I am pleased to resubmit for publication the revised version of ACP paper acp-2014-228. I have incorporated new figures, tables and text into the paper in response to the reviewers' comments. The introduction and background sections have been combined and condensed to better motivate the current study. The results section has been condensed and restructured to frame the discussion of meteorological and other physical and chemical processes through their effects on O_3 distributions. New analyses include an evaluation of the simulated PBL depth and mean O_3 profiles calculated over broad regions to facilitate comparison with other models. The revised paper includes discussion of the potential implications of model biases in biogenic emissions and clarifications of the implications of the aircraft-satellite-model O_3 intercomparison, and numerous other clarifications and corrections to the text. Please find below my responses to specific comments.

Reviewer #1

1. The major criticism I have of this paper is the lack of detailed information about the process controlling chemical production of O3 from the models. At present the model results are compared against the observed O3 but few details are given as to why the model results agree or disagree with the observations from a chemical point of view. There is some focus on the role of NO (from soil) and indeed comparisons are made to NO profiles, but other important O3 precursors (e.g. PAN) are neglected. Similarly there is hardly any mention of the role of VOCs in the paper. For example, isoprene acts as an important O3 precursor. How sensitive are the model results to isoprene emissions and chemistry? A cursory comparison of isoprene fluxes from observations and the MEGAN model is included. But there is little to no discussion on the impacts biases in isoprene oxidation may cause. A large amount of the model observation comparison focuses on comparison with meteorological data. Whilst this is undoubtedly a key component to the story I suggest perhaps some of this could be cut down and more analysis on the O3 budgets could be included. Or more links could be drawn between the chemistry and meteorology. What impact does biases in temperature have on O3? The wet scavenging of soluble species should impact O3 too, the effect of which can be relatively easily tested in the model simulations.

We thank the reviewer for his/her comments. We have added the following text discussing the possible model sensitivities to errors in emissions of isoprene and other BVOCs (lines 567-576 in the Revised Manuscript):

"Emissions of BVOCs can increase O_3 production by the following mechanism. Oxidation of BVOCs can lead to formation of HO_2 and $RO_2\bullet$, which react with NO to form NO_2. NO_2 in turn photolyzes to form $O(^3P)$, which reacts with O_2 to form O_3 (National Research Council, 1991). We expect the polluted east/south regions during

BARCA A to be VOC-sensitive and the clean west, north and around Manaus regions during BARCA A and all regions in BARCA B to be NO_x-sensitive. Kuhn et al. (2010) determined via aircraft transects in the Manaus urban plume that most of the VOC reactivity was provided by isoprene emissions from the surrounding rainforest, and NO_x emissions suppressed O_3 production close to urban sources, but stimulated it downwind."

One limitation of this study is that measurements of only a few gas phase species (CO, O_3) are available from BARCA. Thus, it is not possible to evaluate other important O_3 precursors (PAN, VOCs) in the models using BARCA data. We also agree that wet scavenging of soluble O_3 precursors should impact O_3 production. However, as measurements of only relatively passive/insoluble species (CO, O_3) were taken during BARCA, a detailed evaluation of the impact of wet scavenging falls outside the scope of this study. The meteorological evaluation of the models has been shortened and rewritten to emphasize how biases in meteorological variables (e.g. temperature) impact O_3 (Section 4.2, lines 452-522).

References

National Research Council, 1991. Rethinking the Ozone Problem in Urban and Regional Air Pollution. National Academy Press, Washington, DC, 500pp.

In general the manuscript is well written, however, I think the paper could benefit from a number of changes, below, before being published in ACP.

General comments (line number, page and comment):

2. Line 1, page 14017: The authors have not included the role of VOCs (in particular BVOCs) as O3 precursors in the Amazon basin. Is this because they have no net effect on O3?

We chose to focus on NO_x as the primary O_3 precursor in the Amazon basin under clean conditions based on the study of Jacob and Wofsy (1988), who found that O_3 production in a photochemical model based on ABLE-2A was relatively insensitive to the amount of VOCs present. This was because oxidation of CO provided sufficient HO_x to generate background O_3 values of 20 ppb. Thus, the amount of additional O_3 produced in the boundary layer depended on the amount of NO_x present. However, the polluted regions during BARCA A may be VOC-sensitive, and we have added the following text to discuss the possible implications (lines 760-764):

"In polluted, VOC-sensitive conditions, approximately the correct net amount of O_3 is generated in the PBL. This suggests there is insufficient VOC reactivity in the models, since the correct amounts of O_3 deposition velocities and NO_x emissions would both decrease O_3 production."

3. Line 20-27, page 14020: Are there likely to be any issues with using land use data from c.a. 2000 when comparing to observations made in 2008/9?

Conversion of forest to pasture land cover reduces surface latent heat fluxes and increases sensible heat fluxes, as shown in Figs. 6-7 using data from von Randow et al. (2004). On a local scale, at least during the dry season, these changes decrease moisture content and increase surface temperature and the depth of the convective boundary layer over pasture areas (Fisch et al., 2004). Wang et al. (2009) found that deep convection was stronger over forested areas due to the greater humidity, but that shallow convection was enhanced over pasture areas.

The PROVEG dataset (years 2000-2001) was the most recent available for use in regional models at the time of this study. However, deforestation from 2000-2009 (see figure below) was minimal in the BARCA flight regions. Recently an updated vegetation map based on MODIS observations in 2012 was produced for regional models, and will be used in modeling studies going forward.

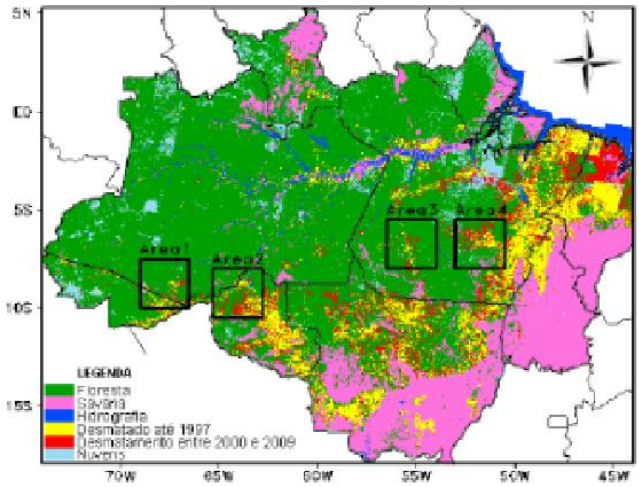

Figure 3.4 from Oliveira (2009): red areas were deforested from 2000-2009 according to data from PRODES (Satellite Monitoring of the Brazilian Amazon) Project (2010, http://www.obt.inpe.br/prodes/)

References:

Fisch, G., Tota, J., Machado, L. A. T., Silva Dias, M. A. F., Lyra, R. F. da F., Nobre, C. A., Dolman, A. J., and Gash, J. H. C.: The convective boundary layer over pasture and forest in Amazonia, Theor. Appl. Climatol. 78, 47–59, DOI 10.1007/s00704-004-0043-x, 2004.

Oliveira, R. A., Análise das Tendências da Precipitação sobre o Brasil e Impactos do Desmatamento no Regime de Chuvas na Amazônia Legal, Master's Thesis in

Meteorology, National Institute for Space Research (INPE), São José dos Campos, Brazil, sid.inpe.br/mtc-m18/2011/12.08.10.56-TDI, 2009.

Wang, J., Chagnon, F. J. F., Williams, E. R., Betts, A. K., Renno, N. O., Machado, L. A. T., Bisht, G., Knox, R., and Bras, R. L.: Impact of deforestation in the Amazon basin on cloud climatology, P. Natl. Acad. Sci. USA, 106(10), 3670-3674, doi:10.1073/pnas.0810156106, 2009.

4. Line 18, page 14022: Other modeling groups will, I hope, find the observations very useful for model evaluation. As it may prove problematic to sample other models in the manner the authors have could the authors comment on the biases from averaging the observed O3 in large areas compared to the sampling they perform in the current manuscript (i.e. if they were to average the model O3 from -3N to 4N, -58E to -68E (roughly speaking the clean sector in Figure 2 (a), how would that compare to the results presented in Figure 2(a)?).

Following the reviewer's suggestion, to facilitate other modeling groups' comparisons with the data and modeling results of this study, a new figure has been added (Fig. 16) which compares the mean observed profiles with large averaged area from the models for: clean (West, North and around Manaus regions) and polluted (East and South regions) regions during BARCA A and all regions during BARCA B.

The following text has been added (lines 350-361) explaining the methodology:

"To facilitate comparison of other models with the data presented in Fig. 2, mean profiles from the large regions corresponding to clean (west, north and around Manaus regions) and polluted (east and south regions) regions during BARCA A and all regions during BARCA B are presented in Fig. 16. From the models, all horizontal grid points falling within the corresponding region's longitude and latitude bounds for each flight day (Table 6) and the closest model output times (12:00-18:00 UTC / 8:00-14:00 LT) were averaged into 500 m vertical bins."

The following text has been added (lines 553-557) presenting the results:

"A similar model behavior is seen as in the mean profiles for individual regions. All simulations over-estimate O_3 throughout the PBL and lower troposphere during clean conditions in BARCA A, but under-estimate O_3 in polluted conditions. This is especially true from 2-4 km where biomass burning plumes detrain O_3 precursors. During BARCA B all simulations show good agreement."

5. Line 5, page 14023: The authors need to include the geographic extent that "west, north etc." refer to in Figure 2 (and Figures 18-21).

A table has been added to include the geographic extents and dates encompassed by the regions (lines 438-440):

"The longitude and latitude bounds and flight dates included in each geographic region from BARCA A and BARCA B are listed in Table 6."

6. Technical corrections (line number, page and comment):

Line 24, page 14013: Typo. "increased" should have "be" inserted before it.

Line 24, page 14015: Typo. "northem" should be "northern".

Line 18, page 14030: Typo. Amazonia needs correcting.

We apologize for these errors, and we have made the suggested corrections in the text.

Reviewer #2

The paper describes an analysis of the temporal and spatial variability in ozone concentrations, fluxes and controlling processes as observed during the BARCA campaigns. This analysis is supported by model simulations done with the regional chemistry transport modelling systems CCATT-BRAMS and WRF-CHEM. I deem this being a very interesting analysis that aims to identify the role of chemical versus physical and dynamical processes in O3 over the Amazon forest for the contrasting meteorological and chemical conditions of the wet and dry seasons. This analysis combines the information gained from both detailed observations as well as model analysis. As such it fits in very well with the scope of ACP but there are, according to me, a number of major issues that must be resolved. For example, in the model application there have been some processes not being considered/not well described (anthrogenic emissions) but that are of potentially large relevance for O3/photo-chemistry over the Amazon forest (see detailed comments below). My most serious concern is about the model application being used too much in a "black box" mode. There are many statements including the term "may" expressing that the models are somewhat being applied as a black box not really being able to really nail down the reasons for the found discrepancies between model simulated and observed chemical and meteorological properties. By the way, from the evaluation of the meteorological parameters is becomes obvious that the model representation of the meteorology for the Amazon region still poses a large limitation to properly simulate the atmospheric chemistry being largely driven by these meteorological (and hydrological) drivers.

We thank the Reviewer for his/her general comments. Numerous modifications were made that are detailed in the responses to the specific comments below.

1. Abstract: "However, O3 simulated by the models was lower than both BARCA observations in mid-levels and total tropospheric O3 retrieved from OMI/MLS, suggesting that the satellites are dominated by middle troposphere and long-range processes and are not a good indication of O3 conditions in the PBL."; Satellites are dominated?? This is apparently a very weird sentence that requires re-writing and re-thinking. The observations should be all right but apparently the models do a relatively poor job on representing the free troposphere-BL gradient in O3.

We thank the reviewer for his/her comment. We did not intend to indicate that the model-satellite discrepancy indicates an error in the satellite retrieval, and have altered the text to specify that the models do a relatively poor job of representing the free troposphere-BL gradient in O_3 compared with aircraft and satellite observations. The new sentence (lines 31-37) now reads:

"In addition, O_3 simulated by the models was either within the error bars or lower than BARCA observations in midlevels (3–5 km a.s.l.), and lower than total tropospheric O_3 retrieved from OMI/MLS, which is primarily comprised of middle troposphere O_3 and thus reflects long-range transport processes. Therefore, the models do a relatively poor job of representing the free troposphere-BL gradient in O_3 compared with aircraft and satellite observations, which could be due to missing long-range and convective transport of O_3 at mid-levels."

2. Introduction; the paper starts straight away on the research questions to be addressed in this paper but where it seems that first indicating why an improved understanding/quantification of ozone temporal and spatial variability in the tropical rainforest environment is important.

We agree with the reviewer that explaining the motivation for the study is important before presenting the specific science questions. The introduction has been revised to start with an explanation of why an improved understanding/quantification of ozone temporal and spatial variability in the tropical rainforest environment is important, followed by the statement of the scientific questions.

2. Introduction, line 65: "high availability of solar radiation"; rephrase to high solar radiation levels

The sentence has been revised to include the reviewer's suggestion.

The new sentence (lines 56-59) now reads:

"The Amazon Basin continues to rapidly urbanize, and urban emissions of O_3 precursors are also expected to grow. Emissions from cities in the tropics may have a larger impact on the upper troposphere due to high solar radiation levels and intense convective transport (Gallardo et al., 2010)."

3. Line 78; here it is stated that in-situ observations of cloud properties and chemical species are the reason that we cannot constrain this system well ; I think it is much more than only cloud properties and chemical species measurements; we need information on many additional parameters; land use changes, boundary layer dynamics, cloud aerosol interactions at the larger scale, etc.

We agree with the reviewer that many parameters/processes affect atmospheric chemistry over Amazonia. The sentence has been revised to include the reviewer's suggestion.

The new sentence (lines 96-98) now reads:

"In-situ data on cloud properties and chemical species, as well as observations of land use changes, boundary layer dynamics and larger-scale cloud-aerosol interactions, are scant in this region."

4. Line 90: "It is interesting to compare BARCA data to observations from the NASA Amazon Boundary Layer Experiments ABLE campaigns (ABLE-2A and -2B), which took place during the dry season of 1985 and wet-to-dry transition of 1987". I also think this is interesting to do but then it should be stated what is expected from such a comparison with these data from the 80's.

We agree that it is important to explain the purpose of comparing data from the current campaign with one which took place three decades ago.

The following text has been added (lines 216-224) to reflect this suggestion from the reviewer:

"Andreae et al. (2012) showed that CO mixing ratios were about 10 ppb higher during ABLE-2B than in BARCA B everywhere except the southern region, reflecting the global trend towards decreasing CO emissions since the 1980s, particularly in the Northern Hemisphere. The CO comparison also showed a similar enhancement of 10–20 ppb in the lowest 1 km above the surface, attributed to diffuse biogenic sources, and also indicated that the much higher enhancements during the dry season in BARCA A must be due to anthropogenic or biomass burning inputs. The O_3 comparison is expected to yield information in long-term trends in O_3 production in the Amazon Basin, as well as the relative importance of biogenic, urban and fire sources."

5. Line 134: "During BARCA A, coarse model aerosols were predominantly from biogenic emissions and biomass burning, while fine mode aerosols consisted of biomass smoke and some Secondary Organic Aerosol (SOA) from biogenic Volatile Organic Compounds (VOCs)". I guess you refer here to coarse mode aerosols but how do you know what the sources are of these coarse mode aerosols?

Numerous studies have focused on aerosol composition and origin in the Amazon (Martin et al., 2010 provides a review). These studies show that the dominant coarse mode source is primary biogenic emissions, while the main fine mode source is biomass burning in the dry season and Secondary Organic Aerosol (SOA) from biogenic Volatile Organic Compounds (bVOCs) in clean conditions. However, the aerosol size distribution was not measured during BARCA, so the following sentence was removed:

"During BARCA A, coarse model aerosols were predominantly from biogenic emissions and biomass burning, while fine mode aerosols consisted of biomass smoke and some Secondary Organic Aerosol (SOA) from biogenic Volatile Organic Compounds (VOCs)."

Reference:

Martin, S. T., Andreae, M. O., Artaxo, P., Baumgardner, D., Chen, Q., Goldstein, A. H., Guenther, A., Heald, C. L., Mayol-Bracero, O. L., McMurry, P. H., Pauliquevis, T., Pöschl, U., Prather, K. A., Roberts, G. C., Saleska, S. R., Dias, M. A. S., Spracklen, D., Swietlicki, E., and Trebs, I.: Sources and properties of Amazonian aerosol particles, Rev. Geophys., 48, RG2002, doi:10.1029/2008RG000280, 2010.

6. Line 142: "The mean contribution from biomass burning to total CO during BARCA-A was about 31%, with a contribution from background (110 ppb) of about 61%"

First of all refer to all flights in a consistent way; BARCA-A (previously it was BARCA A); Furthermore, the second part of the sentence reads weird; rephrase.

The sentence has been corrected to refer to the field campaigns in a consistent way (BARCA A) and to explain the data more clearly.

The revised sentence (lines 161-163) now reads:

"According to analysis of tracer simulations, during BARCA A biomass burning contributed on average about 56 ppb (31%) to the total CO of around 180 ppb, while the background was 110 ppb (61%)."

7. Line 150: "Small boundary layer enhancements were attributed to a source from the oxidation of biogenic VOCs". Would be good to see some reference here.

The reference (Andreae et al., 2012) has been included at the end of this sentence (lines 170-171).

8. Line 152: "The simulated vertical CO profiles matched mean observed values, but were overly vertical (too low near the surface and too high above 3 km), suggesting that the models were overly diffusive or had too much convective transport". Here you already discuss a model result, one that is indicating a quite essential problem with the

models relevant for the presented analysis before you have even introduced in more detail these models and their set-up.

The following sentence was added at the beginning of the paragraph (lines 172-175) to indicate that the model results being discussed are from Andreae et al. (2012), not the current study:

"Andreae et al. (2012) also showed simulated vertical CO profiles from CCATT-BRAMS and WRF-Chem simulations, as well as the Stochastic Time Inverted Lagrangian Transport (STILT) model with two different meteorological field inputs and the WRF Greenhouse Gas Module (WRF-GHG)."

9. In the overview of the O3 observations and role of different mechanisms explaining this behavior I miss the references to studies that have demonstrated/explained the behavior, e.g., line 181 on the role of convection in lofting O3 and a chemical production of 15 ppbv d-1 over Brazil but also already at the beginning of the section on the role of NO/BVOC emissions versus transport, on the observations collected in Rondonia, etc.

We thank the reviewer for his/her suggestion on how to clarify the references in the text. This portion of the background section has been condensed as follows (lines 76-79):

"Previous analyses of satellite ozone data have noted early-year O_3 maximums in the tropical Southern Hemisphere primarily associated with cross-Atlantic transport of biomass burning emissions from Africa (Fishman and Larson, 1987; Thompson et al., 1996), Northern Hemisphere fires and lightning NO_x (Edwards et al., 2003)."

10. Lines 186-193; this is one example of extreme long sentences that make the paper difficult to read; there are many more of those long sentences that require editing.

Numerous sentences were edited to make them shorter and easier to read.

11. Lines 218: "dry deposition in the region was a globally significant O3 sink", dry deposition in the region provides a significant sink in the global O3 budget.

Line 228; "aboard", onboard (?)

The suggested changes have been made in the text.

12. Line 230; where the measurements collected at 1.5m above the soil surface or above the canopy top? and what was the vertical extent over which the profiles were sample? In the forest canopy there are large gradients especially during nighttime and then the reference height becomes very important.

The sentence has been revised to clarify the height and vertical extent at which the measurements were collected. The sentence (lines 208-213) now reads:

"As part of ABLE-2, near-continuous O_3 surface measurements (1.5 m above the soil surface) showed daytime maximums of 3.7 ppb inside a forest and 5.7 ppb in a clearing (typical standard deviations of 0.3 ppbv). Additionally, tower measurements at the clearing site showed higher O_3 values of 6.7 ppb at 7 m above the soil surface and 6.9 ppb at 15 m above the soil surface (Kirchhoff et al., 1990)."

13. Line 281; I appreciate the overview of all the measurements that have informed us about the typical features of O3 and the photochemical and mixing/transport regimes over the Amazon but at the end what can be concluded from this?? Because of the vast amount of information it would be optimal to draw some conclusions about the main findings.

Different O_3 measurement methods enable the observation of different physical and chemical processes affecting O_3 variability in the Amazon, with satellites identifying fire and lightning sources of precursors, ground measurements observing surface processes, and aircraft in the location of convective transport. The following paragraph was added to the Introduction (lines 90-96):

"Thus, satellite observations enable the attribution of tropical O_3 maxima to biomass burning and lightning NO_x sources, while ground-based measurements allow the identification of key surface processes in the Amazon Basin affecting O_3 amounts. These processes include O_3 production from soil NO_x emissions and removal via dry deposition to the forest canopy. Aircraft campaigns complete the suite of observations, allowing the examination of convective lofting of surface emissions, with biomass burning emissions of particular importance on the regional scale."

14. Line 328; I think that indicating the location with 2 numbers behind the comma suffices.

We have corrected the latitude/longitude locations to use two decimal places (lines 428-432).

15. Line 387: "Anthropogenic emissions were estimated from the RETRO, GOCART and EDGAR v4.0 global databases updated with South American inventories (Alonso et al., 2010)". It is rather easy to read over this quite essential part of the analysis. The emissions, especially those of NOx, will ultimately determine to a large extent the photochemistry over the Amazon basin. Than having an estimate of the emissions based on a selection of different emission inventories might introduce a large range in results. I think it is essential to provide the emission inventory as used in this analysis and also show how the numbers compare to the different alternatives; e.g., how do the RETRO and EDGAR v4.0 compare for this domain and how does the actually applied inventory compare to those global inventories for the domain?

In PREP-CHEM-SRC, the emissions are obtained from RETRO if available for that species, then from EDGAR v4.0, otherwise from GOCART. The purpose of this is to use the most consistent emissions inventory possible. The following sentence has been added in order to clarify this point (lines 286-292):

"Emissions are obtained from RETRO if available for that species (CO, NO_x, chlorinated hydrocarbons, acids, esters, alcohols, ethers, benzene, ketones, methanal, other alkanals, other aromatics, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14} plus higher alkanes, other VOCs, toluene, trimethylbenzenes, xylene), then from EDGAR v4.0 (NMVOC, SO_4, CO_2, SF_6, N_2O), otherwise from GOCART (BC, OC, SO_2, DMS), in order to use the most consistent emissions inventory possible."

As the differences between the RETRO emissions and PREP-CHEM-SRC emissions are documented and illustrated in Alonso et al. (2010), we do not feel it is necessary to include another figure in the present paper.

16. I also realized, reading through the rest of the paper, that there is not reference at all to how the atmosphere-biosphere NOx exchange is treated, a component that is essential for the analysis in all the areas without substantial anthropogenic influences.

Biogenic NO emissions were not included in these simulations as NO was not available for the MEGAN 2000 climatology. Future simulations will include online MEGAN emissions of NO and other biogenic species. The following sentence was added to the model description section (lines 294-297) to make this clearer:

"The MEGAN 2000 climatology includes numerous biogenic species (acetaldehyde, formaldehyde, other ketones, acetone, isoprene, propane, methane, propene, ethane, methanol, sesquiterpenes, ethene, monoterpenes and toluene), but not soil NO emissions."

17. Line 410: "while in WRF-Chem, wet deposition and lightning production of NOx were not considered.". Why?? I think this should be explained and then later on it will be important to demonstrate/discuss the consequences of ignoring these quite essential features in the presented analysis

The text was modified to explain why these processes were not included in the WRF-Chem simulation:

(lines 320-322) On the other hand, no wet scavenging is included for cloud water and precipitation resolved by the microphysics scheme, because this option is not currently available in WRF-Chem for the RACM chemical mechanism.

(lines 331-333) "In WRF-Chem, lightning production of NO_x was not included, because these parameterizations have not yet been evaluated for the Amazon region."

The following text discusses the consequences of ignoring these processes:

(lines 322-326): "O_3 production in the upper troposphere is affected by the net convective transport of soluble HO_x precursors (including hydrogen peroxide (H_2O_2), methyl hydroperoxide (CH_3OOH) and formaldehyde (CH_2O)). However, uncertainties remain about the scavenging efficiencies of these and other soluble species by deep convective storms."

(lines 333-337): "In the tropics, over continents, lightning production is comparable to other sources of NO_x, including biomass burning and soil release, and it is the primary source over oceans (Bond et al. 2002). Since lightning NO_x production peaks in the upper troposphere, it could be an important contributor to ozone production."

18. Line 480: "Especially in the case of WRF Chem, the excessive precipitation rate may be due to a too sensitive deep convective trigger function or underestimated shallow convection, leading to a more unstable atmosphere"; Would there be a way that you could indeed confirm this explanation doing some sensitivity experiments?

We thank the reviewer for their suggestion. Sensitivity experiments on parameters of the convective parameterization such as the trigger function would indeed be interesting and provide useful information for tuning the convective parameterization for Amazonia. However, we feel these tests fall outside the scope of this study. Simulations for subsequent field campaigns will use updated versions of the convective schemes and at that point it may be appropriate to tune the parameterizations.

