the initial effects on productivity.'

BUT, for human exposure, it is actually the concentration at 2 m that is relevant. Given the importance of a correct representation of O3 deposition, the paper should contain a comparison between the deposition velocities used in the model and those obtained in field studies, particularly Rummel et al. (2007).

We have included a comparison against Rummel et al. (2007) ozone deposition fluxes in the supplementary material.

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

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Abstract

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

burning on plant productivity. The simulated impact of ozone damage from present-day biomass burning on vegetation productivity is about 230 TgC/yr. Taking into account that uncertainty in these estimates is substantial, this ozone damage impact over the Amazon forest is of the same order of magnitude as the release of carbon dioxide due to fire in South America; in effect to potentially double the impact of biomass burning on the carbon cycle.

435 **Introduction**

436

437 Biomass burning is a global source of aerosol and trace gases, including ozone (O_3) precursors, and
438 can lead to local and regional O_3 pollution. Tropospheric O_3 is a greenhouse gas and, above
439 background concentrations, an air pollutant: it is harmful to human health (e.g. Lippmann 1993;
440 Burnett et al., 1997) and it damages plants (e.g. Rich et al., 1964; Fiscus et al., 2005; Felzer et al.,
441 2007; Ainsworth et al., 2012). Tropospheric O_3 is a product of photochemical reactions whose main
442 precursors are nitrogen oxides (NO_x), carbon monoxide (CO), methane (CH_4) and volatile organic
443 compounds (VOCs) (Seinfeld and Pandis, 1998). VOCs are particularly important in Amazonia
444 because of the large natural biogenic and biomass burning emissions (Karl et al., 2007).

445

446 In the Amazon forest, biomass burning is mostly anthropogenic, and mainly occurs during the dry
447 season (August to October). Biomass burning emissions drastically change the composition of the
448 atmosphere, e.g. diurnal maximum mixing ratios of tropospheric O_3 varies from 12 parts per billion
449 (ppb), during the wet season, to values as high as 100 ppb in the biomass burning affected dry
450 season (Kirkman et al., 2002, Sigler et al., 2002, Artaxo et al., 2002, 2005, Rummel et al., 2007).

451

452 Surface O_3 mixing ratios over 40 ppb are known to produce visible leaf injury and damage to plants,
453 reducing crop productivity and posing a threat to food security; nonetheless different climatic
454 conditions (e.g. soil moisture and water stress) also play a role in determining leaf stomatal closure
455 and hence there will be variable impacts of the same O_3 concentrations (Ashmore, 2005), e.g.
456 tropical rainforest vegetation may be particularly sensitive to surface O_3, even at concentrations
457 below 40ppb (a threshold associated with extra-tropical vegetation), due to high stomatal
458 conductances. Moreover, tropical vegetation evolved in low background O_3 concentrations and
459 could be more sensitive to O_3. In leaves, cellular damage caused by O_3 not only reduces
460 photosynthetic rates but also requires increased resource allocation to detoxify and repair leaves
461 (Ainsworth et al., 2012). Ozone damage to vegetation reduces plant productivity, decreasing the
462 amount of carbon absorbed by plants, hence has an impact on climate via and indirect radiative
463 forcing (Sitch et al., 2007).

464

465 Tropical rain forests play an important role in the global carbon budget, as they cover 12% of the
466 Earth's land surface and contain around 40% of the terrestrial biosphere's carbon (Ometto et al.,
467 2005, Taylor & Lloyd, 1992). It has been estimated that they may account for as much as 50% of
468 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_3 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_3 chemistry via changing photolysis rate. That will be the focus of a separate study. Our specific aim is to estimate the effect of O_3-induced changes on vegetation productivity due to biomass burning.

Importantly, Sitch et al. (2007) performed their assessment of the potential impact of O_3 on vegetation using an offline simulation where monthly mean O_3 concentrations derived with a global chemistry climate model were used in determining the impacts of O_3 damage. Here we use an online flux-gradient approach to quantify the impact of biomass burning on surface O_3 concentration and O_3 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_3 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_3 concentrations and O_3 damage on vegetation for present-day (2001-2009) climate conditions. Our version of HadGEM2 includes the O_3 damage scheme developed by Sitch et al. (2007). We evaluated simulated surface O_3 against observations taken at two sites in the Amazon forest: Porto Velho (Brazil; 8.69°S; 63.87°W), a site heavily impacted by biomass burning emissions, and site ZF2 in the Cuieiras forest reserve in Central Amazonia (Brazil;

2.59°S; 60.21°W). A description of the sites can be found in Artaxo et al. (2013). In a sensitivity study we varied biomass burning emissions over South America by +/-20, 40, 60, 80, 100% to quantify the potential impact of biomass burning on surface O_3 concentrations and O_3 damage over the Amazon forest.

Model description

HadGEM2 is a fully coupled Earth-system model (Collins et al., 2011). It is built around the HadGEM2 atmosphere-ocean general circulation model and includes a number of earth system components: the ocean biosphere model diat-HadOCC (Diatom-Hadley Centre Ocean Carbon Cycle, a development of the HadOCC model of Palmer and Totterdell, 2001), the Top-down Representation of Interactive Foliage and Flora Including Dynamics (TRIFFID) dynamic global vegetation model (Cox, 2001), the land-surface and carbon cycle model MOSES2 (Met Office Surface Exchange Scheme; Cox et al. 1998, 1999; Essery et al. 2003), the interactive Biogenic Volatile Organic Compounds (iBVOC) emission model (Pacifico et al., 2012), the United Kingdom Chemistry and Aerosol (UKCA) model (O'Connor et al., 2014) and an interactive scheme of O_3 damage on vegetation (Sitch et al., 2007; Clark et al., 2011).

The configuration used here is a version of HadGEM2-UKCA with extended tropospheric chemistry (N96L38), the resolution is 1.25° latitude x 1.875° longitude (~200 x 140 km) with 38 vertical levels extending up to 39 km altitude. The land-based anthropogenic, biomass burning, and shipping emissions are taken from Lamarque et al. (2010), and represent a decadal (1997-2006) mean centered on the year 2000. The use of an emission pattern from 1997-2006 can lead to an overestimation of O_3 concentrations by the model, since the emissions vary on a year to year basis and are expected to be lower in recent years due to the reduction in Amazonian deforestation via burning, consequently reducing the amount of O_3 precursors. HadGEM2 runs at a 30 minute time step with the exception of global radiation, which is updated every 3 hours and provides radiative fluxes between those time steps via interpolation. This configuration is described and evaluated in O'Connor et al. (2014) with the exception of the Extended Tropospheric Chemistry (ExtTC) that has been applied in this work. The ExtTC mechanism has been designed to represent the key species and reactions in the troposphere in as much detail as is necessary to simulate atmospheric composition-climate couplings and feedbacks while retaining the capability to conduct decade-long climate simulations. UKCA-ExtTC simulates the spatial distribution and evolution in time of 89

chemical species, 63 of which are model tracers. The model includes emissions from anthropogenic, biogenic, soil, and wildfire sources for 17 species: nitrogen oxides (NO_x = NO +NO_2), CH_4, carbon monoxide (CO), hydrogen (H_2), methanol, formaldehyde, acetaldehyde and higher aldehydes, acetone, methyl ethyl ketone, ethane (C_2H_6), propane (C_3H_8), butanes and higher alkanes, ethene (C_2H_4), propene (C_3H_6), isoprene, (mono)terpenes, and a lumped species representing aromatics (toluene + xylene) from anthropogenic sources.