19. In the discussion about the meteorological conditions I think it is essential to start with the analysis of the shortwave radiation terms since if this parameter is off in the models, then you would also not expect the latent and sensible heat fluxes to be correctly simulated.

We agree that the shortwave radiation will affect the heat fluxes, and we have reordered the text to reflect the reviewer's suggestion (Section 4.2, lines 452-522).

20. Line 513; "The overestimated moisture in CCATT-BRAMS may be due to overactive convective detrainment at midlevels, and could be associated with over-active O3 production"

Here you suggest with this sentence that O3 is somehow responsible for the overestimation of moisture in the model. I guess that you would like to express that the issues on moisture representation in the model coincide with issues on the O3 simulations due to issues on the convective transport.

We did not intend to suggest that overestimated O_3 production causes high moisture bias in the models. Therefore we have altered this sentence to clarify that excessive moisture may stimulate O_3 production (lines 507-510):

"The models generally show good agreement with soundings at Manaus (Figs. 8-9), but excess moisture (positive dewpoint bias of 10 K) in CCATT-BRAMS above 500 hPa may lead to increased photochemical production of O_3."

21. Line 534; Overall the analysis of the meteorological parameters (measurements and models) does not give a lot of confidence in this feature essential to a fair evaluation of the chemistry. There appear to be substantial issues on the representation of some of the key drivers of chemistry (solar radiation), tracer transport and removal processes. I also think that the analysis is not very well structured going back and forth between all the relevant meteorological parameters. Is there a more optimal way to structure this description of the analysis of the meteorology?

We agree that accurate simulation of meteorological parameters in the Amazon continues to be a challenge, and that these parameters will drive some of the main processes that affect O_3 production and transport. We now state this at the beginning of Section 3.2 (lines 452-454):

"Tropospheric O_3 distributions are driven by both chemical processes, including chemistry and emissions of O_3 precursors, and meteorological ones, such as solar radiation, tracer transport and removal."

We also added a new paragraph (lines 477-485) that summarizes the key findings of the model-data meteorological comparison and their implications for chemistry:

"Now we summarize the key findings of the model-data meteorological comparison and their implications for the chemistry simulations. The models capture the seasonal spatial distribution of precipitation over northern South America (Fig. 4), and the signs of NE-SE differences are correctly modeled by both models during both seasons, i.e., the NE is drier than the SE during November and vice-versa during May. For the Amazon, CCATT-BRAMS slightly underestimates the precipitation rates in both seasons, but the rate in WRF-Chem is about twice that of TRMM 3B43 (Table 2). This may lead to errors in the strength and vertical distribution of convective transport and the amount of convective wet removal."

22. Line 551: "Typical model anthropogenic NOx emissions values over the Amazon, primarily from biofuel source..... (Garcia-Montiel et al., 2003)." Another example of a way too long sentence.

This sentence was divided into four sentences to increase readability (lines 585-581):

"Typical model anthropogenic NO_x emissions values over the Amazon, primarily from biofuel sources, were 0.008-13 µg N m^{-2} hr^{-1} N. These NO_x emissions included in the models were less than one third of the mean values of 44 ± 14 µg N m^{-2} h^{-1} NO measured by Kaplan et al. (1988) during ABLE-2A. This is considered a threshold value for NO_x-driven O_3 production to be the dominant O_3 source in the PBL. The model emissions were also much lower than the mean emissions from forest of 35.8 µg N m^{-2} h^{-1} NO measured in the 1998 dry season (Garcia-Montiel et al., 2003)."

23. Line 727: "These discrepancies of models with observations may result from an overly mixed (constant with altitude) profile due to overly active turbulent mixing from 1-2 km or too much downward convective transport of O3 from 2 km to the surface, as observed by Betts et al. (2002)."

This statement is an example of where I think that this analysis would benefit from more in depth analysis of what really explains the observed discrepancies between the models and the measurements. There are many statements including the term "may" expressing that the models are somewhat being applied as a black box not really being able to really nail down the reasons for the misrepresentations. On this particular topic I think it would be very useful to see some analysis of the boundary layer (BL) depth, how this compares to observations of the BL depth over tropical rainforest and also to see, if the BL depth would be different, to what extent this is due to issues on the surface energy balance representation, model representation of entrainment/detrainment processes, etc.

We agree that we would like to better understand what explain the discrepancies between the model and observations. For complex coupled meteorology-chemistry models, with many feedbacks among processes, physical and chemical parameters and input data sources, it is difficult to attribute an error to specific processes. In response to the reviewer's suggestion, we have included an analysis comparing the maximum CBL depth from Fisch et al. (2004) with the models at forest and pasture sites for both seasons. The text describing this analysis is as follows (lines 404-414):

"Fisch et al. (2004) found that in the dry season (14-25 August, 1994), higher sensible heat fluxes over pasture increase the maximum height at 21 UTC (17 LT) of the Convective Boundary Layer (CBL) from around 1100 m for forest (Rebio Jarú) to 1650 m over pasture (FNS). On the other hand, during the wet season (Jan.-Feb. 1999) the height of the CBL is similar for both land types, around 1000 m. The simulated height of the PBL at 21Z above the forest and pasture sites (Table 4) was analyzed from model output using two different methods: *TKE*, the first level above the surface where the Turbulent Kinetic Energy (TKE) from the PBL schemes dropped below 0.01 m^2 s^{-1} and *Theta*, the first level above the surface where theta exceeded theta of the level below by

0.6 K. In addition, *WRF MYNN* is the diagnostic from the WRF PBL scheme which takes into account TKE as well as stability."

Reviewer #3

1. Overall, the paper presents valuable results but would benefit from better organization around the main science questions. For example, the introduction (Section 1) and Previous studies (Section 1.3) could be combined and condensed so that they lead directly into the questions this study will address. Stronger links between the model evaluation and the science questions would also be helpful.

We agree that the previous studies should be presented in order to justify the science questions of this current study. Following the reviewer's suggestion, the introduction and previous studies sections have been combined and condensed, followed by the science questions.

Specific Comments:

2. Abstract Line 15-18: There are a number of reasons ozone might be higher in OMI/MLS than the model besides lack of PBL sensitivity in the satellite data.

We agree that in the scope of this study it is difficult to assess the accuracy of the OMI/MLS data. The too-vertical nature of the model profiles could be due to missing inputs from the boundary conditions and errors in the convective transport. This sentence in the abstract (lines 31-37) has been modified to:

"In addition, O_3 simulated by the models was either within the error bars or lower than BARCA observations in midlevels (3–5 km a.s.l.), and lower than total tropospheric O_3 retrieved from OMI/MLS, which is primarily comprised of middle troposphere O_3 and thus reflects long-range transport processes. Therefore, the models do a relatively poor job of representing the free troposphere-BL gradient in O_3 compared with aircraft and satellite observations, which could be due to missing long-range and convective transport of O_3 at mid-levels."

3. P14010 Line 16: Please explain "The flights consisted of quasi-Lagrangian measurement"

Lagrangian measurements involve following an air parcel as it moves through the atmosphere in order to be able to constrain sources and sinks of chemical species found within the parcel. As it is nearly impossible to do this with an aircraft, the term "quasi-Lagrangian" is used to refer to sampling a parcel, then intercepting what is thought to be the same parcel at a later time and location. The following paragraph (lines 130-138) has been rephrased in order to clarify this terminology:

"In-situ measurements were made of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ozone (O_3), and aerosol number concentration and optical properties. Flask samples were collected to determine CO_2, CH_4, sulfur hexafluoride (SF_6), CO, nitrous oxide (N_2O), hydrogen, and the oxygen-nitrogen ratio (O_2/N_2). The flights consisted of quasi-Lagrangian measurements, which attempt to sample an air parcel at multiple locations along its path in order to constrain regional and basin-wide fluxes of these species. The aircraft had a ceiling of 4500 m, and flights usually consisted of ascending and descending vertical profiles separated by short (5–30 min) horizontal legs."

4. P14022 Line 26-28: What is the advantage of using the 16 boxes instead of just sampling the model at the location of the observation?

The following sentence was inserted to explain this reasoning (lines 342-344):

"As the model output has a much coarser spatial and temporal resolution than the aircraft measurements, the model value is interpolated to the observation time and location."

5. Section 3.3 1st Paragraph: Is this background information or findings of this study? If it is background, please include citations.

This is background information to set up the analysis of the impact of seasonal variations in meteorological and emissions conditions on the chemistry. The paragraph has been edited to include references as follows:

(lines 454-456) "During the dry-to-wet transition season, increased actinic fluxes stimulate the production of OH radicals from O_3 photolysis that can lead to net O_3 production (Seinfeld and Pandis, 2006)."

(lines 459-466) "On the other hand, in the wet-to-dry transition season, lower levels of O_3 are largely associated with increased presence of convective clouds and precipitation. Decreased surface temperatures and incident solar radiation due to cloudiness suppress emissions of biogenic VOCs such as isoprene (Fall and Wildermuth, 1998). In addition, higher surface humidity and precipitation decrease the occurrence of fires (Morton et al., 2013; Chen et al., 2013) that emit NO_x and VOCs (Freitas et al., 2007). O_3 precursors are further decreased by wet removal within the storms (Barth et al., 2007a)."

References:

Barth, M. C., Kim, S.-W., Skamarock, W. C., Stuart, A. L., Pickering, K. E., and Ott, L. E.: Simulations of the redistribution of formaldehyde, formic acid, and peroxides in the

July 10, 1996 STERAO deep convection storm, J. Geophys. Res., 112, D13310, doi:10.1029/2006JD008046, 2007.

Chen, Y., Velicogna, I., Famiglietti, J. S., and Randerson, J. T.: Satellite observations of terrestrial water storage provide early warning information about drought and fire season severity in the Amazon, J. Geophys. Res. Biogeosci., 118, 495–504, doi: 10.1002/jgrg.20046, 2013.

Fall, R., and Wildermuth, M. C.: Isoprene Synthase: From Biochemical Mechanism to Emission Algorithm, J. Geophys. Res., 103(D19), 25599-25609, doi: 10.1029/98jd00808, 1998.

Morton, D. C., Le Page, Y., DeFries, R., Collatz, G. J., and Hurtt, G. C.: Understorey fire frequency and the fate of burned forests in southern Amazonia, Phil. Trans. R. Soc. B, 368(1619), doi: 10.1098/rstb.2012.0163, 2013.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd edition, J. Wiley, New York, 2006.

6. Page 14030 Lines 3-5: The second part of the sentence does not necessarily follow from the first, since there could be errors in the model's vertical distribution of ozone.

We agree with the reviewer that we cannot conclude that the satellite data is missing PBL O_3. The tropospheric O_3 may be lower in the models than satellite due to missing mid-level inflow and sources, as is also indicated by the comparison with the aircraft observations and SHADOZ. This sentence has been revised as follows (lines 768-771):

"In addition, simulated O_3 was lower than both the OMI/MLS total tropospheric O_3 and the BARCA observations in mid-levels, indicating that the models are missing sources at mid-levels from long-range and convective transport."

7. P14034 Lines 6-7: Better agreement than what?

Both sensitivity simulations agreed better with observations than the original simulation. The sentence was revised and now reads (lines 739-741):

"Additional simulations with WRF-Chem showed that O_3 in the lower boundary layer was about twice as sensitive to increases in O_3 deposition velocity as reductions in NO_x emissions, but both simulations achieved better agreement with observations than the base case simulation."

8. P14034 Lines 9-10: Are there other possible sources of model error?

Yes, in clean (NO_x-sensitive) conditions, low ozone deposition and NO_x emissions can contribute to the O_3 overestimate, while in polluted (VOC-sensitive) conditions these

errors may be compensated for by insufficient VOC reactivity. We have added the following sentence to clarify this reasoning (lines 760-766):

"In polluted, VOC-sensitive conditions, approximately the correct net amount of O_3 is generated in the PBL. This suggests there is insufficient VOC reactivity in the models, since the correct amounts of O_3 deposition velocities and NO_x emissions would both decrease O_3 production. Additionally, in clean, NO_x-sensitive conditions, proportionally more O_3 is produced per unit NO_x emissions and the O_3 deposition velocities are still too low, resulting in an overestimate."

9. P14034 Line 24: Could insufficient ozone deposition also contribute?

Yes. See response to Comment #8.

10. P14035 Lines 1-4: While the lack of surface sensitivity in the satellite data is known and is a potential factor in the model/obs mismatch, there can be many sources of model error. This statement, here and in the abstract, needs to be re-worded; one cannot conclude simply from the fact that simulated ozone was lower than OMI/MLS at mid-levels that the O3 observed by satellites is dominated by the mid-troposphere and long-range transport.

These statements were revised as follows in the Abstract (lines 31-37):

"In addition, O_3 simulated by the models was either within the error bars or lower than BARCA observations in midlevels (3–5 km a.s.l.), and lower than total tropospheric O_3 retrieved from OMI/MLS, which is primarily comprised of middle troposphere O_3 and thus reflects long-range transport processes. Therefore, the models do a relatively poor job of representing the free troposphere-BL gradient in O_3 compared with aircraft and satellite observations, which could be due to missing long-range and convective transport of O_3 at mid-levels."

And in the Conclusions (lines 768-771):

"In addition, simulated O_3 was lower than both the OMI/MLS total tropospheric O_3 and the BARCA observations in mid-levels, indicating that the models are missing sources at mid-levels from long-range and convective transport."

11. P14025 Lines 5-8: This sentence is confusing. Please re-word.

Following the suggestion of the reviewer, the sentence was re-worded to be clearer as follows (lines 487-492):

"However, for the southern Amazon forest and pasture sites peak shortwave may be overestimated (underestimated) by 50-100 W m^{-2} by CCATT-BRAMS (WRF-Chem) (Figs. 6-7), suggesting that there is insufficient (excessive) cloudiness in the models."

12. Figure 2 Caption: What statistical test does Matlab use to determine outliers?

The following text was added to the Fig. 2 caption (lines 1157-1162) to include this information:

"the whiskers extend to the most extreme data points not considered outliers and outliers are plotted individually as red plusses. Values are drawn as outliers if their values exceed q3 + w(q3 - q1) or are less than q1 - w(q3 - q1), where q1 and q3 are the 25th and 75th percentiles, respectively, and w is the maximum whisker length with the default value of 1.5. For normally distributed data, the whiskers encompass from approximately the 2.7 to 99.3 percentiles."

Comments about organization:

13. P14008 Lines 8-13: This seems like a separate paragraph and should be moved elsewhere.

A new paragraph was created after the Lelieveld et al. (2008) citation and the remainder of the paragraph was reordered as follows (lines 56-68):

"The Amazon Basin continues to rapidly urbanize, and urban emissions of O_3 precursors are also expected to grow. Emissions from cities in the tropics may have a larger impact on the upper troposphere due to high solar radiation levels and intense convective transport (Gallardo, et al., 2010). In the upper troposphere, O_3 acts as a greenhouse gas, increasing surface radiative forcing (IPCC, 2001). Inhalation of elevated levels of ozone can irritate the lungs; aggravate asthma and cause emphysema, bronchitis, and premature death (Schwela, 2000). High ozone concentrations can also inhibit photosynthesis in plants and damage leaf tissue, harming wild ecosystems and reducing crop productivity (Reich and Amundson, 1985). Thus, an improved understanding/quantification of O_3 temporal and spatial variability in the tropical rainforest environment is important for projecting future impacts of land use and climate change in the Amazon Basin and other tropical rainforest regions worldwide on their expanding human populations and significant biodiversity."

14. P14009 Line 15: Description of BARCA seems like it should be a separate paragraph

A separate section was created for the BARCA description (Section 2, lines 121-224)

15. Are sections 1.1-1.3 all subsections of the introduction? Section 1.3: This section could potentially be combined with the introduction. It contains a lot of detail on past studies, but it would be helpful to relate this information more strongly to the goals of the current study and how the current study will advance our understanding.

Subsection 1.3 was condensed and integrated into the main body of the introduction to create a more coherent justification of the current study.

16. Section 3.2: There is a lot of detail in this section that is difficult for the reader to keep track of and relate to the main chemical processes. The last paragraph provides a nice summary, so perhaps other portions of the text and the number of figures could be reduced. Another possibility would be to combine sections 3.2 and 3.3 but discuss each portion of the campaign separately.

Following the reviewer's suggestion, this section (now 4.2, lines 452-522) has been condensed and reframed in terms of impacts on the chemical processes.

Ozone production and transport over the Amazon Basin during the dry-to-wet and wet-to-dry transition seasons

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Abstract

The Regional Carbon Balance in Amazonia (BARCA) campaign provided the first Amazon Basin-wide aircraft measurements of O_3 during both the dry-to-wet (November and December 2008) and wet-to-dry (May 2009) transition seasons. Extremely low background values (< 20 ppb) were observed to the west and north of Manaus in both seasons and in all regions during the wet-to-dry transition. On the other hand, elevated O_3 levels (40-60 ppb) were seen during the dry-to-wet transition to the east and south of Manaus, where biomass burning emissions of O_3 precursors were present. Chemistry simulations with the CCATT-BRAMS and WRF-Chem models are within the error bars of the observed O_3 profiles in the boundary layer (0-3 km a.s.l.) in polluted conditions. However, the models overestimate O_3 in the boundary layer in clean conditions, despite lacking the predominant NO source from soil. In addition, O_3 simulated by the models was either within the error bars or lower than BARCA observations in midlevels (3–5 km a.s.l.), and lower than total tropospheric O_3 retrieved from OMI/MLS, which is primarily comprised of middle troposphere O_3 and thus reflects long-range transport processes. Therefore, the models do a relatively poor job of representing the free troposphere-BL gradient in O_3 compared with aircraft and satellite observations, which could be due to missing long-range and convective transport of O_3 at mid-levels. Additional simulations with WRF-Chem showed that the model O_3 production is very sensitive to both the O_3 deposition velocities and the NO_x emissions, which were both about one half of observed values. These results indicate the necessity of more realistic model representations of emissions, deposition and convective processes for accurate monitoring and prediction of increases in O_3 production in the Amazon Basin as the regional population grows.

Excluído: indicating that the models do not represent the free troposphere – boundary layer gradient in O_3. Total tropospheric O_3 retrieved from OMI/MLS was higher than that simulated by the models, suggesting that the satellite observations are dominated by the middle troposphere and long-range processes and are not a good indication of O_3 conditions in the PBL.

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1 Introduction

In the Amazon Basin, trace gases from biomass-burning, urban, and biogenic emissions are important sources of ozone precursors, which are efficiently transported by intense convective activity to the upper troposphere, where they can be dispersed over long distances by regional and global circulations. Additionally, convective overshooting may inject heat, moisture and trace gases into the tropical tropopause layer, impacting stratospheric ozone and other aspects of global climate (Fueglistaler et al., 2009). In the dry-to-wet transition season, regional smoke and haze plumes from biomass burning are observed (Longo et al., 2009). On the other hand, in the wet-to-dry transition season, biogenic emission of VOCs, particularly from the Amazon rainforest, may maintain the atmospheric oxidative capacity for generating ozone and other photochemical pollutants (Lelieveld et al., 2008).

The Amazon Basin continues to rapidly urbanize, and urban emissions of O_3 precursors are also expected to grow. Emissions from cities in the tropics may have a larger impact on the upper troposphere due to high solar radiation levels and intense convective transport (Gallardo et al., 2010). In the upper troposphere, O_3 acts as a greenhouse gas, increasing surface radiative forcing (IPCC, 2001). Inhalation of elevated levels of ozone can irritate the lungs, aggravate asthma and cause emphysema, bronchitis, and premature death (Schwela, 2000). High ozone concentrations can also inhibit photosynthesis in plants and damage leaf tissue, harming wild ecosystems and reducing crop productivity (Reich and Amundson, 1985). Thus, an improved understanding and quantification of O_3 temporal and spatial variability in the tropical rainforest environment is important for projecting future impacts of land use and climate change in the Amazon Basin and other tropical rainforest regions worldwide on their expanding human populations and significant biodiversity.

Analyses of satellite, aircraft and ground-based observations of O_3 over Amazonia since the 1980s have demonstrated the influence of long-range transport of African biomass burning and Northern Hemisphere inputs, local fire sources, NO soil and biogenic VOC emissions, and convective transport on spatial and seasonal variability in O_3. In particular, data from the ABLE-2B aircraft and ground campaign during the 1987 wet-to-dry transition season and the BARCA observations offer the opportunity to compare the regional O_3 distribution across decades.

Previous analyses of satellite ozone data have noted early-year O_3 maximums in tropical Southern Hemisphere primarily associated with cross-Atlantic transport of biomass burning emissions from Africa (Fishman and Larson, 1987; Thompson et al., 1996), Northern Hemisphere fires, and lightning NO_x (Edwards et al., 2003). In the Amazon region, ground-based and aircraft campaigns (e.g., Crutzen et al., 1985; Kirchhoff et al.,

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Movido para cima [16]: The Amazon Basin continues to rapidly urbanize, and urban emissions of O_3 precursors are also expected to grow (Gallardo et al., 2010).

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Movido para baixo [14]: Motivated by the impact of O_3 in the Amazon Basin on human and ecosystem health and global climate, we collected aircraft observations of O_3 during BARCA and conducted regional chemistry simulations in order to answer the following scientific questions: how does O_3 vary spatially and seasonally over the Amazon basin? What are the sources and sink of O_3 in this region? How well can state-of-the-art regional chemistry models reproduce O_3 distributions over the Amazon Basin? ¶

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1990; Browell et al., 1996; Kaufman et al., 1998; Longo et al., 1999, Andreae et al., 2001; Andreae et al., 2002; Zhou et al., 2002; Cordova et al., 2003; Rummel et al., 2007; Kuhn et al., 2010; Martin et al., 2010; Toon et al., 2010) have observed daytime background O_3 levels of 10-20 ppb, decreasing to very low values (~5 ppb) at night due to O_3 deposition to the forest. However, nighttime values can be increased up to 30 ppb due to convective downdrafts (Betts et al., 2002; Cordova et al., 2003). Elevated levels of 60-80 ppb are found due to production from regional fire emissions and recirculated urban pollution from SE Brazil, as well as evidence of deep convective transport of boundary layer air to the middle and upper troposphere.

Thus, satellite observations enable the attribution of tropical O_3 maxima to biomass burning and lightning NO_x sources, while ground-based measurements allow the identification of key surface processes in the Amazon Basin affecting O_3 amounts. These processes include O_3 production from soil NO_x emissions and removal via dry deposition to the forest canopy. Aircraft campaigns complete the suite of observations, allowing the examination of convective lofting of surface emissions, with biomass burning emissions of particular importance on the regional scale. In-situ data on cloud properties and chemical species, as well as observations of land use changes, boundary layer dynamics and larger-scale cloud-aerosol interactions, are scant in this region. Therefore, models are essential tools for monitoring and predicting atmospheric chemistry composition, weather, and climate at local, regional and global scales. In turn, the observations help constrain uncertainties in the model representations of parameterized convection, turbulence, land surface and other subgrid scale processes that affect the simulated transport and chemical transformation of the atmospheric composition (Beck et al., 2013).

Motivated by the impact of O_3 in the Amazon Basin on human and ecosystem health and global climate, we collected aircraft observations of O_3 during BARCA and conducted regional chemistry simulations in order to answer the following scientific questions: how does O_3 vary spatially and seasonally over the Amazon basin? What are the sources and sinks of O_3 in this region? How well can state-of-the-art regional chemistry models reproduce O_3 distributions over the Amazon Basin?

The structure of this paper is as follows. In Section 2, the measurements taken during the BARCA aircraft campaign are presented, followed by the meteorological conditions and emissions regimes during the two phases of the campaign. The ABLE-2 campaigns from the 1980s are also described in this section. Sections 3.1-3.3 detail the aircraft observations, the setup of the CCATT-BRAMS and WRF-Chem simulations and the ground-based and remote sensing observations used in the analysis. In Section 4.1, the O_3 aircraft observations are presented, followed by the analysis of observed and

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Movido para baixo [15]: In-situ data on cloud properties and chemical species, as well as observations of land use changes, boundary layer dynamics and larger-scale cloud-aerosol interactions, are scant in this region. Therefore, models are essential tools for monitoring and predicting atmospheric chemistry composition, weather, and climate at local, regional, and global scales. Uncertainties in the model representations of parameterized convection, turbulence, land surface and other subgrid scale processes lead to significant errors in simulated transport and chemical transformation of the atmospheric composition (Beck et al., 2013).

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modeled transition season meteorology in Section 4.2 and the findings from the O_3 simulations and process studies in Section 4.3. Final discussions and conclusions are found in Section 5.

2 BARCA aircraft campaigns

The Regional Carbon Balance in Amazonia (BARCA) Large-Scale Biosphere-Atmosphere (LBA) experiment was an aircraft campaign based in Manaus and conducted during the dry-to-wet (November and December 2008) and wet-to-dry (May 2009) transition seasons. BARCA was the first flight campaign to sample ozone and other trace gases on a regional scale in both transition seasons. It offers a unique opportunity, together with satellite observations and modeling studies, to understand the regional ozone distribution in the Amazon under different meteorological and emissions regimes.