Emissions of biogenic species (isoprene, terpenes, methanol, acetone) are computed by iBVOC and provided to UKCA at every time step. The isoprene emission scheme is that of Pacifico et al. (2011). Terpenes, methanol, and acetone emissions are simulated with the model described in Guenther et al. (1995). Anthropogenic and wildfire emissions are prescribed from monthly mean emission data sets prepared for CMIP5 using the historic scenario (Lamarque et al., 2010). Given the difficulty in prescribing a diurnal cycle for fire emissions, these monthly mean emissions are kept constant during the day. Wetland methane emissions are prescribed from data from Gedney et al. (2004). Soil-biogenic NO_x emissions are prescribed using the monthly distributions provided by the Global Emissions Inventory Activity (http://www.geiacenter.org/inventories/present.html), which are based on the global empirical model of soil-biogenic NO_x emissions of Yienger and Levy (1995). NO_x emissions from global lightning activity are parameterized based on the convective cloud top height following Price and Rind (1992, 1994) and are thus sensitive to the model climate. UKCA also includes a dry deposition scheme based on the resistance in-series approach as outlined in Wesely (1989). Physical removal of soluble species is parameterized as a first-order loss process based on convective and stratiform rainfall rates (Collins et al., 2011).

The TRIFFID vegetation module of HadGEM2 simulates the dynamics of five plant functional types (PFTs): broadleaf trees, needleleaf trees, shrubs, and C_3 and C_4 grass (i.e., grasses using the C_3 and C_4 photosynthetic pathway, respectively). Changes in the extent of croplands over time are not simulated but are prescribed from land use maps prepared for the Coupled Model Intercomparison Project 5 (CMIP5, Taylor et al., 2012). Here we use the historic (1850–2000; Hurtt et al., 2009) data sets, as described in Jones et al. (2011). A further four surface types (urban, inland water, bare soil, and ice) are used in the land-surface scheme for the calculation of water and energy exchanges between the land and the atmosphere. Each model grid box can include varying proportions of several vegetation and/or surface types. The model does not include interactive deforestation due to fire.

The parameterization of O_3 damage on vegetation is that of Sitch et al., (2007). This scheme uses a flux-gradient approach to model O_3 damage, rather than empirical approaches based on the accumulated O_3 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_3 that varies proportionally to the O_3 flux through stomata above a specified critical O_3 deposition flux. The critical deposition flux depends on O_3 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_3 deposition. As the O_3 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_3 deposition flux. This approach to modelling O_3 effects on photosynthesis accounts for the complex interaction between CO_2 and O_3 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_3 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_3, CO, H_2, total reactive nitrogen (NO_y), 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_2 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).

We performed a 9-year (2001-2009) control simulation for present-day climate conditions

initialized from a centennial transient climate simulation with ocean couplings (Jones et al., 2011). We analysed the last 8 years of the simulation, as the first year of simulation was used as spin-up. A single year is considered sufficient for spin-up because one year is around five times longer than the lifetime of the longest lived atmospheric species (with the exclusion of methane) involved in O_3 chemistry. The control simulation was driven by anthropogenic and wildfire emissions of trace gases and aerosols via historical scenarios (Global Fire Emissions Database GFEDv2; Lamarque et al., 2010; Van der Werf et al., 2006) of anthropogenic and wildfire emissions. We also perform 10 experiments that differ from the control simulation in terms of assumed biomass burning emissions, i.e. biomass burning emissions over South America are either increased or decreased by +/-20, 40, 60, 80, 100%, while emissions over the rest of the world are kept unchanged. The vegetation distribution was not adjusted for loss of vegetation due to fire. We define biomass burning emissions as those from wildfires, deforestation fires, agricultural forest burning, residential and commercial combustion, including fuel wood burning, charcoal production and biofuel combustion for cooking and heating (Lamarque et al., 2010). The dominant fire types in South America are from deforestation and degradation fires in an arc around Amazonia, with some regional hotspots of agricultural burning (see Figure 13 in Van der Werf et al., 2010). Between 2001 and 2009 the percentage contribution to annual fire emissions from fire types (deforestation and degradation, grassland and savanna, woodland, forest, agriculture) are (59%, 22%, 10%, 8%, 2%) over Southern Hemisphere South America (Figure 13 van der Werf et al., 2010), with minor differences in this region between this dataset (Global Fire Emissions Database GFEFv3) and the earlier GFEDv2 used in this study (see Fig. 16 in Van der Werf et al., 2010).

This set of experiments allows us to simulate the impact of biomass burning on surface O_3 and vegetation productivity. The control simulation was also used to evaluate surface O_3 mixing ratios against measurements over the Amazon forest.

Model site-level Evaluation

Over the data-sparse Amazonian region, comprehensive spatial data sets of surface O_3 concentration are extremely limited. We evaluated simulated surface O_3 against observations from two sites that have full annual analyses of O_3 concentration: Porto Velho (Brazil; 8.69°S; 63.87°W) and site ZF2 in the Cuieiras forest reserve (Brazil; 2.59°S; 60.21°W). O_3 mixing ratios were

measured with a UV absorption analyser (Thermo 49i, USA). Observations from both sites have an estimated 4% uncertainty, considering zero noise, zero and span drifts reported in the instrument manual, and the frequency of zero and span checks performed along the experiments.

The Porto Velho sampling site is located in a forest reserve about 5 km NE (generally upwind) from the city of Porto Velho. Large land use change and regional biomass burning makes its atmospheric conditions characteristic of those of the Amazon forest with significant human interference (Brito et al., 2014). The whole region of Porto Velho has been subject to land use change since the 1980s. In Porto Velho, the dry season is from June to October and the wet season from November to May. Measurements of surface O_3 mixing ratios were taken from November 2011 to October 2012 in a forest clearance, at 5 m a.g.l..

The Cuieiras forest reserve in Central Amazonia encloses 380 km^2 of pristine tropical rainforest forest. The reserve is located in the central Amazon Basin, 60 km NNW of downtown Manaus and 40 km from the metropolis margins. This site is relatively undisturbed, as no biomass burning occurs in the forest reserve. Here rain showers are frequent with a short dry season from July to October. Measurements were taken at 39 m a.g.l. at the TT34 tower. The forest canopy height near the tower varied between 30 and 35 m, and the site is described in Martin et al. (2010), Rizzo et al. (2013) and Artaxo et al. (2013). Most of the time, the prevailing trade winds blow over 2000 km of the intact tropical forest before reaching the measurement tower. However, the site was also affected by regional transport of pollutants, either from biomass burning or urban (Rizzo et al., 2013). Measurements of surface O_3 mixing ratios were taken from April 2010 to June 2012, with the exclusion of a few months due to instrument maintenance.

We compared simulated (averaged over 8 years of simulations) against observed average diurnal cycle at each site for each available month. The model overestimates observed monthly averaged hourly O_3 mixing ratios at the surface by about 5-15 ppb for all months at the Porto Velho site, but it reproduces the diurnal and seasonal cycle, including those months affected by biomass burning, i.e. August and September, at the Porto Velho site (Figure 1). The model is able to reproduce the diurnal cycle, including magnitude, at the ZF2 site for about 8 months out of 24. The model overestimates surface monthly averaged hourly O_3 mixing ratios by about 5-10 ppb for the rest of months, which are also the months with lower surface O_3 mixing ratios (Figure 2).

672 **Results**

673

674 Our analysis is focused on the region enclosed in the red rectangle in figure 3, this is a highly
675 vegetated region with homogeneous topography, and it includes the two sites used for the model
676 evaluation (Porto Velho and ZF2 in the Cuieiras forest reserve). This region of analysis is covered
677 by two PFTs in HadGEM2: broadleaf trees, which is the predominant, and C_3 grass (Figure 3).

678

679 Surface O_3 mixing ratios simulated with HadGEM2 are higher during the months of August,
680 September and October over the Amazon forest, and in particular over our region of analysis,
681 because of the higher biomass burning emissions in the model during these months. Monthly
682 average surface O_3 mixing ratios in our control simulation peaks at 55-60 ppb in this region (Figure
683 4), while the average over the region of analysis is peaked at about 30 ppb in August and
684 September, less in October (Figure 5a, black line).