The BARCA flights were conducted with the EMB 110 Bandeirante aircraft of the Brazilian National Institute for Space Research (INPE). In-situ measurements were made of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ozone (O_3), and aerosol number concentration and optical properties. Flask samples were collected to determine CO_2, CH_4, sulfur hexafluoride (SF_6), CO, nitrous oxide (N_2O), hydrogen, and the oxygen-nitrogen ratio (O_2/N_2). The flights consisted of quasi-Lagrangian measurements, which attempt to sample an air parcel at multiple locations along its path in order to constrain regional and basin-wide fluxes of these species. The aircraft had a ceiling of 4500 m, and flights usually consisted of ascending and descending vertical profiles separated by short (5-30 min) horizontal legs. A detailed description of the aircraft measurements can be found in Andreae et al. (2012). Figure 1 shows a map of the flight tracks from BARCA A and B. Both experiment periods included flights to the north, south and east of Manaus, as well as local flights near Manaus. Only BARCA A included flights to the west of Manaus, because intense convective activity in that region during BARCA B precluded flying. During BARCA B, fire activity was low throughout the Amazon region due to heavy precipitation, while during BARCA A, intense fire activity occurred on the northern coast of Brazil and scattered fires were present throughout the southeastern Amazon.

Andreae et al. (2012) summarized the BARCA campaign, meteorological background, carbon monoxide and aerosol observations and CO results from several regional transport and chemistry models. These included the CCATT-BRAMS and WRF-Chem simulations analyzed in greater detail in this paper. Meteorological analysis showed that during BARCA A, when the Inter-Tropical Convergence Zone (ITCZ) was to the north of the Amazon Basin, inflow to the Amazon was primarily from the Southern Hemisphere. During BARCA B, the ITCZ extended to 20° S and air at low levels was

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of Northern Hemisphere origin, including some smoke from West African fires. On the other hand, the mid-tropospheric air was of mixed origin.

The highest CO levels were observed on the flights on 25-27 November in the southeastern Amazon, influenced by regional biomass burning, since maximum values were observed from 1-3 km. These are typical of injection heights of smoke plumes from savanna fires (Freitas et al., 2007). The excess CO from biomass burning was between about 30 and 200 ppb, increasing from north to south across the Basin. According to analysis of tracer simulations, during BARCA A biomass burning contributed on average about 56 ppb (31%) to the total CO of around 180 ppb, while the background was 110 ppb (61%). Biomass burning influence was indicated by CO mixing ratios up to 300 ppb, Condensation Nuclei (CN) approaching 10000 cm^{-3}, and a low CN to CO ratio ($\Delta CN/\Delta CO$) signifying aged smoke. This influence was highest in the southern Amazon from 1-3 km. Manaus back trajectories at 500 and 4000 m came from eastern Amazon fires rather than the intense African fires occurring at the same time. During BARCA B, little biomass burning influence was observed. CN counts were 300-500 cm^{-3} and a CO enhancement of ~10 ppb above the mixing ratios in air entering the Basin from the Atlantic was seen. Small boundary layer enhancements were attributed to a source from the oxidation of biogenic VOCs (Andreae et al., 2012).

Andreae et al. (2012) also showed simulated vertical CO profiles from CCATT-BRAMS and WRF-Chem simulations, as well as the Stochastic Time Inverted Lagrangian Transport (STILT) model with two different meteorological field inputs and the WRF Greenhouse Gas Module (WRF-GHG). The simulated CO profiles matched mean observed values, but were overly vertical (too low near the surface and too high above 3 km). This suggested that the models had too much convective transport or vertical mixing from the PBL schemes. However, the probability densities were consistent with observations in the boundary layer, indicating that horizontal dispersion was reasonable. Beck et al. (2013) evaluated different CH_4 wetland emissions schemes and maps using WRF-GHG. They found the best agreement with BARCA CH_4 data for days where convective transport, as evaluated by comparison of upstream TRMM and WRF precipitation amounts, was well represented in the model. This indicates that proper representation of convective transport in models is essential for prediction of vertical distributions of pollutants in the Amazon Basin.

It is interesting to compare BARCA data to observations from the NASA Amazon Boundary Layer Experiments ABLE campaigns (ABLE-2A and -2B), which took place during the dry season of 1985 and wet-to-dry transition of 1987. During the dry season (July-August 1985), the Amazon Boundary Layer Experiment (ABLE-2A) integrated aircraft, ground-based and satellite observations to study the processes affecting the

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chemical composition in mixed layer over Amazonia (Harriss et al., 1988). Jacob and Wofsy (1988) used a photochemical model of the Amazonian boundary layer to study the diurnal cycle of isoprene, NO_y and O_3 during ABLE-2A. They found that photochemical production spurred by NO emissions from soils increased daytime O_3 to about 20 ppb. However, at night, dry deposition to the forest caused O_3 to drop below 5 ppb. Model results were consistent with the NO values of 25-60 ppt observed in the lower boundary layer over central Amazonia (Torres and Buchan, 1988). Isoprene emissions were found to have little effect on O_3 levels, as the oxidation of CO would produce sufficient HO_x to generate 20 ppb of O_3. However, O_3 production in the model was highly sensitive to NO_x emissions, and downward transport from the free troposphere became the dominant source of O_3 in the PBL when NO emissions were decreased below the average value of 44 ± 14 μg N m^{-2} h^{-1} NO measured by Kaplan et al. (1988). Lidar observations during ABLE-2A showed highly variable O_3 levels, with some small regions with up to 30-40 ppb, attributed to variable NO flux from the canopy (Browell et al., 1988). ABLE-2B was conducted during the wet-to-dry transition season (April-May 1987) (Harriss et al., 1990). Periodic inputs from the Northern Hemisphere were found to be a pollution source over Amazonia, and dry deposition in the region provided a significant sink in the global O_3 budget. As part of ABLE-2, near-continuous O_3 surface measurements (1.5 m above the soil surface) showed daytime maximums of 3.7 ppb inside a forest and 5.7 ppb in a clearing (typical standard deviations of 0.3 ppb). Additionally, tower measurements at the clearing site showed higher O_3 values of 6.7 ppb at 7 m above the soil surface and 6.9 ppb at 15 m above the soil surface (Kirchhoff et al., 1990). Furthermore, 20 ozonesondes launched in the clearing showed typical mixing ratios of 40 ppb from 500-300 hPa, with values about 10 ppb lower in the wet than dry season.

Andreae et al. (2012) showed that CO mixing ratios were about 10 ppb higher during ABLE-2B than in BARCA_B everywhere except the southern region, reflecting the global trend towards decreasing CO emissions since the 1980s, particularly in the Northern Hemisphere. The CO comparison also showed a similar enhancement of 10–20 ppb in the lowest 1 km above the surface, attributed to diffuse biogenic sources, and also indicated that the much higher enhancements during the dry season in BARCA_A must be due to anthropogenic or biomass burning inputs. The O_3 comparison is expected to yield information in long-term trends in O_3 production in the Amazon Basin, as well as the relative importance of biogenic, urban and fire sources.

3 Data and Methods

3.1 BARCA aircraft measurements

During the BARCA campaign, in-situ measurements of O_3 were conducted aboard the EMB 110 Bandeirante INPE aircraft using a dual-cell, UV Photometric analyzer (Ozone Analyzer, Model 49i, Thermo Fisher Scientific, United States). During BARCA A, 1 minute averages of the original 1 second data were taken, while during BARCA B 1 second data were stored. The detection limit for both campaigns was 1 ppb. The intake for O_3 was forward-facing, located 185 mm from the fuselage on the lower fuselage in front of the propellers to minimize effects of turbulence. The inlet lines consisted of stainless steel tubes with a bend radius of 100 mm and an inner diameter of 11.5 mm. The sample air was not heated or dried before measurement, so reported values are molar mixing rations, nmol mol^{-1}, abbreviated 'ppb', with respect to ambient humid air (Andreae et al., 2012).

3.2 Model description and simulation setup

Simulations of BARCA A and B were conducted with the Chemistry Coupled Aerosol-Tracer Transport model to the Brazilian developments on the Regional Atmospheric Modeling System (CCATT-BRAMS; Longo et al., 2013; Freitas et al., 2009) and Weather Research and Forecasting with Chemistry (WRF-Chem; Grell et al., 2005) coupled chemistry and meteorology models. The model physics and chemistry options that were used are listed in Table 1. Both models used a two-way nested grid configuration, with a 140 km grid covering Africa and South America (southwest corner: 60°S, 100°W, northeast corner: 20°N, 50°W), to encompass the cross-Atlantic transport of biomass burning emissions from Africa, and a 35 km resolution grid covering most of South America (southwest corner: 35°S 85°W, northeast corner: 15°N, 30°W), as depicted in Fig. 3.

The simulations were initialized on 1 October 2008 00:00 UTC and 1 April 2009 00:00 UTC for BARCA A and B, respectively. Boundary conditions and analysis nudging on the outer domain were given by the NCEP GFS analysis (http://rda.ucar.edu/datasets/ds083.2/) with a 6 hourly time resolution and 1° □ 1° spatial resolution. Chemistry initial and boundary conditions were provided by 6 hourly analyses from the Model of Atmospheric Chemistry at Large Scale (Modélisation de la Chimie Atmosphérique Grande Echelle, MOCAGE) global model (Peuch et al., 1999) with a T42 (~ 2.8°) spatial resolution. Sea surface temperature was provided by the NOAA Optimum Interpolation (OI) Sea Surface Temperature (SST) V2 (available at http://www.esrl.noaa.gov/psd/data/gridded/data.noaa.oisst.v2.html) with 1° □ 1° spatial resolution. Soil moisture was initialized with the TRMM-based soil moisture operational product (GPNR) developed by Gevaerd and Freitas (2006).

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<#>Previous studies of O_3 in the Amazon¶
<#>Analyses of satellite, aircraft and ground-based observations of O_3 over Amazônia since the 1980s have demonstrated the influence of long-range transport of African biomass burning and Northern Hemisphere inputs, local fire sources, NO soil and biogenic VOC emissions, and convective transport on spatial and seasonal variability in O_3. In particular, data from the ABLE-2B aircraft and ground campaign during the 1987 wet-to-dry transition season offers the opportunity to compare the regional O_3 distribution across decades.¶
<#>Several studies of satellite data have reported a seasonal O_3 maximum in the tropical Southern Hemisphere, largely associated with long-range transport of African fire emissions or lightning NOx sources. Fishman and Larsen (1987) combined data from 1979-1980 from the Total Ozone Mapping Spectrometer (TOMS) and the Stratospheric Aerosol and Gas Experiment (SAGE) instruments to construct a climatology of tropospheric O_3 from 15°N to 15°S. They attributed the most elevated O_3 from 60°W to 60°E to biomass burning sources. Thompson et al. (1996) integrated TOMS satellite O_3 data with observations from the Transport and Atmospheric Chemistry near the Equator-Atlantic (TRACE-A) and the southern African Fire-Atmosphere Research Initiative (SAFARI) 1992 experiments. They showed a seasonal maximum in tropospheric O_3 in the south Atlantic, with the highest values (> 90 ppb) between 0-25°S. Back and forward trajectories attributed this elevated O_3 to transport of O_3 from fires in southern Africa by mid-level easterlies or recirculations, with little South American contribution. In Brazil, O_3 was seen to be lofted by deep convective transport, and then transported by high-level westerlies. However, from 0-10°S most of the O_3 was from Africa, since there was a delay of 1-2 months from peak African biomass burning to the O_3 maximum at the coastal site of Natal. O_3 production from the surface to 4 km was estimated to be 15 ppb O_3 per day, with a lower but nonzero rate in the upper troposphere. Using remote sensing observations of fire and lightning flash counts and NO_2, Edwards et al. (2003) identified ... [4]

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The PBL parameterization in CCATT-BRAMS is based on Mellor and Yamada (1982), while in WRF-Chem the Mellor-Yamada-Janjic (MYJ; Janjić, 1994) scheme was used. In CCATT-BRAMS, shallow and deep convection are parameterized based on the mass-flux approach of Grell and Dévényi (2002). CCATT-BRAMS also uses the Turbulent Kinetic Energy (TKE) from the Planetary Boundary Layer (PBL) scheme to determine if convection will be triggered within a grid cell. In WRF-Chem the Grell 3D (G3) scheme was used, which includes shallow convection and subsidence spreading of convective outflow into neighboring grid cells. The Noah land surface model (Koren et al., 1999) was used in WRF-Chem and the Land Ecosystem–Atmosphere Feedback model v.2 (LEAF-2; Walko et al., 2000) was utilized in CCATT-BRAMS. Land use was provided by the United States Geological Survey (USGS) global 1 km vegetation dataset, updated with a land cover map for the Brazilian Legal Amazon Region for use in meteorological models (PROVEG) (Sestini et al., 2003). PROVEG is based on the Thematic Mapper (TM) Landsat images with spatial resolution of 90 m □ 90 m from the year 2000 and deforestation data from the Amazon Deforestation Monitoring Program (PRODES) for the year 1997. For WRF-Chem, albedo and greenness fraction were calculated offline using the updated vegetation dataset, Moderate Resolution Imaging Spectroradiometer (MODIS) Normalized Difference Vegetation Index (NDVI) data from the years 2001-2002 and vegetation parameters from the LEAF-2 land surface model as implemented in CCATT-BRAMS.

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Emissions were generated with PREP-CHEM-SRC (Freitas et al., 2011) Version 1.2. Fire emissions were estimated from GOES, AVHRR and MODIS fire count data using the Brazilian Biomass Burning Emission Model (3BEM; Longo et al., 2009). Anthropogenic emissions were estimated from the RETRO, GOCART and EDGAR v4.0 global databases updated with South American inventories (Alonso et al., 2010). Emissions are obtained from RETRO if available for that species (CO, NO_x, chlorinated hydrocarbons, acids, esters, alcohols, ethers, benzene, ketones, methanal, other alkanals, other aromatics, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14} plus higher alkanes, other VOCs, toluene, trimethylbenzenes, xylene), then from EDGAR v4.0 (NMVOC, SO_4, CO_2, SF_6, N_2O), otherwise from GOCART (BC, OC, SO_2, DMS), in order to use the most consistent emissions inventory possible. Biogenic emissions were provided by a monthly climatology for the year 2000 produced with the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006). The MEGAN 2000 climatology includes numerous biogenic species (acetaldehyde, formaldehyde, other ketones, acetone, isoprene, propane, methane, propene, ethane, methanol, sesquiterpenes, ethene, monoterpenes and toluene), but not soil NO emissions. In WRF-Chem, the same Gaussian diurnal cycle with peak at 15:00 UTC (11:00 LT) is applied to both anthropogenic and biogenic emissions, while in CCATT-

BRAMS the diurnal cycle of biogenic emissions follows the solar radiation cycle. In both models, the biomass burning daily cycle peaks at 18:00 UTC (15:00 LT).

In both CCATT-BRAMS and WRF-Chem, the Regional Atmospheric Chemistry Mechanism (RACM) was used (Stockwell et al., 1997). In WRF-Chem, the Goddard Chemistry Aerosol Radiation and Transport (GOCART; Chin et al., 2002) aerosol scheme was used with aerosol direct radiative effects. CCATT-BRAMS has a smoke aerosol scheme with intensive optical properties (extinction efficiency, single scattering albedo and asymmetry parameter) calculated in an offline Mie code based on observations of climatological size distribution and complex refractive index from AERONET sites in the southern Amazon (Rosario et al., 2011, 2013).

CCATT-BRAMS includes scavenging of soluble species in the convective scheme following Berge (1993), as described in Freitas et al. (2005), where the wet removal rates are a function of the precipitation rate, liquid water content and precipitable water. In the cloud microphysics scheme the wet deposition follows Barth et al. (2001), whereby low solubility species partition into the liquid phase according to Henry's Law and high solubility species by diffusion-limited mass transfer. In WRF-Chem, at the convective-parameterizing scale, a constant fraction of gas and aerosol species in convective updrafts are removed (complete removal for sulfur dioxide – SO_2, sulfate – H_2SO_4, ammonium – NH_3, nitric acid – HNO_3 and sea salt; no removal for hydrophobic organic (OC) and black carbon (BC) and dimethyl sulfide (DMS); and 50% removal for all other aerosol species). On the other hand, no wet scavenging is included for cloud water and precipitation resolved by the microphysics scheme, because this option is not currently available in WRF-Chem for the RACM chemical mechanism. O_3 production in the upper troposphere is affected by the net convective transport of soluble HO_x precursors (including hydrogen peroxide (H_2O_2), methyl hydroperoxide (CH_3OOH) and formaldehyde (CH_2O)). However, uncertainties remain about the scavenging efficiencies of soluble species by deep convective storms. Simulations of an idealized thunderstorm by several cloud-resolving models yielded varying results for CH_2O, H_2O_2 and HNO_3 in convective outflow due to differing microphysics and assumptions about retention of chemical species during cloud drop freezing (Barth et al., 2007).

The CCATT-BRAMS simulations employ a lightning NO_x parameterization based on convective cloud top height (Stockwell et al., 1999). In WRF-Chem, lightning production of NO_x was not included, because these parameterizations have not yet been evaluated for the Amazon region. In the tropics, over continents, lightning production is comparable to other sources of NO_x, including biomass burning and soil release, and it is the primary source over oceans (Bond et al. 2002). Since lightning NO_x production

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peaks in the upper troposphere, it could be an important contributor to ozone production. The roles of wet deposition and lightning NO_x production will be more closely examined in future modeling studies of tropospheric chemistry in the Amazon.

For model results evaluation, the mean vertical O_3 profiles for observations, CCATT-BRAMS and WRF-Chem were calculated for the regions to the west, north, south, east, and around Manaus. Horizontal flight legs were excluded from analysis to eliminate the influence of plumes in the boundary layer. As the model output has a much coarser spatial and temporal resolution than the aircraft measurements, the model value is interpolated to the observation time and location. To calculate the mean simulated profiles, the four grid points closest in latitude and longitude to each observation were determined at the two model hours that bracket the observations. At each of these grid points and hours, vertical profiles were extracted from the model output and then linearly interpolated to the observed GPS height. The four points from each time were averaged, weighting by the inverse distance to the observed longitude and latitude. Finally, the prior and posterior hour values were averaged with appropriate weights. Thus, 16 model points were used with spatial and temporal weights to obtain each model value for comparison to observations. The observed and model time series were then separated into five regions to the west, north, east, and south of Manaus, and in the region of Manaus itself. The mean value and standard deviation were calculated for each region and 500 m vertical bin. To facilitate comparison of other models with the data presented in Fig. 2, mean profiles from the large regions corresponding to clean (west, north and around Manaus regions) and polluted (east and south regions) regions during BARCA A and all regions during BARCA B are presented in Fig. 16. From the models, all horizontal grid points falling within the corresponding region's longitude and latitude bounds for each flight day (Table 6) and the closest model output times (12:00-18:00 UTC / 8:00-14:00 LT) were averaged into 500 m vertical bins.

3.3 Meteorological and satellite and ground-based O_3 data

Monthly mean precipitation over the Amazon region was obtained from the 3B43 Tropical Rainfall Monitoring Mission (TRMM) and Other Data Precipitation Product at a spatial resolution of 0.25° □ 0.25° (obtained from http://trmm.gsfc.nasa.gov/) (Kummerow et al., 1998; Kawanishi et al., 2000). TRMM 3B43 is derived from retrievals of 3-hourly precipitation amount from the Precipitation Radar (PR), TRMM Microwave Imager (TMI), and Visible and Infrared Scanner (VIRS) aboard the TRMM satellite, merged with rain gauge data from Climate Anomaly Monitoring System (CAMS) and the Global Precipitation Climatology Project (GPCP). Satellite estimates of precipitation are used for model evaluation due to their more complete spatial and temporal coverage compared to rain gauge data. Buarque et al. (2011) found that mean

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Excluído: In addition to the in-situ O_3 data, the model results were compared with OMI/MLS monthly mean tropospheric ozone mixing ratios and total column ozone (http://acd-ext.gsfc.nasa.gov/Data_services/cloud_slice/#pub) (Ziemke et al., 2006). Tropospheric values were estimated by subtracting the stratospheric contribution from total column measurements. A cloud-slicing method was used to detect O_3 inside optically thick clouds. This method was able to detect elevated O_3 levels of around 50 ppb in the upper parts of convective clouds over South America and Africa, comparable to background cloud-free levels in the tropics (Ziemke et al., 2009). The model total tropospheric O_3 column and mean tropospheric O_3 mixing ratio were calculated by summing O_3 mixing ratios, weighted by the model level air density, from the first model level to the level below the tropopause. The tropopause level was determined by the World Meteorological Organization (WMO) definition of a temperature lapse rate less than 2 K km^{-1} (Logan, 1999).¶
The models were also compared with soundings measuring O_3, temperature, and relative humidity conducted at sites in Paramaribo, Surinam (5.8°N, 55.2W) and Natal, Brazil (5.4°S, 5.4°W) during the BARCA periods as part of the Southern Hemisphere ADditional OZonesondes (SHADOZ) network (http://croc.gsfc.nasa.gov/shadoz/) (Thompson et al., 2003a, b, 2007). ¶

annual rainfall from Brazilian rain gauge and TRMM 3B42 3-hourly data at 488 sites in the Amazon Basin for the years 2003-2005 agreed within 5%. Other characteristics of the rainfall distribution, such as the number of days with rainfall, differed more substantially. Mean precipitation during the dry-to-wet (Nov. 2008) and wet-to-dry (May 2009) transition seasons was calculated for the TRMM 3B43 data and the CCATT-BRAMS and WRF-Chem models for three regions: the Amazon (15°S – 10°N, 50°W – 80°W), northeast Brazil (15°S – 0°N, 35°W – 50°W), and southeast South America (15°S – 35°S, 35°W – 65°W). The values are listed in Table 2. The mean precipitation on the 35 km resolution domain for the two months is shown in Fig. 4, as well as the delineations of the subregion boxes.

Surface downward shortwave radiation (Level 1.5) obtained with a Kipp and Zonen CM-21 pyranometer (305-2800 nm) were obtained from the Solar Radiation Network (SolRad-Net) site at Manaus (2.56°S, 60.04°W, 93 m a.s.l.) (http://aeronet.gsfc.nasa.gov/cgi-bin/bamgomas_interactive) (Fig. 5).

Mean daily cycles of fluxes of sensible and latent heat and radiation were obtained from flux tower measurements for the wet (February - March 1999, January - March 2000) and dry (July - September 1999-2000) seasons at forest (Rebio Jarú, 10.08°S, 61.93°W, 145 m a.s.l.) and pasture (Fazenda Nossa Senhora, 10.75°S, 62.37°W, 293 m a.s.l) tower sites (von Randow et al., 2004) (Figs. 6-7).

Surface meteorological station data was obtained for the BARCA region for October - November 2008 and April - May 2009 from 52 SYNOP (INMET) and 26 METAR (airport) stations, the locations of which are depicted in Fig. 10. The models were also evaluated against TRMM 3B42 3-hourly precipitation rates at the 78 surface station locations in the Amazon. Mean observations and values of Root Mean Squared Error (RMSE) and bias for the CCATT-BRAMS and WRF-Chem simulations are shown in Table 3.

Meteorological soundings from the Manaus airport (3.15°S, 59.98°W) were conducted at 00:00 UTC (12 in October-November 2008, 60 in April-May 2009) and 12:00 UTC (49 in October - November 2008, 60 in April - May 2009). During BARCA A, 13 additional soundings were conducted at 18:00 UTC from 18 November – 1 December 2008 (Figs. 8-9).