685

686 Monthly total Net Primary Productivity (NPP) in our control simulation reaches its minimum
687 during the months of August and September (Figure 5b, black line), at about 300 TgC/month,
688 corresponding to the end of the dry season.

689

690 Decreasing biomass burning emissions over South America by -20%, -40%, -60%, -80%, -100%
691 decreases surface O_3 mixing ratios and increases net productivity. Vice versa, increasing biomass
692 burning emissions over South America by +20%, +40%, +60%, +80%, +100% increases surface O_3
693 mixing ratios over the region of analysis and subsequently reduces net productivity because of O_3
694 damage on vegetation (Figure 5c).
695 These sensitivity tests suggest that decreasing biomass burning emission by 100% over South
696 America brings monthly mean surface O_3 mixing ratios averaged over the region of analysis to
697 about the observed 15 ppb for each month (Figure 5a, dark blue line), even during the dry season,
698 with no values over 35 ppb for any grid-cell (Figure 6). Increasing biomass burning emissions by
699 100% suggests that monthly mean mixing ratios of surface O_3 averaged over the region of analysis
700 reach 40 ppb in August (Figure 5a), with peaks of about 65-70 ppb in some grid-cells (Figure 6a).
701 For both increases and decreases of between 20 and 80% in South American biomass burning the
702 model simulates almost linear changes in surface O_3 mixing ratios (Figure 6, the figure shows
703 increases and reductions by 40, 60 and 100%).

704

Suppressing biomass burning emissions (i.e. decreasing biomass burning emission by 100%) over South America increases total NPP over the region of analysis by about 15%, to about 350-370 TgC/month, with peak increases of 60% for a few grid-cells, in August and September (Figure 6b): this quantifies the impact of present-day biomass burning on vegetation productivity. When increasing biomass burning emissions over South America by 100%, monthly total NPP over the region of analysis is reduced by about 10%, i.e. to about 250 TgC/month, in August and September (Figure 5b), with peak values of 50-60% reductions for few grid-cells (Figure 6c). For reductions by 20 to 80% in South American biomass burning the model varies NPP almost linearly (Figure 5c). However, the increase in South American biomass burning by 20 to 80% determine a very similar decrease in NPP, e.g. between 7 and 10% decrease in August (Figure 5c). Both increasing and reducing South American biomass burning from 20 to 80% increases the number of grid-cells where a significant variation of NPP takes place (Figure 6b). The percentages given above are significant against inter-annual variability in the control simulation, i.e. we only take into account of the variations above one standard deviation in the control simulation. We also exclude from our analysis the grid-cells with low productivity, i.e. where NPP in the control simulation is below 50 gC/m^2/month (i.e. we focus on high productivity regions, e.g. forests).

Discussion and Conclusions

The HadGEM2 model overestimates the magnitude of the O_3 diurnal cycle at the two sites used in the evaluation. Overestimation of simulated O_3 in the Amazonian boundary layer has been observed in other modelling studies, especially in clean air conditions (Bela et al., 2014). Nonetheless, our model reproduces the main features of the diurnal and seasonal cycle. In particular, the model is able to reproduce the increase in surface O_3 during the biomass burning season.

As stated earlier in the model description section, biomass burning emissions are prescribed as monthly mean and kept constant during the day, and this can have an impact on the hourly and day-to-day variation of surface O_3. For example, O_3 production will respond differently if biomass burning emissions occur during the day or at night, affecting simulated surface O_3 mixing ratios. These issues can be improved by modelling fire and biomass burning emissions interactively. The inclusion of an interactive fire model in HadGEM is currently under development.