Fisch et al. (2004) found that in the dry season (14-25 August, 1994), higher sensible heat fluxes over pasture increase the maximum height at 21:00 UTC (17:00 LT) of the Convective Boundary Layer (CBL) from around 1100 m for forest (Rebio Jarú) to 1650 m over pasture (FNS). On the other hand, during the wet season (January-February 1999) the height of the CBL was similar for both land types, around 1000 m. The simulated height of the PBL at 21:00 UTC above the forest and pasture sites (Table 4)

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Movido para cima [10]: Simulations of BARCA A and B were conducted with the Chemistry Coupled Aerosol-Tracer Transport model to the Brazilian developments on the Regional Atmospheric Modeling System (CCATT-BRAMS; Longo et al., 2013; Freitas et al., 2009) and Weather Research and Forecasting with Chemistry (WRF-Chem; Grell et al., 2005) coupled chemistry and meteorology models. The model physics and chemistry options that were used are listed in Table 1. Both models used a two-way nested grid configuration, with a 140 km grid covering Africa and South America (southwest corner: 60°S, 100°W, northeast corner: 20°N, 50°W), to encompass the cross-Atlantic transport of biomass burning emissions from Africa, and a 35-km resolution grid covering most of South America (southwest corner: 35°S 85°W, northeast corner: 15°N, 30°W), as depicted in Fig. 3.¶
The simulations were initialized on 1 October 2008 00:00 UTC and 1 April 2009 00:00 UTC for BARCA A and B, respectively. Boundary conditions and analysis nudging on the outer domain were given by the NCEP GFS analysis (http://rda.ucar.edu/datasets/ds083.2/) with a 6 hourly time resolution and 1° □ 1° spatial resolution. Chemistry initial and boundary conditions were provided by 6 hourly analyses from the Model of Atmospheric Chemistry at Large Scale (Modélisation de la Chimie Atmosphérique Grande Echelle, MOCAGE) global model (Peuch et al., 1999) with a T42 (~ 2.8°) spatial resolution. Sea surface temperature was provided by the NOAA Optimum Interpolation (OI) Sea Surface Temperature (SST) V2 (available at http://www.esrl.noaa.gov/psd/data/gridded/data.noaa.oisst.v2.html) with 1° □ 1° spatial resolution. Soil moisture was initialized with the TRMM-based soil moisture operational product (GPNR) developed by Gevaerd and Freitas (2006).¶
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was analyzed from model output using two different methods: *TKE*, the first level above the surface where the Turbulent Kinetic Energy (TKE) from the PBL schemes dropped below 0.01 $m^2 s^{-1}$ and *Theta*, the first level above the surface where theta exceeded theta of the level below by 0.6 K. In addition, *WRF MYNN* is the diagnostic from the WRF PBL scheme which takes into account TKE as well as stability.

In addition to the in-situ O_3 data, the model results were compared with OMI/MLS monthly mean tropospheric ozone mixing ratios and total column ozone (http://acd-ext.gsfc.nasa.gov/Data_services/cloud_slice/#pub) (Ziemke et al., 2006) (Fig. 20-21). In this product, the tropospheric values are estimated by subtracting the stratospheric contribution from total column measurements. A cloud-slicing method is used to detect O_3 inside optically thick clouds. This method is able to detect elevated O_3 levels of around 50 ppb in the upper parts of convective clouds over South America and Africa, comparable to background cloud-free levels in the tropics (Ziemke et al., 2009). In this study, the model total tropospheric O_3 column and mean tropospheric O_3 mixing ratio were calculated by summing O_3 mixing ratios, weighted by the model level air density, from the first model level to the level below the tropopause. The tropopause level was determined by the World Meteorological Organization (WMO) definition of a temperature lapse rate less than 2 K km^{-1} (Logan, 1999).

The models were also compared with soundings measuring O_3, temperature, and relative humidity conducted at sites in Paramaribo, Surinam (5.8°N, 55.2W) and Natal, Brazil (5.4°S, 5.4°W) during the BARCA periods as part of the Southern Hemisphere ADditional OZonesondes (SHADOZ) network (http://croc.gsfc.nasa.gov/shadoz/) (Thompson et al., 2003a, b, 2007) (Fig. 22).

4 Results and discussion

4.1 BARCA O_3 Observations

The vertical distributions of O_3 measured by the aircraft during BARCA A and B are depicted in Fig. 2. Observations during the dry-to-wet transition (BARCA A) are plotted separately for clean (west, north and around Manaus regions) and fire-influenced polluted (east and south regions) conditions. The longitude and latitude bounds and flight dates included in each geographic region from BARCA A and BARCA B are listed in Table 6. The O_3 distributions are similar during BARCA A in the clean regions and BARCA B, with median values ranging from 10-25 ppb. However, there is more variability, as measured by the difference between the 25th and 75th percentiles, in the BARCA A data. This may be due to downward mixing of O_3 transported long-range from fires in Africa or recirculated from the polluted southeast Brazil region. In the fire-influenced regions during BARCA A, medians range from 25-45 ppb, peaking at a typical plume injection height for savanna fires of 2-3 km. The highest variability is

seen in polluted conditions during BARCA A, particularly at 2-3 km, indicating the influence of small-scale fire plumes. This variability of O_3 in the PBL presents a challenge to the regional models, since the effects of small-scale processes such as plume rise and convection are parameterized and averaged across the grid cell.

4.2 Observed and Simulated Meteorology

Tropospheric O_3 distributions are driven by both chemical processes, including chemistry and emissions of O_3 precursors, and meteorological ones, such as solar radiation, tracer transport and removal. During the dry-to-wet transition season, increased actinic fluxes stimulate the production of OH radicals from O_3 photolysis that can lead to net O_3 production (Seinfeld and Pandis, 2006). In November 2008, a band of increased precipitation extended in TRMM 3B43 observations from the northwest Amazon to southeast Brazil but the northern Amazon between Manaus and Belém was relatively dry (Fig. 4a). On the other hand, in the wet-to-dry transition season, lower levels of O_3 are largely associated with increased presence of convective clouds and precipitation. Decreased surface temperatures and incident solar radiation due to cloudiness suppress emissions of biogenic VOCs such as isoprene (Fall and Wildermuth, 1998). In addition, higher surface humidity and precipitation decrease the occurrence of fires (Morton et al., 2013; Chen et al., 2013) that emit NO_x and VOCs (Freitas et al., 2007). O_3 precursors are further decreased by wet removal within the storms (Barth et al., 2007a). In May 2009, increased precipitation as observed by TRMM 3B43 extended from the western Amazon to the northeast coast of Brazil (Fig. 4b). In radiosoundings at Manaus, a more pronounced decrease in dew point temperature from 0:00 UTC to 12:00 UTC is observed in May 2009 (Fig. 9) than Nov. 2008 (Fig. 8) in upper levels (300-400 hPa), likely due to more precipitation.

Land cover also impacts surface heat and moisture exchange and can thus affect convective triggering. In both transition seasons, surface sensible heat fluxes are higher and latent heat fluxes are lower at the pasture compared to forest sites (Figs. 6a-b and 7a-b). However, incident solar radiation and thereby peak sensible heat flux (Fig. 7) are lower in the wet-to-dry than dry-to-wet transitions (Fig. 6) for both forest and pasture sites.

Now we summarize the key findings of the model-data meteorological comparison and their implications for the chemistry simulations. The models capture the seasonal spatial distribution of precipitation over northern South America signs of NE-SE differences are correctly modeled by both models during both seasons, i.e., the NE is drier than the SE during November, and vice-versa during May. For the Amazon, CCATT-BRAMS slightly underestimates the precipitation rates in both seasons, but the rate in WRF-Chem is about twice that of TRMM 3B43 (Table 2). This may lead to errors in the

Excluído: In addition to surface emissions and chemical sources and sinks of O_3, several meteorological processes are key drivers of tropospheric O_3 distributions, including solar radiation, tracer transport and removal. Thus, first we evaluate the ability of the models to represent these processes and their seasonalities.¶

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Excluído: Incident solar radiation is higher in the dry than wet season for both sites (Figs. 6-8). At the forest and pasture sites, peak sensible heat flux is higher in the dry-to-wet than wet-to-dry transition seasons, and higher at forest than pasture sites for both seasons, while latent heat flux is higher in the wet-to-dry than dry-to-wet transition seasons for both sites, and higher at the pasture site for both seasons (Figs. 7 and 8).

Movido para cima [9]: In radiosoundings, a decrease in dew point temperature is observed in upper levels (300-400 hPa) from 0 to 12 or 18Z, likely due to precipitation, more pronounced in the wet-to-dry transition season (Figs. 9 and 10).

Excluído: Mean precipitation during the dry-to-wet (November 2008) and wet-to-dry (May 2009) transition seasons was calculated for the TRMM 3B43 data and the CCATT-BRAMS and WRF-Chem models for three regions: the Amazon (15°S – 10°N, 50°W – 80°W), northeast Brazil (15°S – 0°N, 35°W – 50°W), and southeast South America (15°S – 35°S, 35°W – 65°W). The values are listed in Table 2. The mean precipitation on the 35-km resolution domain for the two months is shown in Figs. 3 and 4, respectively, as well as the delineations of the subregion boxes. The signs of NE-SE differences are correctly modeled by both models during both seasons, i.e., the NE is drier than the SE during November, and vice-versa during May. For the Amazon, CCATT-BRAMS slightly underestimates the precipitation rates in both seasons, but the rate in WRF-Chem is about twice that of TRMM ... [6]

Movido (inserção) [8]

Excluído: , although the mean precipitation rates are slightly lower (CCATT-BRAMS) and substantially ... [7]

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strength and vertical distribution of convective transport and the amount of convective wet removal.

Peak surface shortwave radiation during the dry-to-wet transition at Manaus is within the error bars of the observations for both models (Fig. 5). However, for the southern Amazon forest and pasture sites peak shortwave may be overestimated (underestimated) by 50-100 W m^{-2} by CCATT-BRAMS (WRF-Chem) (Figs. 6-7), suggesting that there is insufficient (excessive) cloudiness in the models. This will increase (decrease) surface temperature and evaporation, and therefore increase (decrease) O_3 production from photolysis.

In the dry-to-wet transition season (Fig. 7), the observed Bowen ratio (sensible/latent heat flux) is lower at the forest site than the pasture site (0.23-0.38 vs. 0.8). However, in WRF-Chem, the Bowen ratio at 13:00 LT shows a smaller contrast between the forest and pasture sites (0.40 vs. 0.51), due to underestimated sensible heat flux at the pasture site. In the wet-to-dry transition season (Fig. 8), the observed Bowen ratio is lower at both forest and pasture sites for this season (0.18-0.39 vs. 0.33-0.59). On the other hand, in WRF-Chem, latent and sensible heat flux and thus the Bowen ratio are nearly constant at the forest and pasture sites (0.39 vs. 0.38). This indicates that the Noah land surface model is not properly representing the impact of conversion of forest to pasture and the resulting increase in sensible heat flux.

At the surface stations (Table 3), both models overestimate precipitation on average. Dew point temperature is underestimated by 1-2 K and temperature is underestimated in all cases by 0.1 - 2.4 K except by CCATT-BRAMS during BARCA A, which overestimated temperature by about 1 K. All of these biases will decrease photochemical O_3 production at the surface. The models generally show good agreement with soundings at Manaus, but excess moisture (positive dewpoint bias of 10 K) in CCATT-BRAMS above 500 hPa may lead to increased O_3 production at mid-levels.

Next we compare the CBL heights for wet and dry seasons reported by Fisch et al. (2004) with the simulated PBL heights in the dry-to-wet and wet-to-dry transitions (Table 4). The models represent the pattern of lower PBL heights in the wet-to-dry than dry-to-wet transitions, and similar PBL heights at the forest and pasture sites. However, for the dry-to-wet transition, the PBL heights are indistinguishable between forest and pasture sites for both models, and generally closer to the observed forest (1.1 km) than pasture (1.65 km) values. Additionally, for the wet-to-dry transition, the mean PBL height for all models and diagnostics except *Theta* for CCATT-BRAMS are lower than observed (1 km). Overall the models underestimate the PBL depth, which may contribute to an overestimate of O_3 near the ground. Despite these limitations, the

Movido (inserção) [7]

Excluído: Peak shortwave radiation is slightly overestimated by both models, which may be related to low cloudiness (convection is triggering too early) or AOD (too much aerosol wet removal). This will increase O_3 production from photolysis, as well as increase surface temperature and evaporation. Although biogenic emissions are not coupled with meteorology in these simulations, this may increase biogenic emissions in future studies that include online biogenic emissions. WRF-Chem predicts a nearly constant Bowen ratio at forest and pasture sites. This indicates that the Noah land surface model is not properly representing the impact of conversion of forest to pasture and the resulting increase in sensible heat flux.¶
In the dry-to-wet transition season, for both CCATT-BRAMS and WRF-Chem, the mean daily cycle of surface incident shortwave radiation calculated for the Manaus AERONET site for October–November 2008, falls within one standard deviation of the mean AERONET observations (Fig. 6), but is closer to the upper limit, possibly due to underestimated cloudiness or AOD in the models. For the forest and pasture sites, both models represent the daily cycles of incident ... [8]

Excluído: peak latent heat flux at 13:00 LT is higher at the forest site than at the pasture site (460 W m^{-2} vs. 268 W m^{-2}) whereas the sensible heat flux shows ... [9]

Movido para cima [7]: Both models represent the daily cycles of incident shortwave and ingoing and outgoing longwave radiation, although incid ... [10]

Excluído: as for the dry-to-wet transition, peak latent heat flux at 13:00 LT is higher at the forest site than at the pasture site (401 W m^{-2} vs. 324 W m^{-2}). However, th ... [11]

Excluído: Mean vertical profiles at Manaus from radiosoundings, CCATT-BRAMS and WRF-Chem for October - November 2008 at 0, 12 and 18Z a ... [12]

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Excluído: , with a RMSE of 2.4 - 3.0 mm h^{-1} and bias of 0.3-3.5 mm h^{-1} for CCATT-BRAMS, and RMSE of 4.5 - 7.1 mm h^{-1} and bias of 3.5-5.8 mm h^{-1} for WRF-Chem

Excluído: surface pressure is underestimated by 1 - 2 hPa. Wind speed is underestimated by CCATT-BRAM ... [13]

Movido (inserção) [6]

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Movido para cima [8]: Now we summarize the key findings of the model-data meteorological comparison and their implications for the chemistry simu ... [14]

Movido para cima [6]: The models generally show good agreement with soundings, but excess moisture in C ... [15]

models are able to capture the meteorological contrast between the dry-to-wet and wet-to-dry transition seasons.

4.3 Observed and Simulated Chemistry

4.3.1 Mean O_3 Profiles

An example of observed and simulated O_3 during the flight legs between Manaus and Belém in BARCA A and B is shown in Fig. 17. While the models capture the pattern of increasing O_3 values with height, the models underestimate elevated O_3 values from 2.5-4.5 km, and overestimate low values near the surface (1-1.5 km). The models also do not reproduce the variability in the high values, likely due to the aircraft intersection of biomass burning plumes. This is expected given the coarse horizontal grid resolution. Thus, mean profiles are analyzed in order to study differences among the regions and seasons and to assess the models' abilities to capture the impacts of such small-scale processes on regional O_3 distributions.

The mean vertical O_3 profiles for observations, CCATT-BRAMS and WRF-Chem for the regions to the west, north, south, east and around Manaus are shown for BARCA A and B in Figs. 12 and 14, respectively, and NO profiles corresponding to the aircraft tracks are depicted in Figs. 13 and 15, respectively. Mean profiles from longitudinal surveys over Amazonia of O_3 during ABLE-2A (Browell et al., 1988) and ABLE-2B (Harriss et al., 1990) and NO during ABLE-2A (Torres and Buchan, 1988) are included for comparison. In BARCA B, O_3 values were at or near background values in all regions, ranging from 8 - 15 ppb at the surface to 2 - 15 ppb at 4 - 4.5 km, and the models are generally within 5 - 10 ppb of the observations. During BARCA A, while the W region still had low O_3 values (5 ppb at the surface to 20 ppb at 4 - 4.5 km), the N, S and M regions ranged from 15 - 20 ppb at the surface to 30 - 35 ppb at 4 - 4.5 km, and the E region presented the most elevated values, from 25 - 55 ppb. ABLE-2A O_3 profiles are similar in all regions, ranging from 15 - 20 ppb near the surface to 30 - 40 ppb from 4 - 6 km, so that the BARCA values are higher in the fire-influenced east and south regions, lower in the north and west regions, and very similar around Manaus. The profiles from ABLE-2B are within one standard deviation of the BARCA B measurements, except for the north region, where they are lower (5-15 ppb). These results suggest an increasing influence of fire emissions to the east and south of Manaus, but that O_3 in clean regions has not changed much.

A similar model behavior is seen in the broad regional mean profiles (Fig. 16). All simulations over-estimate O_3 throughout the PBL and lower troposphere during clean conditions in BARCA A, but under-estimate O_3 in polluted conditions. This is especially true from 2-4 km where biomass burning plumes detrain O_3 precursors. During BARCA B all simulations show good agreement.

Movido (inserção) [5]

Excluído: Lower levels of O_3 in the rainy season are largely associated with increased presence of convective clouds and precipitation. Decreased surface temperatures and incident solar radiation due to cloudiness suppress emissions of biogenic VOCs such as isoprene. In addition, higher surface humidity and precipitation decrease the occurrence of fires that emit NO_x and VOCs. O_3 precursors are further decreased by wet removal within the storms. On the other hand, during the dry-to-wet transition season, increased solar radiation, latent heat and temperature stimulate the production of OH and other HO_x radicals that can stimulate net O_3 production.¶

Movido para cima [5]: Lower levels of O_3 in the rainy season are largely associated with increased presence of convective clouds and precipitation. Decreased surface temperatures and incident solar radiation due to cloudiness suppress emissions of biogenic VOCs such as isoprene. In addition, higher surface humidity and precipitation decrease the occurrence of fires that emit NO_x and VOCs. O_3 precursors are further decreased by wet removal within the storms. On the other hand, during the dry-to-wet transition season, increased solar radiation, latent heat and temperature stimulate the production of OH and other HO_x radicals that can stimulate net O_3 production.

Movido (inserção) [4]

Excluído: However, the BARCA observations are generally lower than the models in the boundary layer, indicating that the satellites appear here to be dominated by the middle troposphere and long-range transport.

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Both models generally overestimate O_3 from 1-2 km and underestimate O_3 from 3-4.5 km. As seen in the CO results shown in Andreae et al. (2012), the model profiles have steeper slopes than the observations, except in the polluted south, possibly due to excessive vertical mixing of precursors. In addition, the models may be missing sources of O_3 and/or precursors at 3-4.5 km in the model inflow boundary conditions. In general the models overestimate O_3 in the PBL compared to aircraft measurements, but underestimate the total column values relative to the OMI/MLS satellite product. This suggests that the total column values in Amazonia are dominated by global pollution from Africa, rather than local O_3 production from biomass burning. ¶

In order to understand the possible sources of model error, we now individually examine the contributions of different chemical sources and sinks, including surface emissions and deposition, boundary inflow and chemistry within the PBL.

4.3.2 Emissions

The relative sensitivities of O_3 production to NO_x or BVOC emissions depend upon the relative amounts of VOCs and NO_x present. Under clean conditions with a high VOC:NO_x ratio, O_3 production is NO_x sensitive, whereby increases in NO_x will lead to increases in O_3 while increased VOCs will have little impact. On the other hand, in polluted areas with a high NO_x:VOC ratio, the system is VOC-sensitive, that is, increased VOCs contribute to O_3 production but an increase in NO_x actually depletes O_3. Emissions of BVOCs can increase O_3 production by the following mechanism. Oxidation of BVOCs can lead to formation of HO_2 and $RO_2\bullet$, which react with NO to form NO_2. NO_2 in turn photolyzes to form $O(^3P)$, which reacts with O_2 to form O_3 (National Research Council, 1991). We expect the polluted east/south regions during BARCA A to be VOC-sensitive and the clean west, north and around Manaus regions during BARCA A and all regions in BARCA B to be NO_x-sensitive. Kuhn et al. (2010) determined via aircraft transects in the Manaus urban plume that most of the VOC reactivity was provided by isoprene emissions from the surrounding rainforest, and NO_x emissions suppressed O_3 production close to urban sources, but stimulated it downwind.

For BARCA, the simulated mean monthly emission rates for two O_3 precursors, NO_x (anthropogenic and biomass burning) and isoprene (biogenic) are shown in Fig. 17. In Nov. 2008, elevated NO_x emission rates of up to 5 x 10^{-5} kg m^{-2} day^{-1} are seen from an area of intense biomass burning in the northeast Amazon, as well as from more scattered fires in the southeast Amazon. These are both regions that were overflown by the aircraft (Fig. 1). In May 2009, the Amazon region is largely free of fire. Because biogenic NO emissions (e.g., from soil) were not included in the MEGAN climatology used in this study, background NO emissions (in absence of fire) are likely too low. Typical model anthropogenic NO_x emissions values over the Amazon, primarily from biofuel sources, were 0.008-13 µg N m^{-2} hr^{-1} N. This NO_x emissions included in the modles were less than one third of the mean values of 44 ± 14 µg N m^{-2} h^{-1} NO measured by Kaplan et al. (1988) during ABLE-2A. This is considered a threshold value for NO_x-driven O_3 production to be the dominant O_3 source in the PBL. The model emissions were also much lower than the mean emissions from forest of 35.8 µg N m^{-2} h^{-1} NO measured in the 1998 dry season (Garcia-Montiel et al., 2003). Wetting the forest soil resulted in small pulses of NO and therefore the mean emissions are expected to be higher in the wet season than dry season.

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Isoprene emissions are highest in the western and southern Amazon, reaching 15 x 10^{-5} kg m^{-2} d^{-1} in November ~~2008 and 5-10 x 10^{-5} kg m^{-2} d^{-1} in the aircraft sampling region.~~ Due to decreased surface temperature and incident solar radiation in the rainy season, isoprene emissions in the Amazon Basin are much lower during BARCA B, 3-5 x 10^{-5} kg m^{-2} d^{-1}. The MEGAN emissions are consistent with isoprene emission measurements above the Amazonian canopy: a normalized flux of 5.76 x 10^{-5} kg m^{-2} d^{-1} in July 2000 at the end of the rainy season (Rinne et al., 2002) and an average noontime flux of 18.7 ± 5.5 x 10^{-5} kg m^{-2} d^{-1} in September 2004 during the dry season (Karl et al., 2007).

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4.3.3 Deposition

Figures 18 and 19 show the average O_3 dry deposition flux and median daytime deposition velocity, respectively, as simulated on the 35 km resolution domain by the CCATT-BRAMS and WRF-Chem models for November 2008 and May 2009. In the Amazon Basin, O_3 deposition fluxes are higher in the dry-to-wet transition season, with values reaching 3.5 nmol m^{-2} s^{-1} for CCATT-BRAMS and 6 nmol m^{-2} s^{-1} for WRF-Chem in the northeast Amazon, near the region of concentrated biomass burning. These values are also seen along the northern Andes and Southeast Brazil, due to recirculation of O_3–rich air. In the wet-to-dry transition season, O_3 deposition is at a minimum in the western Amazon, with values of 0.5-1 nmol m^{-2} s^{-1} for CCATT-BRAMS and 2 nmol m^{-2} s^{-1} for WRF-Chem. For both models, deposition velocities are higher over the rainforest than in the savanna to the east or south of the Amazon Basin, and higher in the wet-to-dry transition than in the dry-to-wet transition. These patterns are also seen in the tower observations in Table 5.

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O_3 surface fluxes and dry deposition velocities predicted by the models were compared with observations from several field campaigns (Table 5). These include during the dry (May 1999) and wet (September–October 1999) seasons at Reserva Biológica Jarú (RBJ, forest) and Fazenda Nossa Senhora (FNS, pasture) from LBA-EUSTACH (Rummel et al., 2009; Kirkman et al., 2002) and during the wet season at Reserva Ducke (RD, forest tower near Manaus, 2.95°S, 59.95°W°) from ABLE 2B (April-May 1987) (Fan et al., 1990) and at FNS from LBA-TRMM (January - February 1999 (Sigler et al., 2002). For the observations, the means of the hourly (WRF-Chem) and 3-hourly (CCATT-BRAMS) O_3 dry deposition fluxes (nmol m^{-2} s^{-1}) and the medians of the daytime (11:00 – 21:00 UTC) hourly mean deposition velocities (cm s^{-1}) are shown. The values were extracted from the grid points closest to the tower locations. In the observations, O_3 fluxes are larger in the dry season, due to higher O_3 mixing ratios. However, deposition velocities are higher in the wet season, and O_3 deposition to the Amazon forest constitutes a globally significant O_3 sink (Rummel et al., 2009). Both models capture these patterns, but the models underestimate the deposition velocities by

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15-75%, which may be partially responsible for the low O_3 fluxes at the Jarú forest site in both seasons and the pasture site in the dry season.

4.3.4 Boundary Conditions

The mean tropospheric and total tropospheric column O_3 from OMI/MLS, CCATT-BRAMS and WRF-Chem for November 2008 and May 2009 are shown in Figs. 20 and 21, respectively. The models significantly underestimate the total columns from satellite and middle altitudes from BARCA. For both BARCA A and B, the models represent the pattern of lower O_3 over the Amazon and higher values over northeast Brazil (BARCA A only) and at 30°S, although the values are strongly underestimated. In November 2008, OMI/MLS mean tropospheric O_3 concentrations show an inflow of elevated O_3 (mean ca. 55 ppb, total 40-45 DU) on the northeast Brazilian coast due to cross-Atlantic transport from biomass burning in southern and sub-Saharan Africa. Additionally, a band of elevated O_3 (mean 55-60 ppb, total 35-40 DU) passes over the South American continent at around 30°S, also from cross-Atlantic transport. During this month, Northern Hemisphere O_3 levels to the north of South America are relatively low (mean 35-40 ppb, total 25-30 DU). On the other hand, the tropospheric ozone distribution in May 2009 (Fig. 16) is characterized by a band of low ozone extending over the Amazon Basin and northeast Brazil between 10°S and 10°N (mean 25-35 ppb, total 20-25 DU). In addition, slightly elevated values at around 30°S, primarily over the oceans (40-55 ppb, 30-35 DU) and higher ozone in the Northern Hemisphere (mean 50-55 ppb, total 35-40 DU north of 10°N). Both models capture the overall distribution (inflow in NE Brazil in Nov. 2008, lower values over the Amazon Basin, elevated at 30°S) but values are underestimated relative to OMI/MLS. In general the models overestimate O_3 in the PBL compared to aircraft measurements, but underestimate the total column values relative to the OMI/MLS satellite product. This suggests that the total column values in Amazonia are dominated by global pollution from Africa, rather than local O_3 production from biomass burning. A typical OMI averaging kernel (cloud-free ocean conditions) shows maximum sensitivity from 594-416 hPa (Zhang et al., 2010). Therefore, OMI may not be detecting O_3 in the PBL from local sources, but rather primarily seeing global pollution from Africa.