738 The model overestimates surface O_3 mixing ratios by 5-15 ppb for several months at the ZF2 site in
739 the Cuieiras forest reserve and for all available months at the Porto Velho site. The reasons for these
740 systematic biases in surface O_3 mixing ratio are likely manifold. In a complex, highly coupled
741 system such as the HadGEM2 Earth System Model (ESM) it is not always easy to disentangle all
742 processes and attribute model biases to specific components.
743 We attribute the systematic biases in the surface O_3 mixing ratio to the following, most likely
744 reasons:
745 1. Model resolution in both the horizontal and the vertical dimension
746 2. Uncertainties in emissions, both magnitude, seasonality and location
747 3. Uncertainties in the O_3 dry deposition at the surface
748 Other factors such as photolysis rates, lightning NO_x production over the area and transport of O_3
749 and precursors will certainly contribute. We will briefly discuss the three most important (in our
750 opinion) factors that contribute to the systematic biases.
751
752 The relatively coarse resolution of a global ESM simulates mixing ratios of trace species (both trace
753 gases and aerosols) that represent averages over large areas. This issue has been discussed
754 previously in the literature, mostly in relation to air quality modelling (see, e.g., Valari and Menut,
755 2008; Tie et al., 2010; Appel et al. 2011; Thompson and Selin, 2012). In our case one grid box
756 equals approximately 30,000 km^2 (i.e., 200x150 km^2 in longitude and latitude). The implicit
757 averaging pertains both to emission and concentration fields; the predominant consequence is a
758 dilution in each grid-cell. Depending on the chemical regime, this can lead to reduced or enhanced
759 net O_3 production. Additionally, HadGEM2-ES has a relatively coarse vertical resolution.
760 HadGEM2-ES has a lowest model layer depth of 48m (global average) and the vertical profile of O_3
761 will undoubtedly show a gradient as the loss mechanism for O_3 is dominated by the surface (e.g.
762 Colbeck and Harrison, 1967). The measurement level may explain part of the model overestimation,
763 since it is well known that O_3 mixing ratios strongly decrease with height due to deposition within
764 the canopy. The lowest layer of the model is 48 m (which corresponds to canopy top over vegetated
765 grid-cells), while measurements were taken at 5 m and 39 m a.g.l. respectively at Porto Velho and
766 ZF2. Rummel et al. (2007) reports a 5-15 ppb O_3 decrease from 52 to 11 m a.g.l. in a forest site in
767 Amazonia.
768
769 The remote environment of the Amazon forest is dominated by relatively high concentrations of
770 VOC, particularly of biogenic origin, and low concentrations of nitrogen oxides, NO_x. It is a NO_x-
771 limited environment. In such an environment O_3 is destroyed by reactions with BVOC (mainly

isoprene and (mono-)terpenes). This destruction is more pronounced the higher the BVOC concentration becomes. Consequently, conditions in the global model are likely to differ from that of a measurement at a specific point such as those we compare to in Figures 1 and 2. It is a known problem in model evaluation.

Another issue related to model resolution, when comparing global models to point-like observations, is the uncertainty in global emission inventories, both with respect to magnitude and location. In particular the latter will result in discrepancies between modelled concentrations of O_3 and its precursors and point-like observations. But the uncertainties in emission magnitude are also substantial and can reach a factor of two or more in case of biogenic VOC (e.g., Guenther et al., 2006; Arneth et al., 2008, 2011; Pacifico et al., 2011, 2012).

Thirdly, and again related to model resolution, is the representation of O_3 dry deposition at the surface. Its magnitude and diurnal cycle will depend on boundary layer turbulence, surface roughness, land surface type, vegetation type, soil moisture, photosynthetic activity, and more. In a recent sensitivity study by Folberth et. al (in preparation) O_3 surface concentrations showed the largest sensitivity to perturbations in O_3 surface dry deposition fluxes. Underestimating O_3 surface dry deposition, in particular during the night preventing a complete flush of the PBL with respect to O_3, will lead to systematic biases.