Above the boundary layer, from 3-4 km a.g.l., chemical inflow at the eastern boundary of South America may contribute to O_3 elevated above background. In order to evaluate the model representation of this inflow, vertical profiles from SHADOZ soundings on the northeast coast of South America during the BARCA A and B periods were compared with CCATT-BRAMS and WRF-Chem (Fig. 22). In addition, 120 h back trajectories from the sounding locations at heights of 1500 m, 6000 and 9000 m above ground level (gal) were calculated with the HYSPLIT model

Movido para baixo [3]: <#>The mean tropospheric and total tropospheric column O_3 from OMI/MLS, CCATT-BRAMS and WRF-Chem for November 2008 and May 2009 are shown in Figs. 15 and 16, respectively. The models significantly underestimate the total columns from satellite and middle altitudes from BARCA. For both BARCA A and B, the models represent the pattern of lower O_3 over the Amazon and higher values over northeast Brazil (BARCA A only) and at 30°S, although the values are strongly underestimated. In November 2008, OMI/MLS mean tropospheric O_3 concentrations show an inflow of elevated O_3 (mean ca. 55 ppb, total 40-45 DU) on the northeast Brazilian coast due to cross-Atlantic transport from biomass burning in southern and sub-Saharan Africa. Additionally, a band of elevated O_3 (mean 55-60 ppb, total 35-40 DU) passes over the South American continent at around 30°S, also from cross-Atlantic transport. During this month, Northern Hemisphere O_3 levels to the north of South America are relatively low (mean 35-40 ppb, total 25-30 DU). On the other hand, the tropospheric ozone distribution in May 2009 (Fig. 16) is characterized by a band of low ozone extending over the Amazon Basin and northeast Brazil between 10°S and 10°N (mean 25-35 ppb, total 20-25 DU). In addition, lightly elevated values at around 30°S, primarily over the oceans (40-55 ppb, 30-35 DU) and higher ozone in the Northern Hemisphere (mean 50-55 ppb, total 35-40 DU north of 10°N). Both models capture the over ... [16]

Movido para cima [4]: <#>However, the BARCA observations are generally lower than the models in the boundary layer, indicating that the satellites appear here to be dominated by the middle troposphere and long-range transport. An example of observed and simulated O_3 during the flight legs between Manaus and Belém in BARCA A and B is shown in Fig. 17. While the models capture the pattern of ... [17]

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Movido para baixo [2]: The excess O_3 in the PBL in the models could be due to either a low deposition sink, as O_3 dry deposition velocities in the models are about half of observed values, or excessive model sensitivity to NO_x emissions, or both. Two additional simulations were conducted with WRF-Chem to evaluate the model sensitivity to these processes: (1) doubling the calculated deposition velocity for O_3 only (2DEPVEL) and (2) halving the NO_x surface emission rates (0.5ENOx). ... [18]

(http://ready.arl.noaa.gov/hypub-bin/trajtype.pl?runtype=archive) using meteorological data from the NCEP/NCAR global reanalysis. Inflow at Paramaribo originated either in the Caribbean or the tropical Atlantic, while at Natal, air parcels came from anti-cyclonic recirculation from southeastern Brazil or the tropical Atlantic. Both models generally represent the SHADOZ O_3 profiles up to 600 hPa, but do not capture layers of elevated O_3 above 500 hPa. These are likely to be either from pollution recirculated from southeast Brazil or possibly from African biomass burning. The models also do not reproduce thinner layers of high O_3 below 600 hPa. For example, at Natal on 7 November 2008 (Fig. 22c, air of African origin at ~850 hPa and ~470 hPa) and 19 November 2008 (Fig. 22d, air from the central African coast at ~850 hPa and recirculation from southeastern Brazil at ~470 hPa and ~310 hPa) and at Paramaribo on 11 May 2009 (Fig. 22f, air of tropical Atlantic origin at all three levels), both models underestimate O_3 above 500 hPa by 40-60 ppb (model values of 30-50 ppb versus observations maximum values of 80-100 ppb). A previous analysis of ozone soundings and aircraft measurements at Natal suggested that increases in tropospheric ozone in the Southern Hemisphere springtime may be due to stratospheric intrusion (Logan, 1985). This is consistent with the November 2008 profiles at Natal; the models may not be capturing the intrusion of stratospheric air masses seen in the observations, indicated by upper tropospheric (> 500 hPa) layers with elevated O_3 and very low relative humidity (< 20%). On the other hand, at Paramaribo on 6 November and 25 November 2008 and at Paramaribo on 4 May 2009, when air masses at all levels were of Northern Hemisphere origin, the models reproduced the nearly constant with altitude O_3 values of 30-40 ppb.

4.3.5 Chemistry

The excess O_3 in the PBL in the models could be due to either a low deposition sink, as O_3 dry deposition velocities in the models are about half of observed values, or excessive model sensitivity to NO_x emissions, or both. Two additional simulations were conducted with WRF-Chem to evaluate the model sensitivity to these processes: (1) doubling the calculated deposition velocity for O_3 only (2DEPVEL) and (2) halving the NO_x surface emission rates (0.5ENOx). The O_3 profiles corresponding to BARCA flights for these two simulations are also included in Figs. 12 and 14. The corresponding NO profiles from all model simulations as well as a mean profile over Amazônia from ABLE-2A are depicted in Figs. 13 and 14. The 0.5ENOx simulation reduces O_3 more than 2DEPVEL throughout the entire profile. In the dry-to-wet transition, 2DEPVEL reduces O_3 in the lower PBL by about 25%, while 0.5ENOx decreases O_3 by around 40%, and in the wet-to-dry-transition the reductions are about 10% and 30%, respectively. In general the 0.5ENOx O_3 profiles are lower than observed in the first 500 m above the surface, but they provide the best representation of the data for the north

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and west regions in the dry-to-wet transition. They also provide a similarly good fit as 2DEPVEL for the east, Manaus and south regions, while in the wet-to-dry transition 0.5ENOx is closer to the observed value from 0-500 m in all regions except the north. During BARCA A, NO in all WRF-Chem simulations in the north, west, and Manaus regions is 10-15 ppt from 0-500 m above the surface, increasing to a maximum of 20-50 ppt at 2 km a.g.l., and is generally lower than the ABLE-2A observations in the PBL. In the east and south, where biomass burning influence was seen, NO in 0-500 m a.g.l. increased from 20-50 ppt in the base simulation to 35-60 ppt in 2DEPVEL due to decreased O_3 and conversion of NO to NO_2, and was generally within one standard deviation of the ABLE-2A measurements in the PBL. In BARCA B, NO simulated by WRF-Chem is very low, 5-10 ppt in the entire profile, except for the west region, where a mean NO of 30 ppt is seen from 0-500 m a.g.l. This is again due to very low O_3, and for the Manaus region, where anthropogenic NO_x sources may have contributed to NO values of 20 ppt. These results suggest that adjustment of dry deposition parameterizations are needed to increase O_3 deposition velocities by about a factor of two in agreement with ground observations. Future research will compare simulated NO_x fields with observations from more recent field campaigns, as the results of these simulations also suggest that O_3 in WRF-Chem is very sensitive to NO_x emissions.

In summary, chemistry simulations of the BARCA periods with CCATT-BRAMS and WRF-Chem overestimated O_3 in the PBL by 5-10 ppb in the wet-to-dry transition (BARCA B), with background levels observed (10-20 ppb) in all regions. In the dry-to-wet transition (BARCA A), the models generally reproduced elevated O_3 levels in the northeast and southeast Amazon where biomass burning emissions of precursors led to significant enhancements of ambient O_3. However, the models overestimate O_3 in the PBL by 5-10 ppb, whereas from 2-4 km the modeled values are generally lower than observations. These discrepancies of models with observations may result from an overly-mixed (constant with altitude) profile due to overly active turbulent mixing from 1-2 km or too much downward convective transport of O_3 from 2 km to the surface, as observed by Betts et al. (2002). In addition, the models may be missing sources of O_3 and/or precursors at 3-4.5 km in the model inflow boundary conditions. The surface sink of O_3 (dry deposition) may be too low, or overestimation of NO_x sources may produce too much O_3. In the lower boundary layer, the surface sink of O_3 (dry deposition) may be too low, or overestimation of NO_x sources may produce too much O_3. Additional simulations with WRF-Chem showed that O_3 in the lower boundary layer was about twice as sensitive to increases in O_3 deposition velocity as reductions in NO_x emissions, but both simulations achieved better agreement with observations. Although NO emissions over the forest were less than half of observed values, likely due to the lack of inclusion of soil emissions, sufficient O_3 production occurred to match

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or exceed aircraft observations, suggesting that the model chemistry is overly NO_x-sensitive.

5 Conclusions

The BARCA campaign offered the first regional aircraft survey of O_3 in the Amazon Basin in both the dry-to-wet and wet-to-dry transition seasons. In both seasons, extremely low background O_3 values (< 20 ppb) were observed to the west and north of Manaus, and in the wet-to-dry transition low O_3 was also measured to the east and south and in the region around Manaus. These background values are the lowest observed on Earth, due to a combination of isolation from anthropogenic and biomass burning NO_x sources and O_3 deposition to the forest canopy, and the ecosystem and atmospheric chemistry is adjusted to these very low values. According to the models, the chemistry in the Amazon is very sensitive to NO_x emissions from soils, so that even a small overestimate of NO_x emissions generates too much O_3 in the PBL. However, it is likely that the model chemistry is incorrect in the PBL, because the models have about the right amount of NO_x but far too much O_3 in the PBL. Further simulations with WRF-Chem showed that the model O_3 production is very sensitive to both the O_3 deposition velocities, which were about one half of observed values, and the NO_x emissions. In polluted, VOC-sensitive conditions, approximately the correct net amount of O_3 is generated in the PBL. This suggests there is insufficient VOC reactivity in the models, since the correct amounts of O_3 deposition velocities and NO_x emissions would both decrease O_3 production. Additionally, in clean, NO_x-sensitive conditions, proportionally more O_3 is produced per unit NO_x emissions and the O_3 deposition velocities are still too low, resulting in an overestimate. Therefore, we conclude that the current model chemistry produces much more O_3 per unit NO_x than the atmosphere at very low NO_x, but may be about right in polluted conditions. In addition, simulated O_3 was lower than both the OMI/MLS total tropospheric O_3 and the BARCA observations in mid-levels, indicating that the models are missing sources at mid-levels from long-range and convective transport.

As the regional population grows in the Amazon basin, leading to increases in both urban and fire NO_x sources, this is indeed a big concern because PBL O_3 is lower in clean areas than the models predict, so that the change to polluted conditions is larger, and that the chemistry to define the path to higher NO_x conditions is poorly represented. Future modeling studies can include more complete organic chemistry and biogenic emissions, including NO emissions from soil, as well as improved representation of lightning NO_x production, dry deposition, convective transport and wet scavenging processes, to address this NO_x sensitivity. Additionally, future field campaigns in the Amazon that include aircraft observations of nitrogen oxides and hydrocarbons and

Movido (inserção) [1]

Movido para cima [1]: Further simulations with WRF-Chem showed that the model O_3 production is very sensitive to both the O_3 deposition velocities, which were about one half of observed values, and the NO_x emissions.

Excluído: the O_3 retrieved by satellites is dominated by the middle troposphere and long-range transport and does not represent well boundary layer O_3 values

ground-based measurements of NO flux from the forest canopy may allow better constraints on the Amazonian O_3 budget.

Acknowledgements

The authors are grateful to the entire BARCA team, including E. Gottlieb, V.Y. Chow, M.D.P. Longo, G.W. Santoni, F. Morais, A.C. Ribeiro, N. Jürgens, J. Steinbach, H. Chen, O. Kolle, L.V. Gatti, J.B. Miller, and the two INPE Bandeirante airplane pilots, P. Celso and D. Gramacho. We would also like to thank the GMAI group at INPE for indispensable support with the modeling and analysis, including M. Alonso, R. Braz, D. Franca, H. Lopez, R. Mello, R. Oliveira, V. Oliveira, M. Sanchez, F. Santos and R. Stockler. Many thanks to Anne Thompson, Neusa Paes Leme, Rinus Scheele, and Francis J. Schmidlin for the SHADOZ ozone sounding data. We thank B. Holben for his effort in establishing and maintaining the Manaus AERONET site. This work was supported by an IIE Fulbright Scholarship and PCI CNPQ, and the flight campaign was supported by the Max Planck Society, NASA grants NASA NNX08AP68A and NASA NNX10AR75G, FAPESP thematic project AEROCLIMA 2008/58100-2, CNPq Millennium Institute of the Large Scale Biosphere – Atmosphere Experiment in Amazonia (LBA) (CNPq Project 477575/2008-0), and MCT and INPE. Finally, we would like to express our gratitude to the three anonymous reviewers for their generous comments and revisions which greatly improved the manuscript.

Excluído: F. Santos, R. Stockler, R. Mello, M. Alonso, M. Sanchez, D. Franca, R. Braz, H. Lopez, and V. Oliveira

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	CCATT-BRAMS	WRF-Chem
Short/longwave radiation	Based on CARMA	RRTMG
Cloud microphysics	Single moment bulk	WSM-5
Deep/shallow convection	Grell and Dévényi (GD)	Grell 3D
Trace gas chemistry	RACM	RACM
Photolysis	F-TUV	F-TUV
Aerosol scheme	Smoke aerosol	GOCART
Wet deposition	convective and grid scales	convective scale only

Table 1. CCATT-BRAMS and WRF-Chem physics and chemistry options for the BARCA simulations.

	Nov. 2008			May 2009		
Region	**TRMM 3B43**	**CCATT-BRAMS**	**WRF-Chem**	**TRMM 3B43**	**CCATT-BRAMS**	**WRF-Chem**
Amazon	0.24	0.22	0.51	0.20	0.15	0.40
Northeast	0.12	0.07	0.08	0.37	0.23	0.49
Southeast	0.19	0.11	0.24	0.10	0.06	0.07

Table 2. Monthly mean precipitation (mm h^{-1}) for TRMM 3B43, CCATT-BRAMS and WRF-Chem models for three regions: the Amazon (15°S – 10°N, 50°W – 80°W), northeast Brazil (15°S – 0°N, 35°W – 50°W), and southeast South America (15°S – 35°S, 35°W – 65°W).

		Oct-Nov 2008			May-Apr 2009		
			CCATT-BRAMS	**WRF-Chem**		**CCATT-BRAMS**	**WRF-Chem**
T (K)	*Mean Obs.*	*295.97*			*293.89*		
	RMSE		2.30	2.81		1.70	2.44
	Bias		1.04	-2.42		-0.06	-2.28
T_d (K)	*Mean Obs.*	*289.26*			*288.49*		
	RMSE		2.68	1.72		1.76	1.67
	Bias		-1.92	-0.81		-0.99	-0.83
Wind Spd.	*Mean Obs.*	*3.00*			*2.59*		
(m s^{-1})	RMSE		1.41	1.33		1.15	1.00
	Bias		-0.60	0.16		-0.51	0.07
Sfc. Press.	*Mean Obs.*	*1013.17*			*1016.09*		
(hPa)	RMSE		2.16	1.43		1.09	1.34
	Bias		-2.01	-1.02		-0.79	-1.17
Precip. TRMM	Mean Obs.	*0.49*			*0.62*		
(mm h^{-1})	RMSE		2.42	4.50		3.03	7.12
	Bias		0.28	3.47		0.25	5.84

Table 3. Values of RMSE and bias for CCATT-BRAMS and WRF-Chem simulations for 26 METAR and 52 SYNOP stations in the Amazon Basin for BARCA A (October-November 2008) and BARCA B (April-May 2009).

			Forest			Pasture		
PBL Height (km)		**Method**	**TKE**	**Theta**	**WRF MYNN**	**TKE**	**Theta**	**WRF MYNN**
BARCA A	CCATT-BRAMS	Mean	**1.103**	**1.610**	---	**1.143**	**1.636**	---
(Nov. 2008)		Std. Dev.	0.621	0.646	---	0.581	0.640	---
	WRF-Chem	Mean	**1.211**	**1.131**	**0.983**	**1.258**	**1.087**	**0.991**
		Std. Dev.	0.655	0.390	0.423	0.665	0.470	0.455
BARCA B	CCATT-BRAMS	Mean	**0.628**	**1.067**	---	**0.669**	**1.049**	---
(May 2009)		Std. Dev.	0.515	0.554	---	0.527	0.564	---
	WRF-Chem	Mean	**0.828**	**0.922**	**0.815**	**0.845**	**0.933**	**0.766**
		Std. Dev.	0.443	0.336	0.288	0.432	0.282	0.272

Table 4. PBL height at 21:00 UTC (17:00 LT) estimated from CCATT-BRAMS and WRF-Chem using methods based on Turbulent Kinetic Energy (TKE) and theta (θ) and the diagnostic from the WRF MYNN PBL scheme.

		Dry Season			Wet Season		
Site		**Observed**	**CCATT-BRAMS**	**WRF-Chem**	**Observed**	**CCATT-BRAMS**	**WRF-Chem**
RBJ (forest)	Flux	-5.69	-2.43	-3.25	-2.93	-1.59	-2.39
	v_d	0.6	0.3	0.5	1.2	0.4	0.8
FNS (pasture)	Flux	-4.68	-3.06	-2.49	-2.04	-2.07	-2.04
	v_d	0.6	0.4	0.4	0.7	0.4	0.7
RD (forest)	Flux				-1.82	-1.63	-2.68
	v_d				1.6	0.4	0.6

Table 5. Average O_3 dry deposition flux (nmol m^{-2} s^{-1}) and daytime (11:00-21:00 UTC) median deposition velocity (cm s^{-1}) in the dry and wet seasons (Rummel et al., 2007), and WRF-Chem and CCATT-BRAMS simulations from November 2008 (dry-to-wet transition) and May 2009 (wet-to-dry transition) for Reserva Biológica Jarú (RBJ), Fazenda Nossa Senhora (RNS) and Reserva Ducke (RD).

Excluído: 4

	BARCA A (Nov. 2008)					*BARCA B (May 2009)*				
Region	**Longitude**		**Latitude**		**Days**	**Longitude**		**Latitude**		**Days**
west	-60.06	-54.24	-12.00	-3.03	29, 30	-61.16	-59.46	-3.71	-2.39	28
north	-62.00	-59.11	-3.04	2.89	23	-61.81	-60.00	-3.04	3.71	19
around Manaus	-61.52	-58.50	-4.39	1.00	16, 22	-62.14	-60.00	-4.07	-2.16	15, 17
east	-108.73	-48.45	-3.04	-1.33	18, 19	-60.34	-44.82	-4.39	0.14	21, 22, 23, 26
south	-67.69	-60.01	-3.40	0.12	25, 26	-63.93	-60.01	-8.77	-3.04	27

Table 6. Longitude and latitude bounds and dates for each region of the BARCA A and B campaigns.

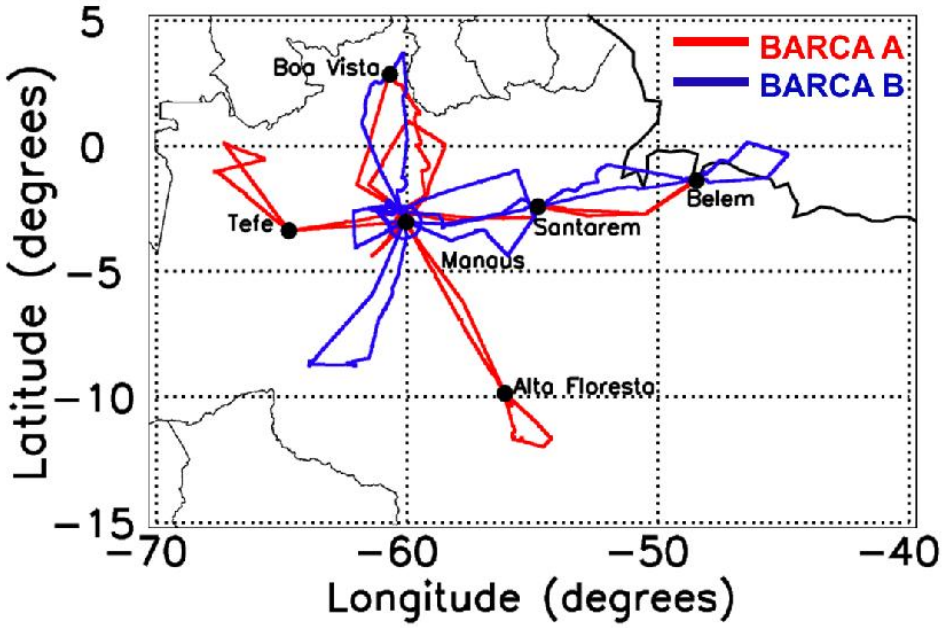

Figure 1. Flight tracks during BARCA.

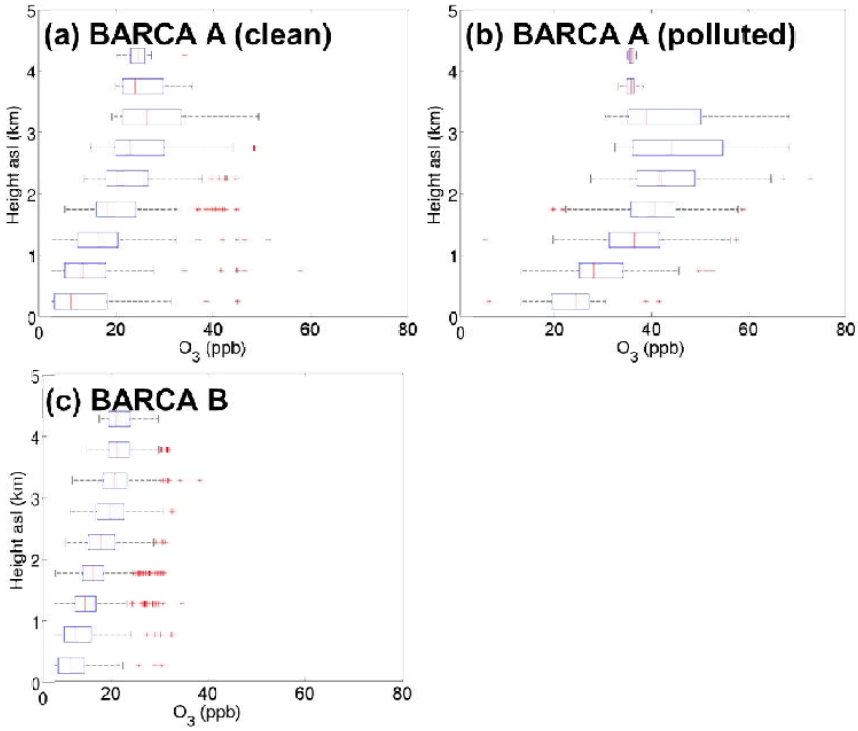

Figure 2. O_3 observations during (a) BARCA A, clean conditions (West, North and around Manaus regions), (b) BARCA A, polluted conditions (East and South regions) and (c) BARCA B. The central mark is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers (as defined by Matlab) and outliers are plotted individually as red plusses. Values are drawn as outliers if their values exceed $q_3 + w(q_3 - q_1)$ or are less than $q_1 - w(q_3 - q_1)$, where q_1 and q_3 are the 25th and 75th percentiles, respectively, and w is the maximum whisker length with the default value of 1.5. For normally distributed data, the whiskers encompass from approximately the 2.7 to 99.3 percentiles.

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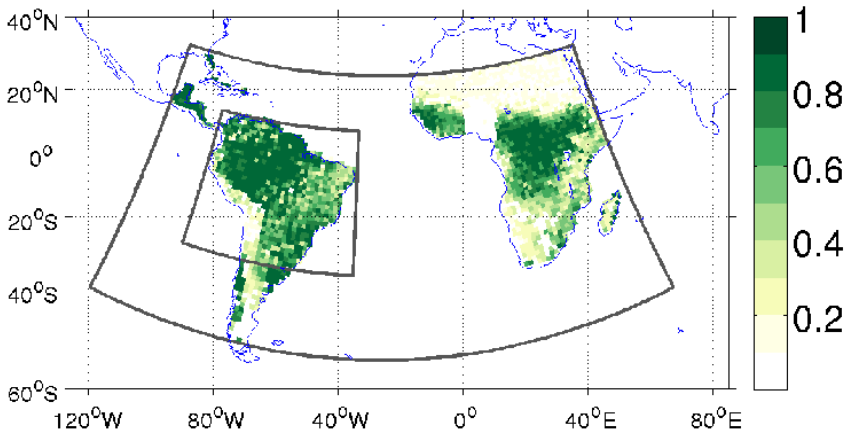

Figure 3. Land surface albedo (fraction) and locations of the coarse (140 km resolution) and nested (35 km resolution) domains for WRF-Chem simulations.