Interestingly, however, the latter process may also represent a redeeming feature of the model. According to our model of O_3 plant damage it is the total O_3 flux into the plant that determines the amount of damage caused to the photosynthetic activity and, hence, carbon assimilation. However, the total O_3 flux (or dose) is a function of both O_3 surface concentrations and dry deposition, i.e. for plants there is a compensation effect when concentrations are overestimated while deposition velocities are underestimated. Underestimating the O_3 dry deposition flux implies reduced O_3 plant uptake, and consequently an underestimation of the plant damage and productivity losses. However, it also leads to higher O_3 concentrations, which subsequently act to increase plant O_3 uptake and damage, compensating for the initial effects on productivity. Still, a detailed assessment and quantification of this interdependence of O_3 concentration and dry deposition fluxes is beyond the scope of this study and must be referred to future research.

August, September and October are the months when biomass burning and surface O_3 concentrations are higher over the Amazon forest, but also the months when plant productivity is at

its lowest which will tend to suppress the impact of O_3 damage on plant productivity. This is because stomatal conductance is reduced due to water limitations (also accounted for in the model) during the dry season, thus reducing the flux of both carbon dioxide and O_3 into the leaves, and consequently reducing O_3 plant damage.

Ashmore (2005), noted how O_3 exposure is poorly correlated with flux into leaves and also the potential for damagingly high O_3 fluxes in leaves at concentrations significantly below 40 ppb at maximum stomatal conductance. Consequently, global vegetation models as used in this study have adopted flux-based parameterizations to represent O_3 impacts on vegetation, moving away from application of the earlier exposure based metrics, e.g. accumulated O_3 exposure above a threshold of 40 ppb, AOT40.

The parameterization of O_3 damage used in this study is calibrated for high-latitude vegetation. Unfortunately data for calibrating this O_3 damage scheme for tropical vegetation are currently not available and observations of O_3 damage in the Amazon forest are very limited. Observations of O_3 damage on tropical forests are urgently needed, including observations at moderate (e.g. 20-30 ppb) and high surface O_3 mixing ratios.

The simulated impact of present-day biomass burning on vegetation productivity over our area of analysis is about 230 TgC/yr (i.e. the difference between the dark blue line and the black line in Fig. 5b) using the "high" sensitivity mode in the O_3 damage scheme. Taking into account that the uncertainty in these estimates is substantial, this O_3 damage impact over the Amazon forest is of the same order of magnitude as the release of CO_2 due to land fire in South America, as quantified in van der Werf et al., (2010; 293 TgC/yr from table 7 of that paper); in effect to potentially double the impact of biomass burning on the CO_2 fluxes. This highlights the urgent need for more tropical data on plant O_3 damage to better constrain estimates.

Despite overestimating surface O_3 mixing ratios our model simulates only a moderate reduction in NPP associated with elevated O_3 due to biomass burning emissions. Given that our model systematically overestimates O_3 mixing ratio, assuming accurate dry deposition, and that we use our model in the high sensitivity mode, our simulations where we increase biomass burning emissions by 100% suggest a maximum 10% average reduction in monthly plant productivity, and peak reductions of 50-60% reductions in few grid-cells. This is because, despite the increase in biomass burning, monthly average surface O_3 mixing ratios do not exceed a moderate 40 ppb. Moreover, our

model does not include deforestation due to fire, which would reduce vegetation cover when increasing biomass burning emissions in our sensitivity experiments, reducing NPP, and BVOC emissions, further. However, local and daily/hourly impact of O_3 damage on plant productivity can be higher.

Estimates of the magnitude of the reduction in plant productivity due to O_3 damage can be improved with additional field studies and improving the representation of tropospheric O_3 in ESMs (sources, chemistry and sinks). Nevertheless, considering these processes in a coupled system can provide an improvement in robustness of conclusions, as e.g. it can treat processes with a specific diurnal cycle, like photosynthesis and surface O_3, interactively on a short time scale (e.g. half an hour in our model).

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Figures

1. Comparison of measured (dots) and simulated (stars) monthly averaged diurnal cycle of surface O_3 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_3 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_3 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_3 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_3 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.