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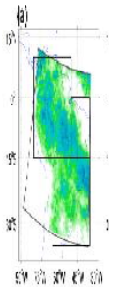

Figure 4. Monthly mean precipitation (mm h^{-1}) for November 2008 on the 35 km resolution domain (dark gray line) from (a) TRMM 3B43, (b) CCATT-BRAMS and (c) WRF-Chem. The subregions for precipitation comparison are indicated by black lines.

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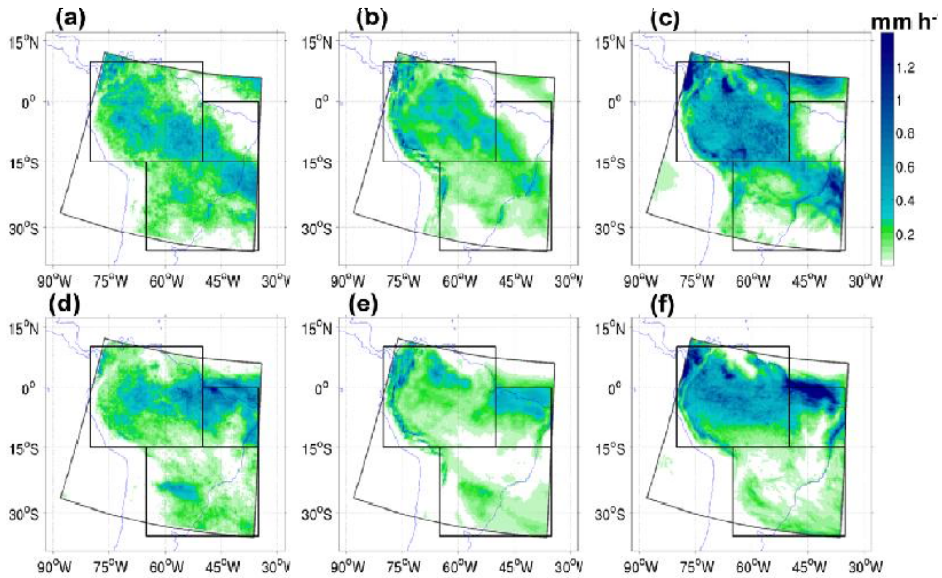

Figure 4. Monthly mean precipitation (mm h^{-1}) on the 35-km resolution domain (dark gray line) for November 2008 from (a) TRMM 3B43, (b) CCATT-BRAMS and (c) WRF-Chem and for May 2009 from (c) TRMM 3B43, (d) CCATT-BRAMS and (f) WRF-Chem. The subregions for precipitation comparison are indicated by black lines.

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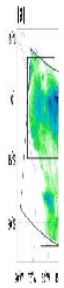

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Excluído: Same as Fig. 4, but for May 2009.¶

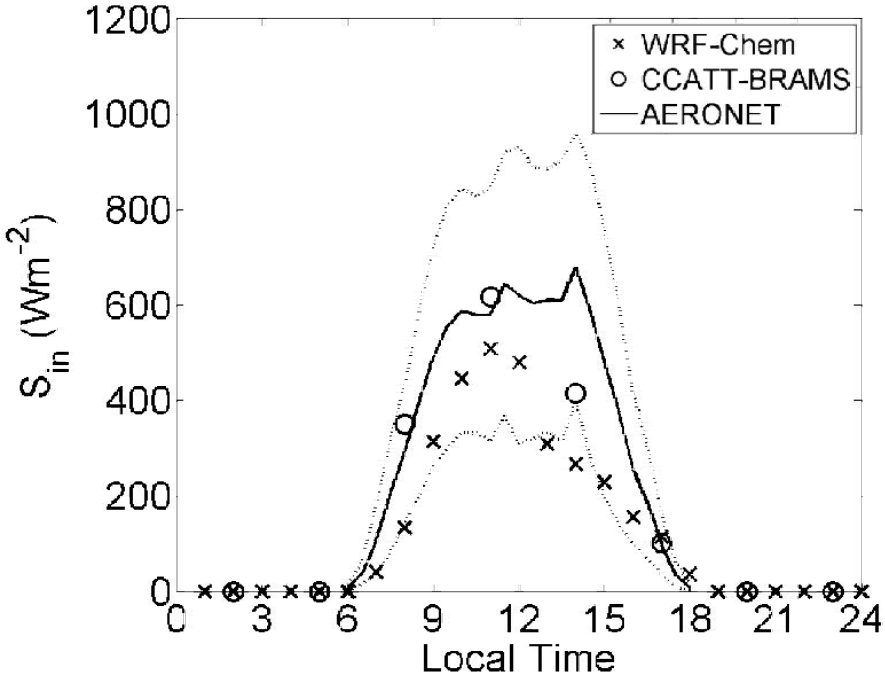

Figure 5. Mean daily cycle of surface incident shortwave radiation from the Manaus AERONET site (solid line, dotted line denotes one standard deviation), WRF-Chem (crosses) and CCATT-BRAMS (circles) for the BARCA A period (October-November 2008).

Excluído: 6

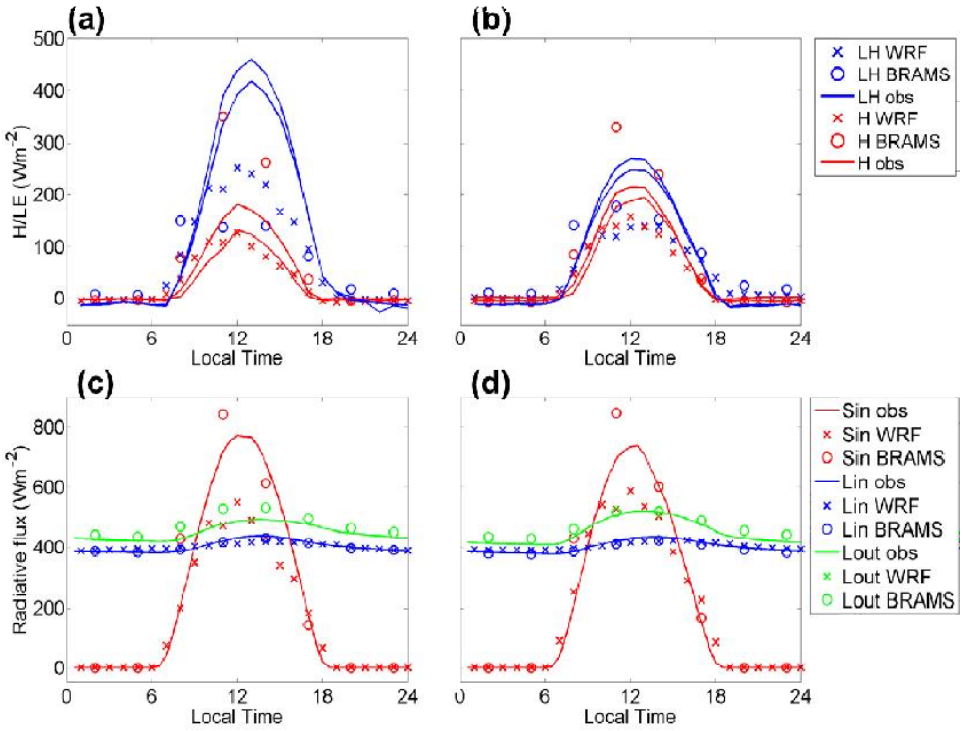

Figure 6. Mean daily cycles of surface (a) latent (LE) and sensible (H) heat and (c) incident shortwave (S_{in}) and incoming (L_{in}) and outgoing (L_{out}) longwave radiation fluxes for a forest site and (b) heat and (d) radiation fluxes for a pasture site, comparing observations (solid lines) from von Randow et al. (2004) for the dry-to-wet transition season (July-September 1999-2000) and from WRF-Chem (crosses) and CCATT-BRAMS (circles) for the BARCA A period (October-November 2008).

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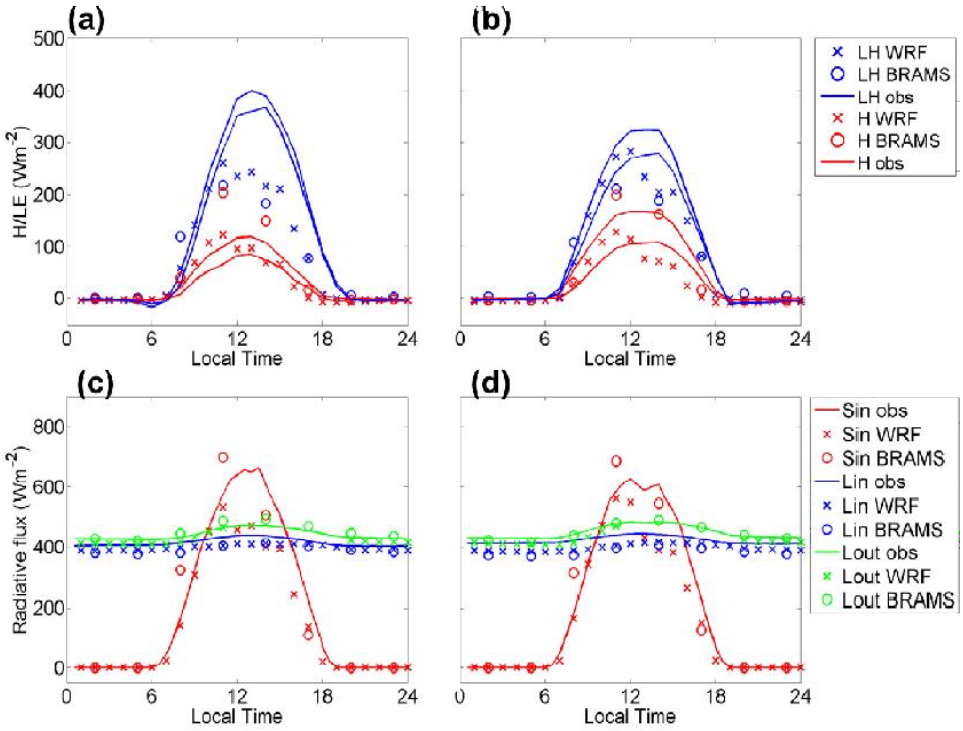

Figure 7. Mean daily cycles of surface (a) latent (LE) and sensible (H) heat and (c) incident shortwave (S_{in}) and incoming (L_{in}) and outgoing (L_{out}) longwave radiation fluxes for a forest site and (b) heat and (d) radiation fluxes for a pasture site, comparing observations (solid lines) from von Randow et al. (2004) for the wet-to-dry transition season (February-March 1999, January-March 2000) and from WRF-Chem (crosses) and CCATT-BRAMS (circles) for the BARCA B period (April-May 2009).

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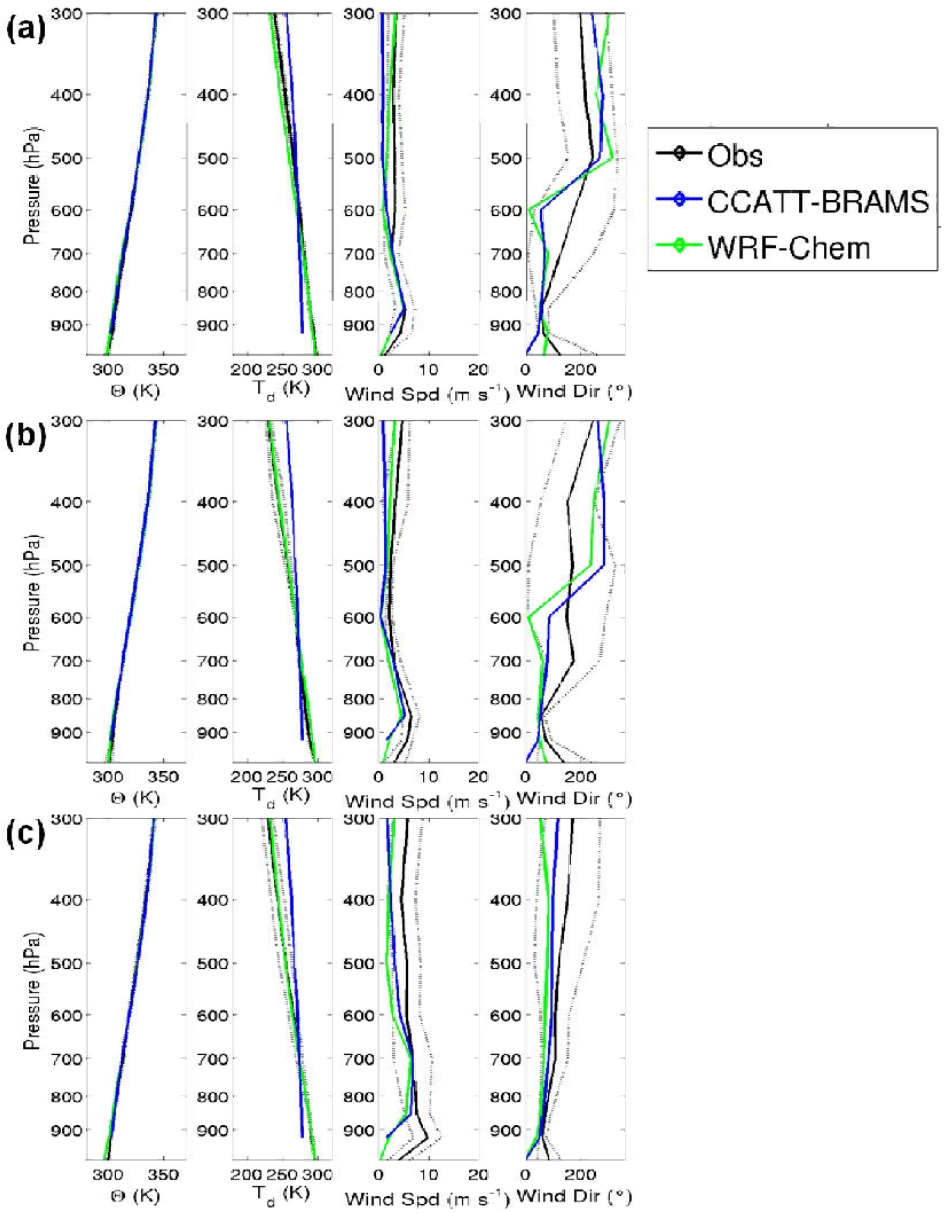

Figure 8. Mean vertical profiles at Manaus from radiosoundings (black, gray line denotes one standard deviation), CCATT-BRAMS (blue) and WRF-Chem (green) for October-November 2008 at (a) 0:00, (b) 12:00 and (c) 18:00 UTC.

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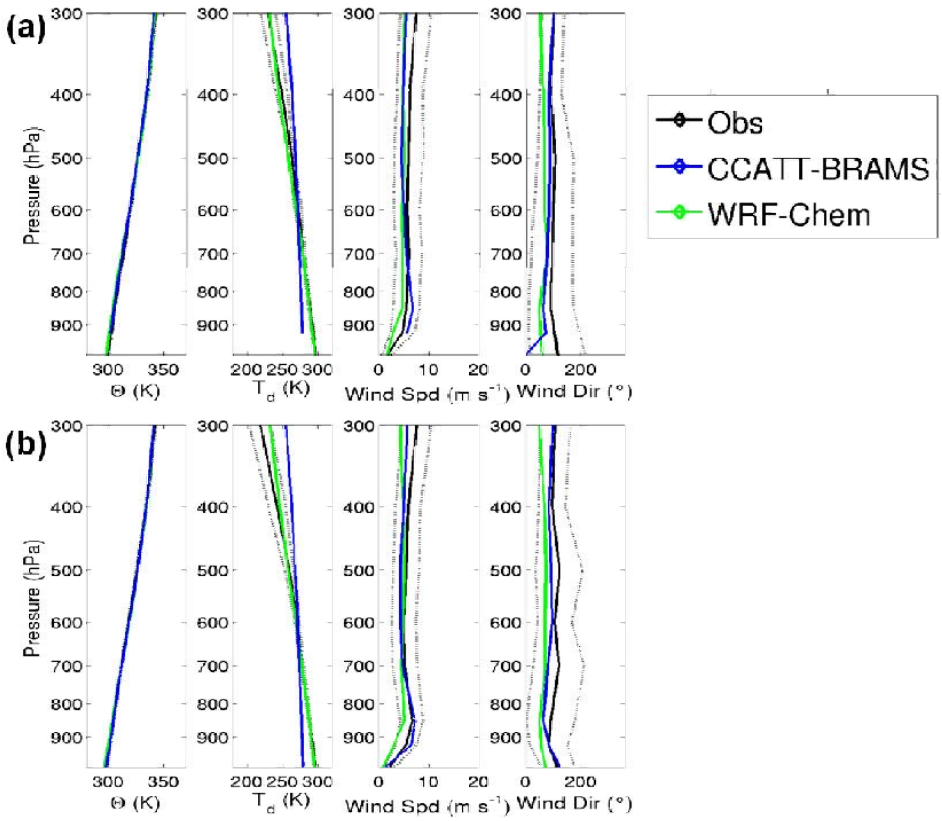

Figure 9. Mean vertical profiles at Manaus from radiosoundings (black, gray line denotes one standard deviation), CCATT-BRAMS (blue) and WRF-Chem (green) for April-May 2009 at (a) 0:00 and (b) 12:00 UTC.

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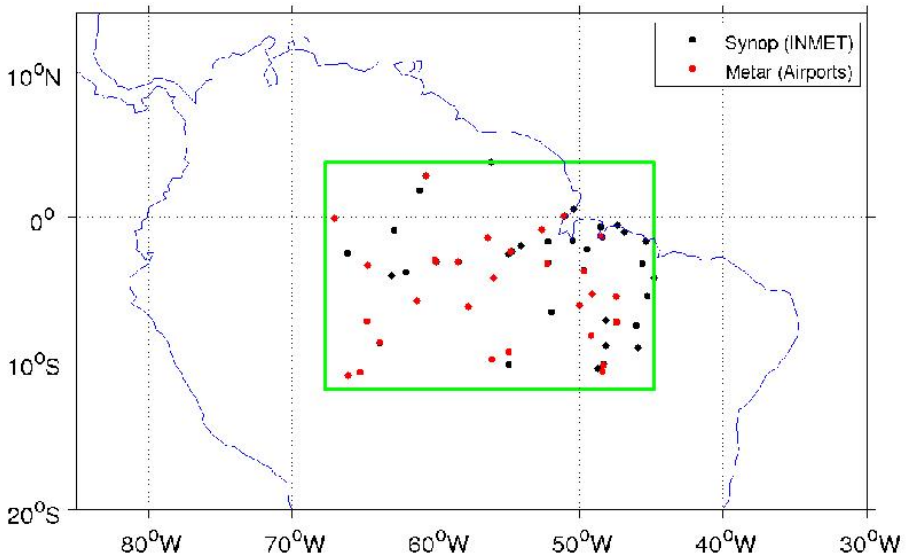

Figure 10. Locations of surface meteorological stations for model evaluation.

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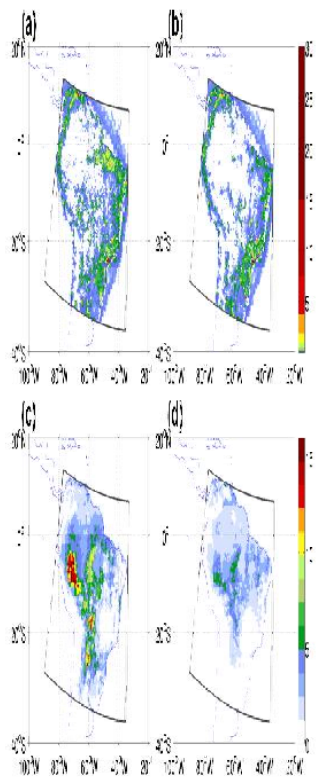

Figure 12. Mean emission rates (10^{-5} kg m^{-2} day^{-1}) from PREP-CHEM-SRC for the 35 km domain (dark gray outline) for NO_x for (a) BARCA A (November 2008) and (b) BARCA B (May 2009) and isoprene for (c) BARCA A and (d) BARCA B peri... [19]

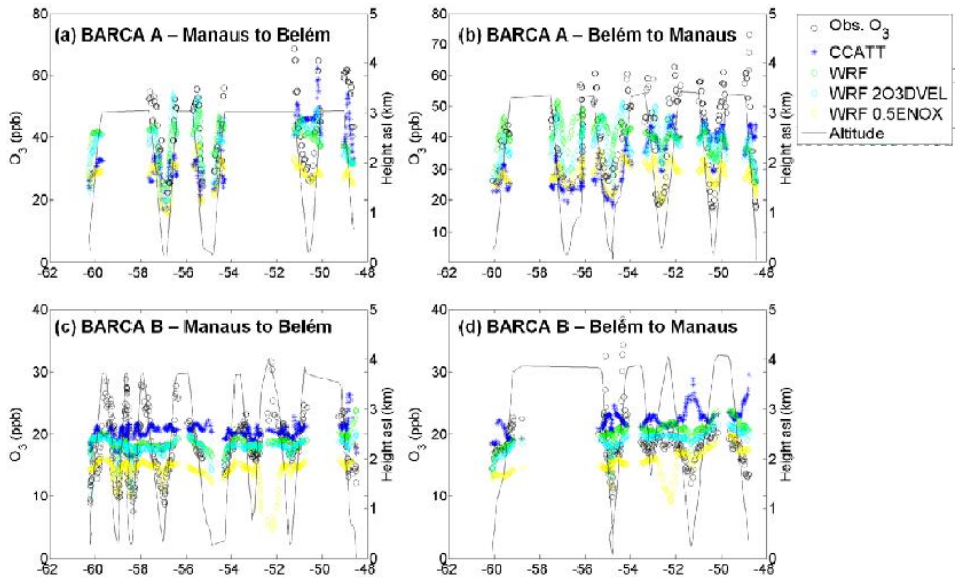

Figure 11. O_3 as observed (black circles) and simulated with CCATT-BRAMS (blue stars) and WRF-Chem (base case – green diamonds, 2DEPVEL – cyan circles and 0.5ENOx – yellow squares) from BARCA flights (a) from Manaus to Belém on 18 November 2008, (b) Belém to Manaus on 19 November 2008, (c) Manaus to Belém on 21 May 2009 and (d) Belém to Manaus on 23 November 2009.

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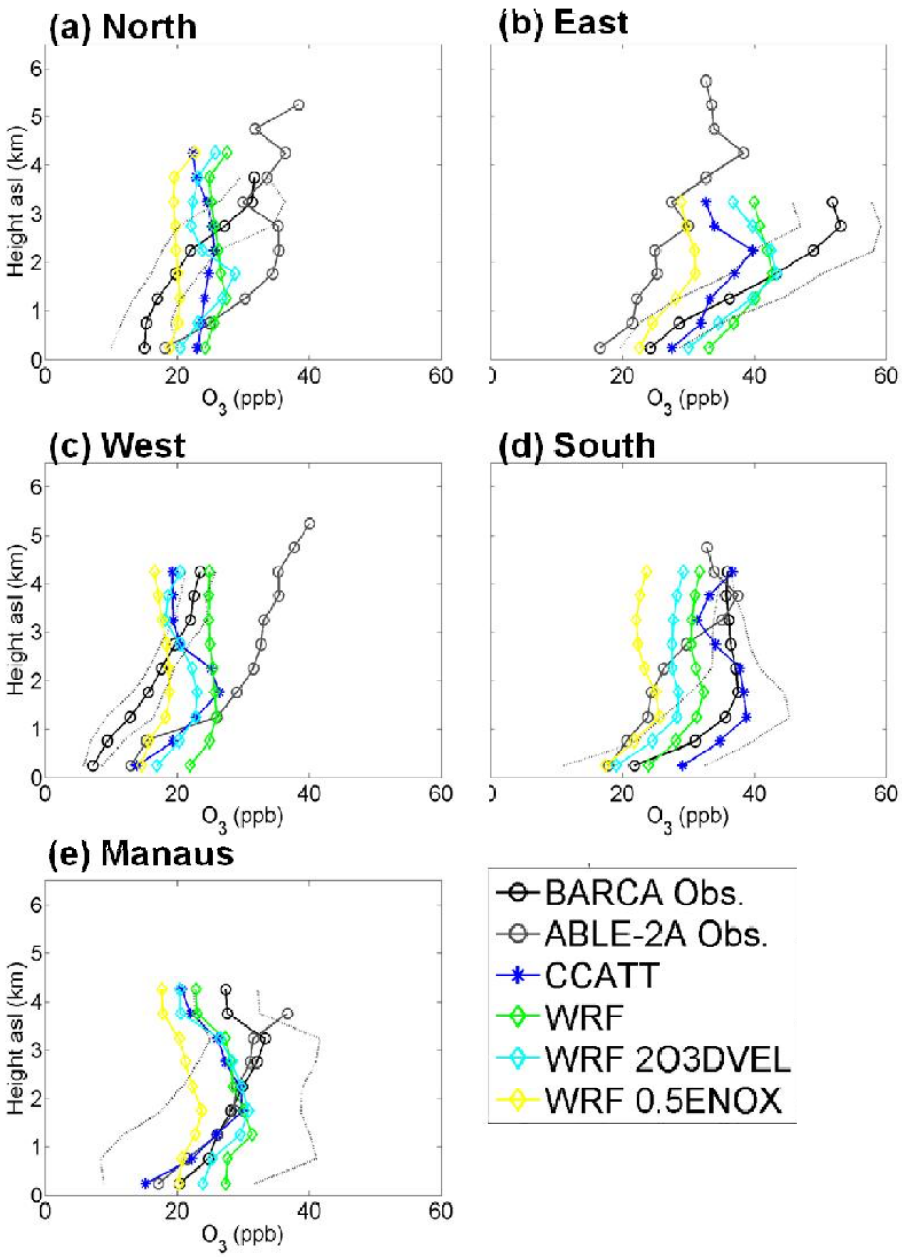

Figure 12. Mean vertical O_3 profiles for BARCA A flights for observations (black, gray line denotes one standard deviation), CCATT-BRAMS (blue) and WRF-Chem (base case – green, 2DEPVEL – cyan and 0.5ENOx – yellow) simulations by region: (a) north, (b) east, (c) west, (d) south and (e) around Manaus. ABLE-2A observations (gray) from the same regions are included for comparison.

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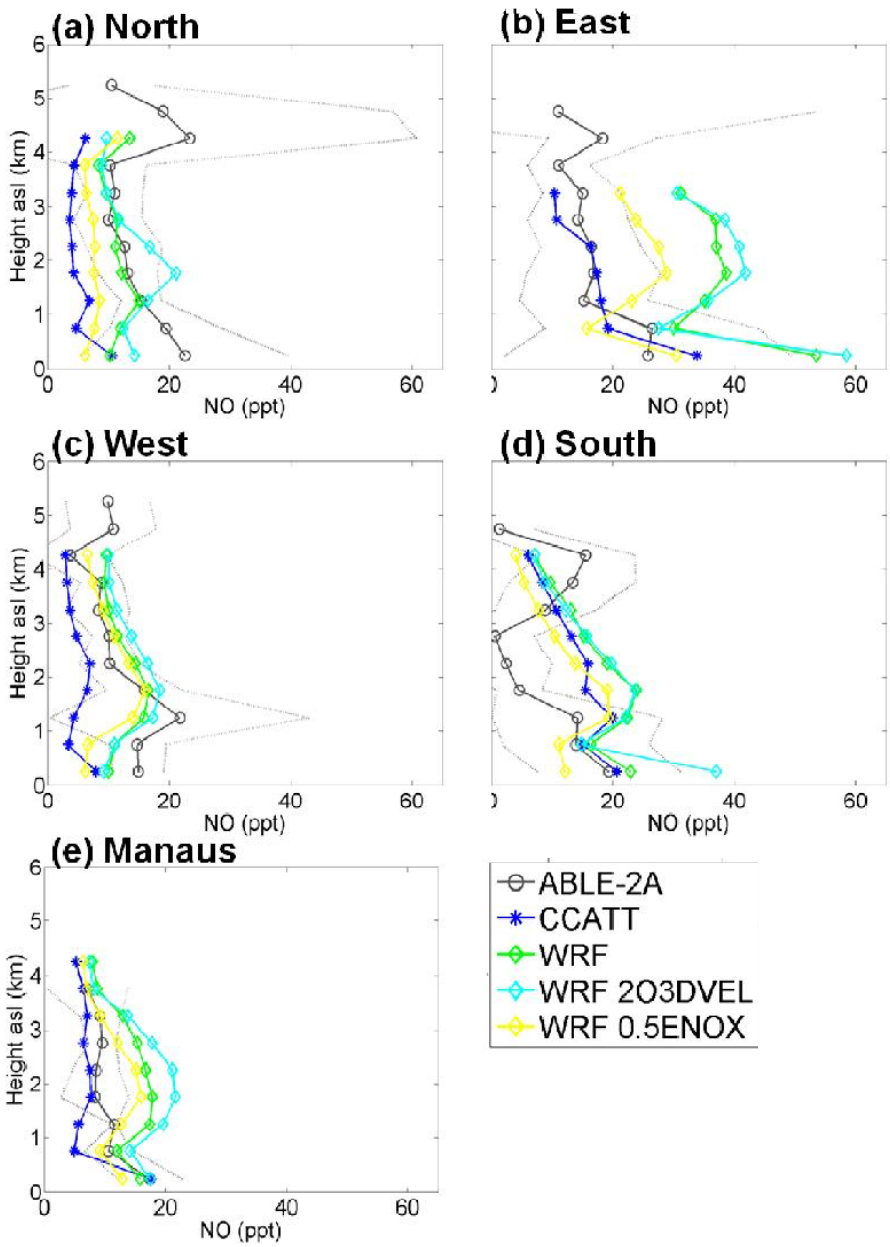


Figure 13. Mean vertical NO profiles corresponding to BARCA A flights for CCATT-BRAMS (blue) and WRF-Chem (base case – green, 2DEPVEL – cyan and 0.5ENOx – yellow) simulations by region: (a) north, (b) east, (c) west, (d) south and (e) around Manaus. ABLE-2A observations (gray) from the same regions are included for comparison.

Excluído: 9

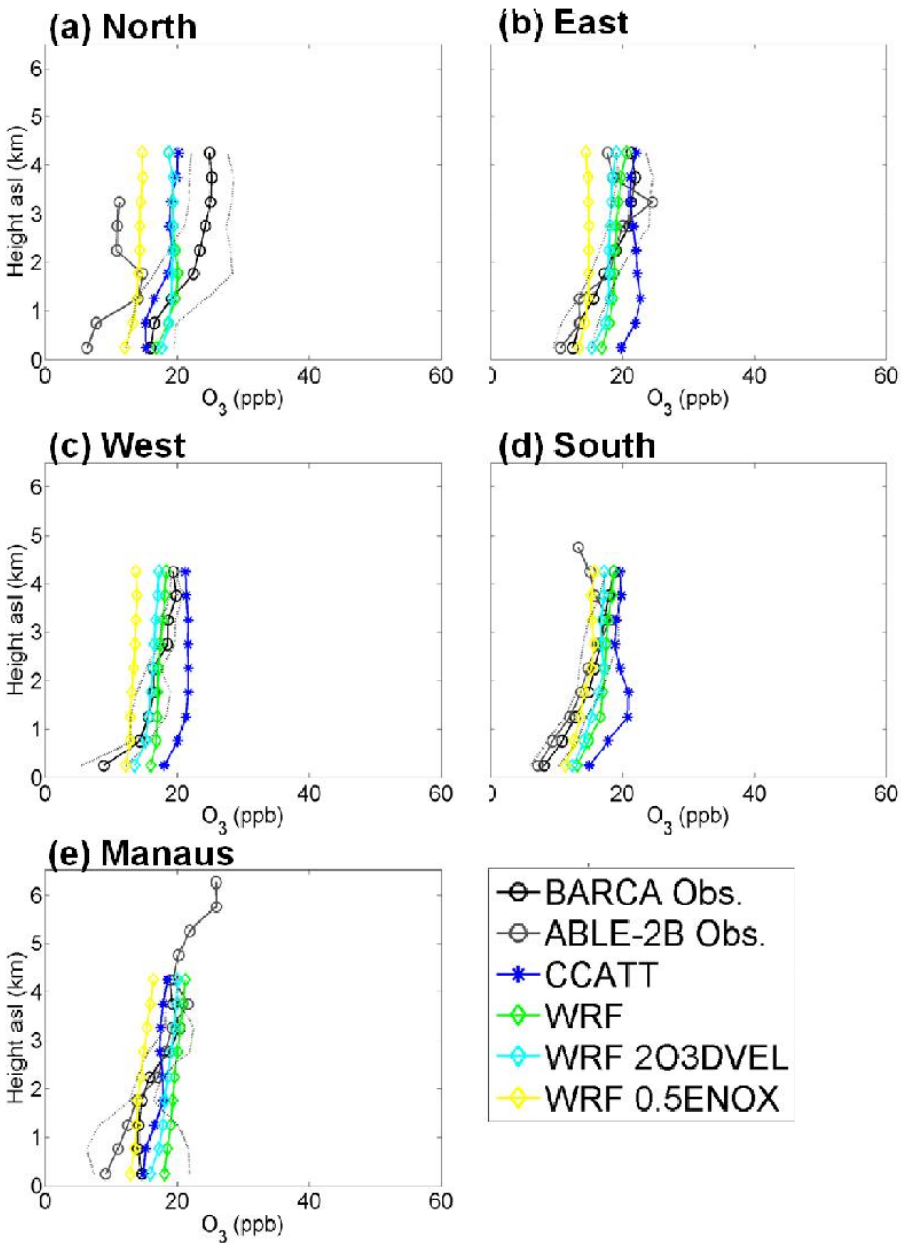


Figure 14. Mean vertical O_3 profiles for BARCA B flights for observations (black, gray line denotes one standard deviation), CCATT-BRAMS (blue) and WRF-Chem (base case – green, 2DEPVEL – cyan and 0.5ENOx – yellow) simulations by region: (a) north, (b) east, (c) west, (d) south and (e) around Manaus. ABLE-2A observations (gray) from the same regions are included for comparison.

Excluído: 20

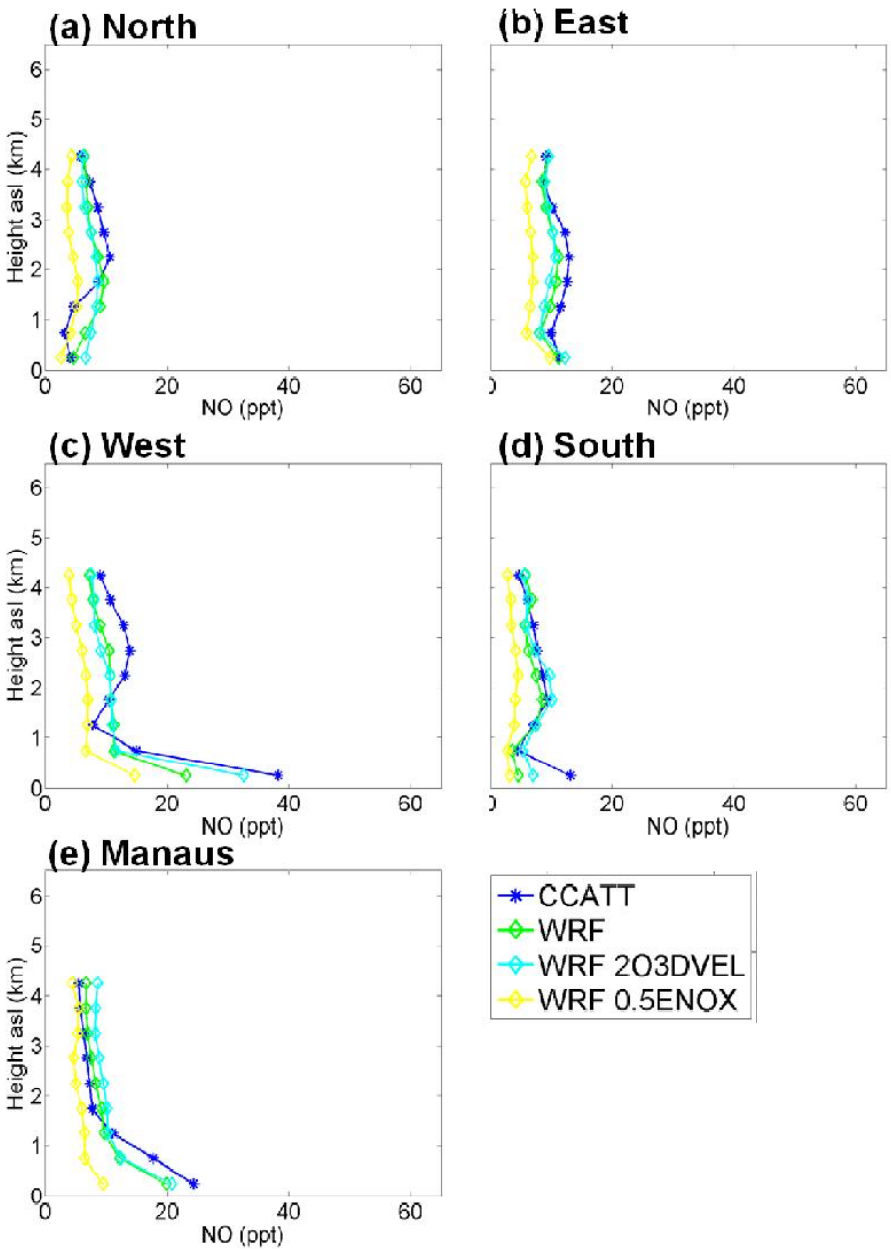


Figure 15. Mean vertical NO profiles corresponding to BARCA B flights for CCATT-BRAMS (blue) and WRF-Chem (base case – green, 2DEPVEL – cyan and 0.5ENOx – yellow) simulations by region: (a) north, (b) east, (c) west, (d) south and (e) around Manaus.

Excluído: 21

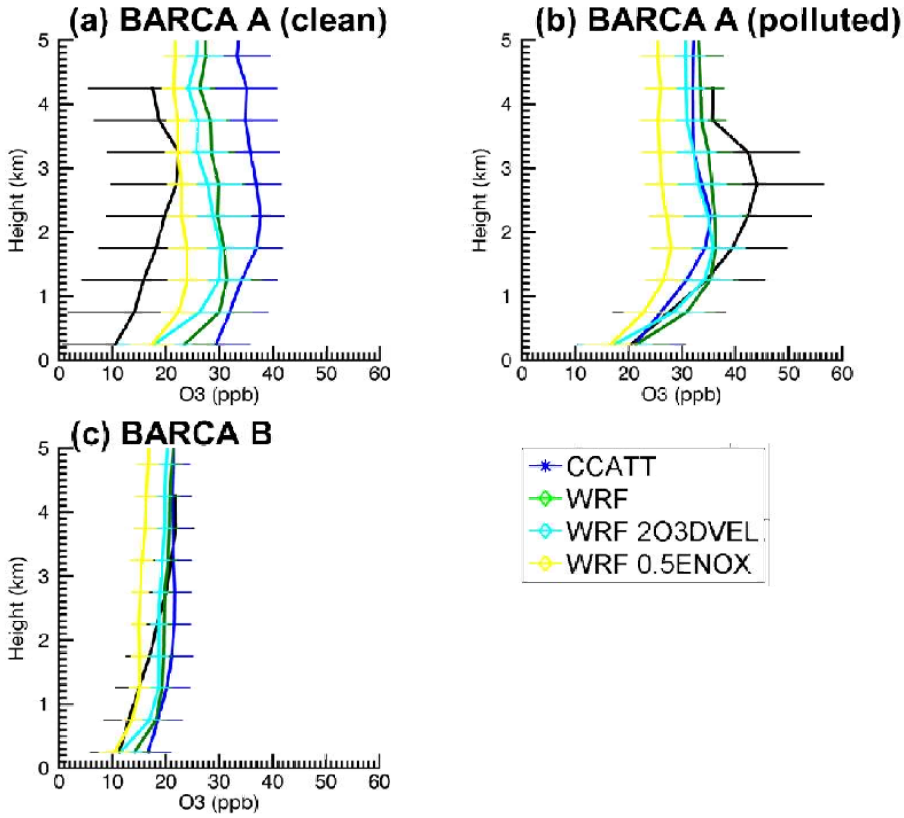


Figure 16. O_3 as observed (black circles) and simulated with CCATT-BRAMS (blue stars) and WRF-Chem (base case – green diamonds, 2DEPVEL – cyan circles and 0.5ENOx – yellow squares) during (a) BARCA A, clean conditions (west, north and around Manaus regions), (b) BARCA A, polluted conditions (east and south regions) and (c) BARCA B.

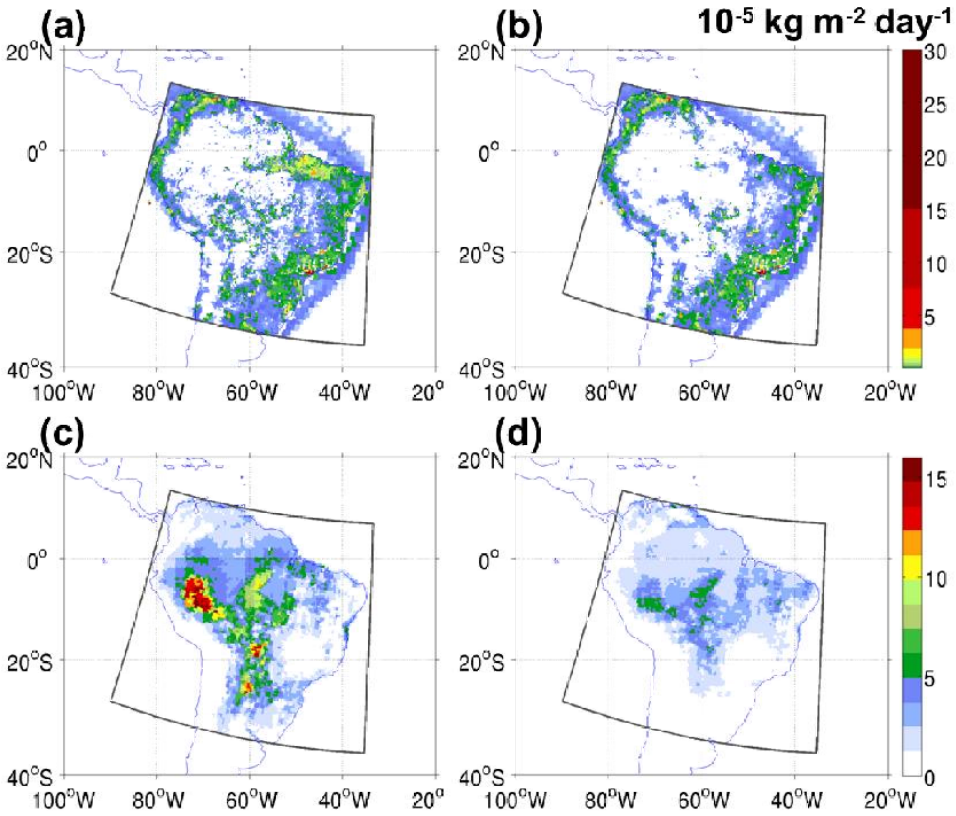


Figure 17. Mean emission rates (10^{-5} kg m^{-2} d^{-1}) from PREP-CHEM-SRC for the 35 km domain (dark gray outline) for NO_x for (a) BARCA A (November 2008) and (b) BARCA B (May 2009) and isoprene for (c) BARCA A and (d) BARCA B periods.

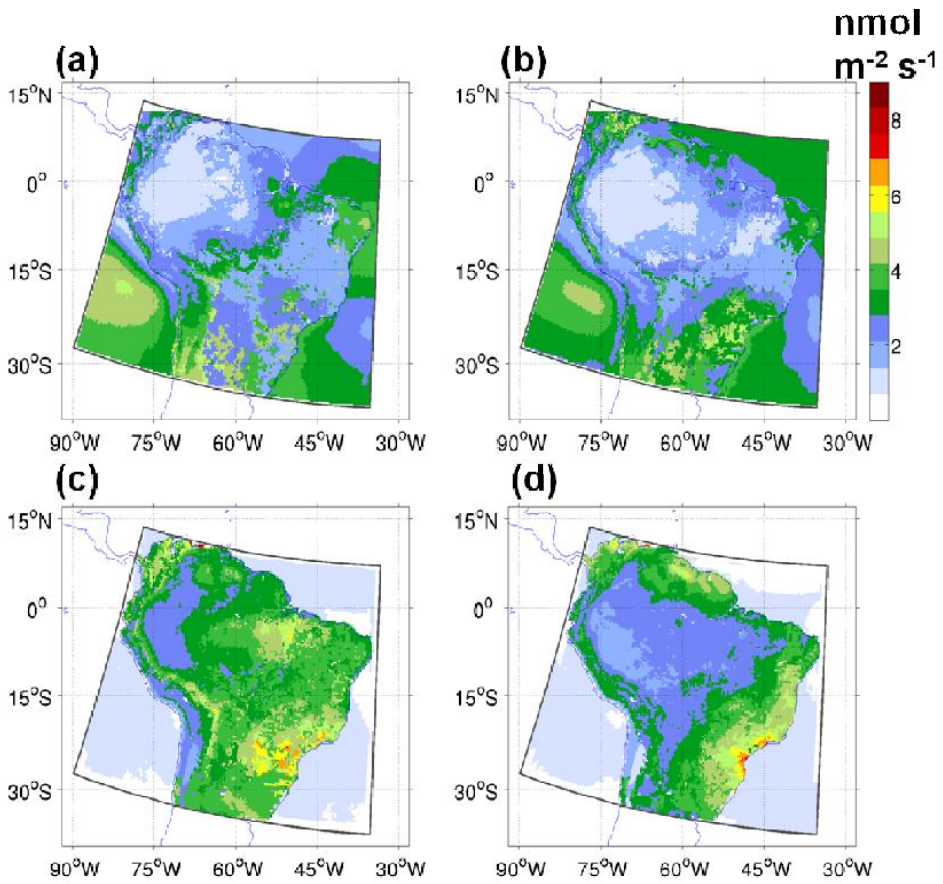


Figure 18. Average O_3 dry deposition flux (nmol m^{-2} s^{-1}) as simulated on the 35 km resolution domain (dark gray outline) by the CCATT-BRAMS model for (a) November 2008 and (b) May 2009 and by the WRF-Chem model for (c) November 2008 and (d) May 2009.

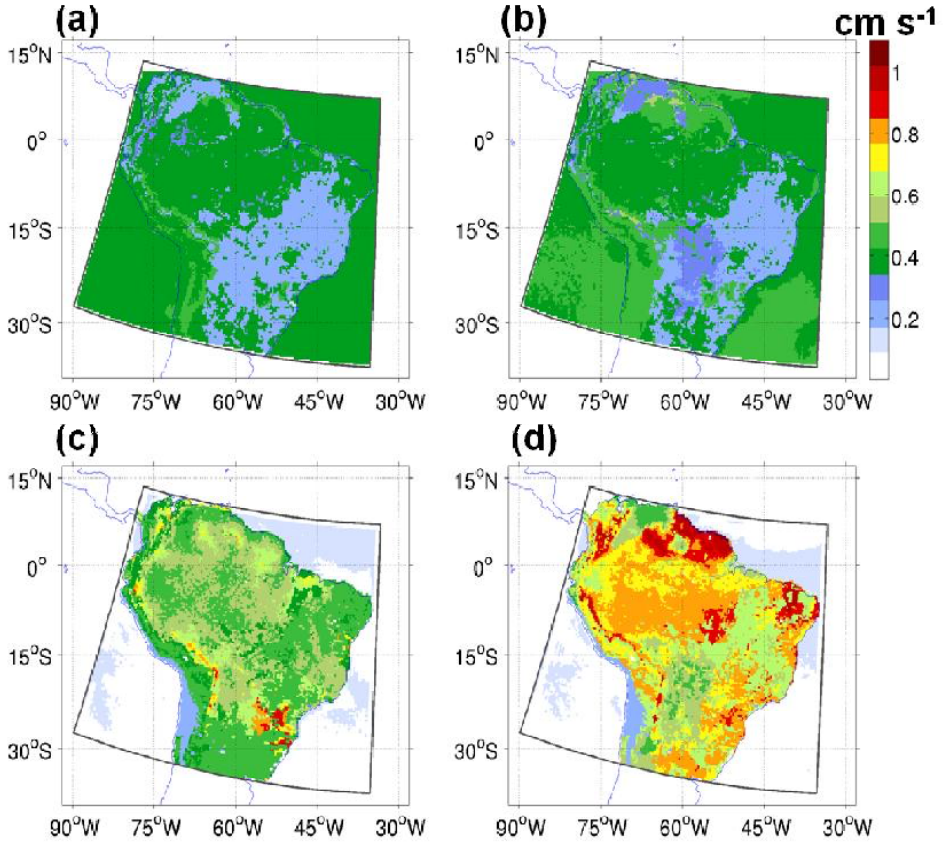


Figure 19. Same as Fig. 18, but daytime (11:00-21:00 UTC) median deposition velocity (cm s^{-1}).

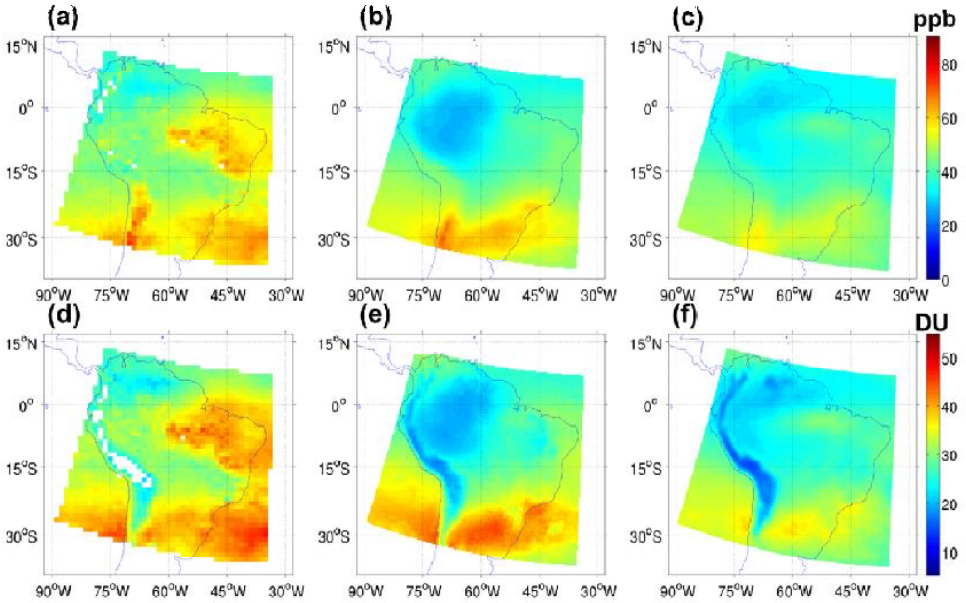


Figure 20. Mean tropospheric O_3 (ppb) on the 35 km domain from (a) OMI/MLS, (b) CCATT-BRAMS and (c) WRF-Chem and total tropospheric column O_3 (Dobson units) from (d) OMI/MLS, (e) CCATT-BRAMS and (f) WRF-Chem for November 2008.

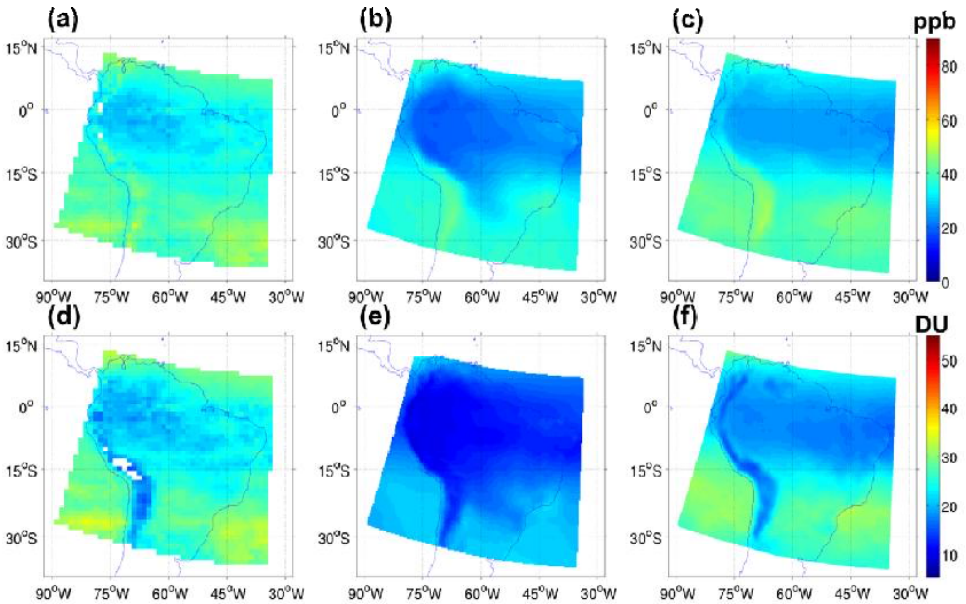
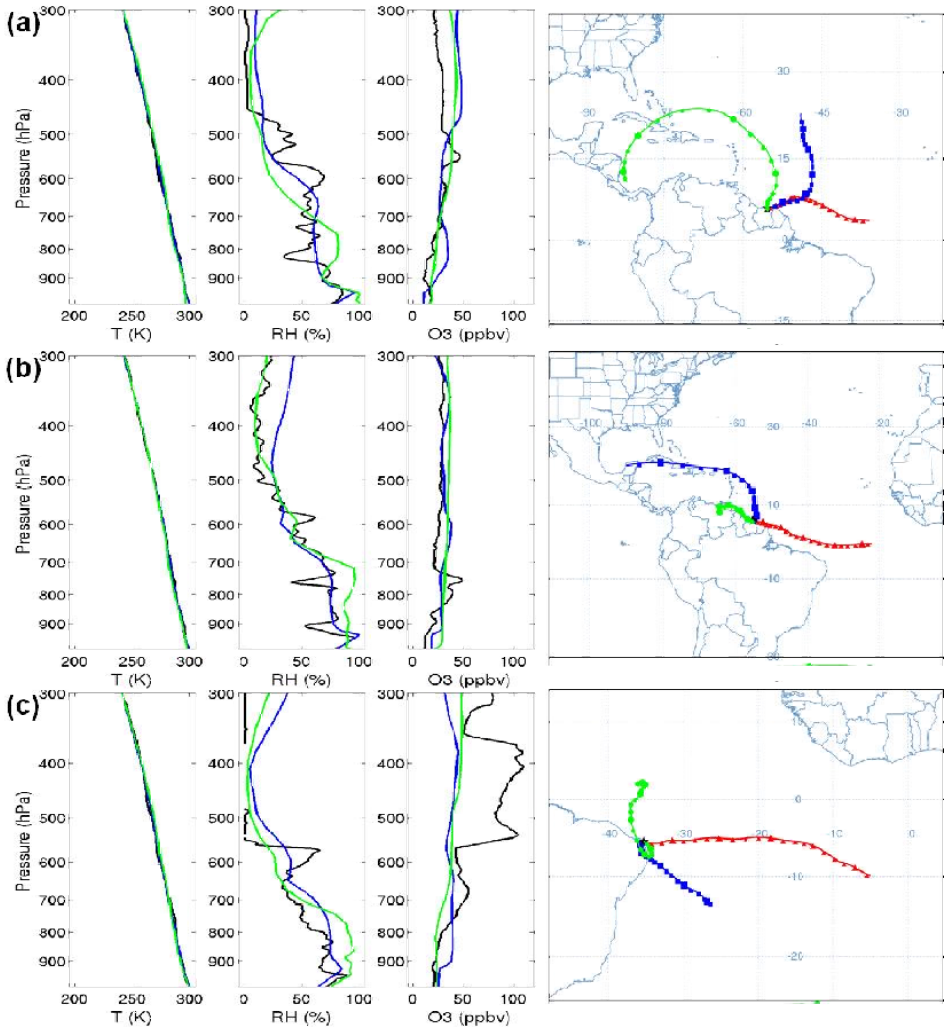


Figure 21. Same as Fig. 20, but for May 2009.


(a)
(b)
(c)
Pressure (hPa)
T (K)
RH (%)
O3 (ppbv)

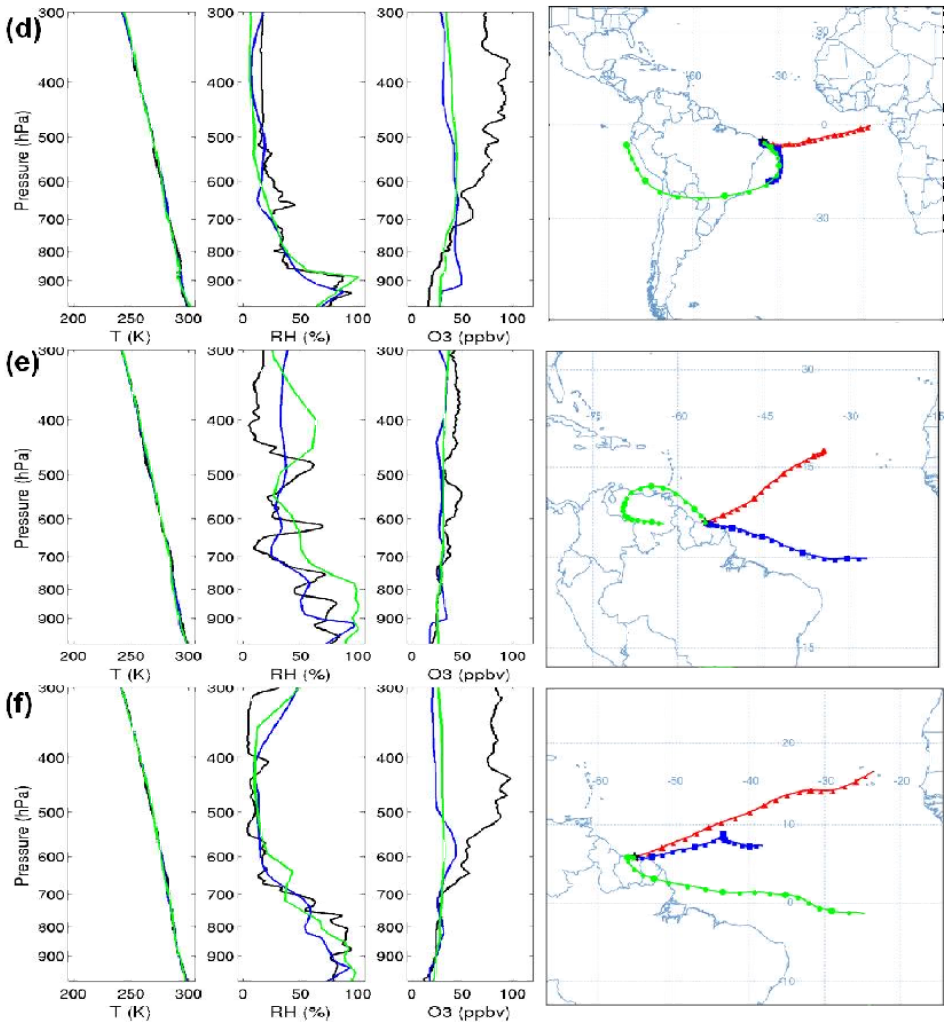


Figure 22. Vertical profiles of potential temperature, relative humidity, and O_3 from SHADOZ soundings (black), CCATT-BRAMS (blue) and WRF-Chem (green) and HYSPLIT back trajectories at 13:00 UTC at 1500 m (~850 hPa, red), 6000 m (~470 hPa, blue) and 9000 m (~310 hPa, green) for: Paramaribo on (a) 6 November and (b) 25 November 2008, Natal on (c) 7 November and (d) November 19 2008 and Paramaribo on (e) 4 May and (f) 11 May 2009.

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It is interesting to compare BARCA data to observations from the NASA Amazon Boundary Layer Experiments ABLE campaigns (ABLE-2A and -2B), which took place during the dry season of 1985 and wet-to-dry transition of 1987. Andreae et al. (2012) showed that CO mixing ratios were about 10 ppb higher during ABLE-2B than in BARCA B everywhere except the southern region, reflecting the global trend towards decreasing CO emissions since the 1980s, particularly in the Northern Hemisphere. The CO comparison also showed a similar enhancement of 10–20 ppb in the lowest 1 km above the surface, attributed to diffuse biogenic sources, and also indicated that the much higher enhancements during the dry season in BARCA A must be due to anthropogenic or biomass burning inputs. The O3 comparison is expected to yield information in long-term trends in O_3 production in the Amazon Basin, as well as the relative importance of biogenic, urban and fire sources.

Página 24: [2] Excluído **mbela** **12/10/2014 16:07:00**

Section 1.3 reviews previous observational and remote sensing studies of O_3 distributions and seasonality in the Amazon. Section 2 describes

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, as well as the setup of the CCATT-BRAMS and WRF-Chem simulations

Página 28: [4] Excluído **mbela** **12/10/2014 16:06:00**

Previous studies of O_3 in the Amazon

Analyses of satellite, aircraft and ground-based observations of O_3 over Amazônia since the 1980s have demonstrated the influence of long-range transport of African biomass burning and Northern Hemisphere inputs, local fire sources, NO soil and biogenic VOC emissions, and convective transport on spatial and seasonal variability in O_3. In particular, data from the ABLE-2B aircraft and ground campaign during the 1987 wet-to-dry transition season offers the opportunity to compare the regional O_3 distribution across decades.

Several studies of satellite data have reported a seasonal O_3 maximum in the tropical Southern Hemisphere, largely associated with long-range transport of African fire emissions or lightning NOx sources. Fishman and Larsen (1987) combined data from 1979-1980 from the Total Ozone

Mapping Spectrometer (TOMS) and the Stratospheric Aerosol and Gas Experiment (SAGE) instruments to construct a climatology of tropospheric O_3 from 15°N to 15°S. They attributed the most elevated O_3 from 60°W to 60°E to biomass burning sources. Thompson et al. (1996) integrated TOMS satellite O_3 data with observations from the Transport and Atmospheric Chemistry near the Equator-Atlantic (TRACE-A) and the southern African Fire-Atmosphere Research Initiative (SAFARI) 1992 experiments. They showed a seasonal maximum in tropospheric O_3 in the south Atlantic, with the highest values (> 90 ppb) between 0-25°S. Back and forward trajectories attributed this elevated O_3 to transport of O_3 from fires in southern Africa by mid-level easterlies or recirculations, with little South American contribution. In Brazil, O_3 was seen to be lofted by deep convective transport, and then transported by high-level westerlies. However, from 0-10°S most of the O_3 was from Africa, since there was a delay of 1-2 months from peak African biomass burning to the O_3 maximum at the coastal site of Natal. O_3 production from the surface to 4 km was estimated to be 15 ppb O_3 per day, with a lower but nonzero rate in the upper troposphere. Using remote sensing observations of fire and lightning flash counts and NO_2, Edwards et al. (2003) identified an early-year tropical Atlantic tropospheric O_3 maximum in January 2001 with two peaks, the first in the lower troposphere from northern hemisphere fires and the second in the southern tropical Atlantic mid-troposphere from lightning NO_x.

For the Amazon region, observations of O_3 and other trace gases were made in several aircraft and ground-based campaigns. These observations identified background (absent of urban and fire influence) O_3 values of around 20 ppb originating from soil NO emissions, decreasing to very low values (~ 5 ppb) at night due to O_3 deposition to the forest. However, nighttime values can increased due to convective downdrafts, and free troposphere enhancements from biomass burning sources are seen.

The earliest O_3 measurements over the Amazon Basin were made during aircraft campaigns in the dry seasons 1979 and 1980 (Crutzen et al., 1985). Mixing ratios of 20-30 ppb and 40-50 ppb were observed in the boundary layer and the free troposphere, respectively, and elevated O_3 was attributed to photochemical reactions and biomass burning. During the dry season (July-August 1985), the Amazon Boundary Layer Experiment (ABLE-2A) integrated aircraft, ground-based and satellite observations to study the processes affecting the chemical composition in mixed layer over Amazonia (Harriss et al., 1988). Jacob and Wofsy (1988) used a photochemical model

of the Amazonian boundary layer to study the diurnal cycle of isoprene, NO_y and O_3 during ABLE-2A. They found that photochemical production spurred by NO emissions from soils increased daytime O_3 to about 20 ppb. However, at night, dry deposition to the forest caused O_3 to drop below 5 ppb. Model results were consistent with the NO values of 25-60 ppt observed in the lower boundary layer over central Amazonia (Torres and Buchan, 1988). Isoprene emissions were found to have little effect on O_3 levels, as the oxidation of CO would produce sufficient HO_x to generate 20 ppb of O_3. However, O_3 production in the model was highly sensitive to NO_x emissions, and downward transport from the free troposphere became the dominant source of O_3 in the PBL when NO emissions were decreased below the average value of 44 ± 14 µg N m^{-2} h^{-1} NO measured by Kaplan et al. (1988). Lidar observations during ABLE-2A showed highly variable O_3 levels, with some small regions with up to 30-40 ppb, attributed to variable NO flux from the canopy (Browell et al., 1988). ABLE-2B was conducted during the wet-to-dry transition season (April-May 1987) (Harriss et al., 1990). Periodic inputs from the Northern Hemisphere were found to be a pollution source over Amazonia, and dry deposition in the region provides a significant sink in the global O_3 budget.

Aircraft measurements from TRACE-A over the South Atlantic in the 1992 dry season attributed high O_3 (> 100 ppb) in the upper troposphere to photochemical production from convectively lofted Brazilian biomass burning emissions. Elevated O_3 (> 75 ppb) originated in lower altitude (< 6 km) plumes from African fires (Browell et al., 1996). During the Smoke, Clouds, and Radiation-Brazil (SCAR-B) campaign (Kaufman et al., 1998), elevated ozone was observed in ozone soundings, launched at Cuiabá from 16 August - 10 September 1995. Elevated ozone was attributed to both local biomass burning pollution and recirculation of urban emissions from SE Brazil. Aerosol backscatter coefficient measurements aboard the ER-2 aircraft during two flights between Cuiabá and Vilhena confirmed the co-occurrence of layers of elevated O_3 with smoke (Longo et al., 1999).

As part of ABLE-2, near-continuous surface O_3 measurements (1.5 m above the surface) showed daytime maximum of 5.7 and 3.7 ppb in a clearing and forest, respectively, and measurements in a tower in a clearing showed an increasing gradient of O_3 with height, up to 6.9 ppb at 15 m above the surface (Kirchhoff et al., 1990). Furthermore, 20 ozonesondes launched in the clearing showed typical mixing ratios of 40 ppb from 500–300 hPa, with values about 10 ppb lower in the wet than dry season.

Observations of O_3, NO_x and CO at a pasture site in the state of Rondônia and forest sites in the states of Pará and Amazonas showed elevated (3x) O_3 and NO_2 levels in the dry-to-wet transition season at the pasture site due to the influence of biomass burning. This was shown by correlations with black carbon and aerosol number concentrations at the surface. On the other hand, NO levels were much lower in the dry-to-wet transition season due to the conversion of NO_2 to NO favored by elevated levels of VOCs, O_3, and radicals, and by higher temperatures. In addition, nighttime ozone was increased in the wet season by transport of ozone-rich cold air from the mid- and upper-troposphere by convective downdrafts, as shown by an anti-correlation of O_3 with equivalent potential temperature (Cordova et al., 2003).

During the LBA-CLAIRE-98 experiment (Andreae et al., 2001) in March 1998, elevated levels of trace gases and biomass burning aerosol were observed at high altitudes (> 9 km) during a flight off the coast of Suriname. Model simulations of CO transport later confirmed the measurements to be the outflow of a deep convective system which had transported biomass burning emissions originating from the northern Amazon (Freitas et al., 2000; Andreae et al., 2001; Gevaerd et al., 2006). During the same experiment, trace gases and CCN spectra were also measured continuously at a ground station in Balbina, near Manaus (Zhou et al., 2002). During the experiment, air masses with origin over undisturbed rainforest and little anthropogenic influence, were sampled at Balbina, yielding O_3 values always less than 20 ppb. Photochemical production of O_3 of up to 15 ppb h^{-1} was detected via aircraft transects in the Manaus urban plumes (Kuhn et al. 2010). Most of the VOC reactivity was provided by isoprene emissions from the surrounding rainforest, and NO_x emissions suppressed O_3 production close to urban sources, but stimulated it downwind.

Observations at a pasture site in Rondônia in January–February 1999 during the LBA Wet Season Atmospheric Mesoscale Campaign (WETAMC) showed that downwardconvective transport events increased nighttime surface O_3 up to 30 ppb, compared to a background of 3–5 ppb (Betts et al., 2002). During the LBA-EUSTACH experiments, CCN and trace gases (including O_3, NO_x and VOCs) were measured at forest and pasture sites in Rondônia in the wet-to-dry (27 April–29 May 1999) and dry-to-wet (12 September–27 October 1999) seasons (Andreae et al., 2002; Rummel et al., 2007). The observations showed VOC (isoprene, formaldehyde,

acetaldehyde, acetic and formic acid) concentrations 4-5 times higher in the dry than wet-to-dry transition season as a result of both enhanced biogenic emissions and photochemical decomposition due to increased solar radiation. In addition, VOC and O_3 concentrations peaked in the afternoon (around 15:00 LT) in both seasons and at both sites. Peak O_3 rose from ca. 15 to almost 60 ppb from the wet to dry-to-wet transition season. During the Amazonian Aerosol Characterization Experiment (AMAZE-08), O_3 was measured at the TT34 tower site from 14 February–14 March 2008 (Martin et al., 2010), with observed values of 1-20 ppb (Ebbon et al., 2011). The Tropical Composition, Clouds and Climate Coupling (TC4) experiment, based in Costa Rica in July and August of 2007, involved coordinated flights, including one over the Colombian Amazon, with the NASA ER-2, WB-57 and DC-8 aircraft to study convective processes in the ITCZ region (Toon et al., 2010). Using low ozone as an indicator of convective transport of boundary layer air, a maximum convective outflow height of 10-11 km was estimated (Avery et al., 2010). A flight in the boundary layer over the Columbian Amazon on August 8, 2007 measured O_3 of 10-20 ppb (Jimenez, personal communication, November 12, 2012).

Thus, satellite observations enable the attribution of tropical O_3 maxima to biomass burning and lightning NO_x sources, while ground-based measurements allow the identification of key surface processes in the Amazon Basin affecting O_3 amounts. These processes include O_3 production from soil NO_x emissions and removal via dry deposition to the forest canopy. Aircraft campaigns complete the suite of observations, allowing the examination of convective lofting of surface emissions, with biomass burning emissions of particular importance on the regional scale.

Página 32: [5] Movido para a página 28 (Mover #10) mbela
12/10/2014 15:57:00

Simulations of BARCA A and B were conducted with the Chemistry Coupled Aerosol-Tracer Transport model to the Brazilian developments on the Regional Atmospheric Modeling System (CCATT-BRAMS; Longo et al., 2013; Freitas et al., 2009) and Weather Research and Forecasting with Chemistry (WRF-Chem; Grell et al., 2005) coupled chemistry and meteorology models. The model physics and chemistry options that were used are listed in Table 1. Both models used a two-way nested grid configuration, with a 140 km grid covering Africa and South America (southwest corner: 60°S, 100°W, northeast corner: 20°N, 50°W), to encompass the cross-Atlantic transport of biomass burning emissions from Africa, and a 35-km resolution grid

covering most of South America (southwest corner: 35°S 85°W, northeast corner: 15°N, 30°W), as depicted in Fig. 3.

The simulations were initialized on 1 October 2008 00:00 UTC and 1 April 2009 00:00 UTC for BARCA A and B, respectively. Boundary conditions and analysis nudging on the outer domain were given by the NCEP GFS analysis (http://rda.ucar.edu/datasets/ds083.2/) with a 6 hourly time resolution and 1° □ 1° spatial resolution. Chemistry initial and boundary conditions were provided by 6 hourly analyses from the Model of Atmospheric Chemistry at Large Scale (Modélisation de la Chimie Atmosphérique Grande Echelle, MOCAGE) global model (Peuch et al., 1999) with a T42 (~ 2.8°) spatial resolution. Sea surface temperature was provided by the NOAA Optimum Interpolation (OI) Sea Surface Temperature (SST) V2 (available at http://www.esrl.noaa.gov/psd/data/gridded/data.noaa.oisst.v2.html) with 1° □ 1° spatial resolution. Soil moisture was initialized with the TRMM-based soil moisture operational product (GPNR) developed by Gevaerd and Freitas (2006).

The PBL parameterization in CCATT-BRAMS is based on Mellor and Yamada (1982), while in WRF-Chem the Mellor-Yamada-Janjic (MYJ; Janjić, 1994) scheme was used. In CCATT-BRAMS, shallow and deep convection are parameterized based on the mass-flux approach of Grell and Dévényi (2002). CCATT-BRAMS also uses the Turbulent Kinetic Energy (TKE) from the Planetary Boundary Layer (PBL) scheme to determine if convection will be triggered within a grid cell. In WRF-Chem the Grell 3D (G3) scheme was used, which includes subsidence spreading of convective outflow into neighboring grid cells. The Noah land surface model (Koren et al., 1999) was used in WRF-Chem and the Land Ecosystem–Atmosphere Feedback model v.2 (LEAF-2; Walko et al., 2000) was utilized in CCATT-BRAMS. Land use was provided by the United States Geological Survey (USGS) global 1 km vegetation dataset, updated with a land cover map for the Brazilian Legal Amazon Region for use in meteorological models (PROVEG) (Sestini et al., 2003). PROVEG is based on the Thematic Mapper (TM) Landsat images with spatial resolution of 90 m □ 90 m from the year 2000 and deforestation data from the Amazon Deforestation Monitoring Program (PRODES) for the year 1997. For WRF-Chem, albedo and greenness fraction were calculated offline using the updated vegetation dataset, Moderate Resolution Imaging Spectroradiometer (MODIS) Normalized Difference Vegetation Index (NDVI) data from the year 2002-2002 and vegetation parameters from the LEAF-2 land surface model as implemented in CCATT-BRAMS.

Emissions were generated with PREP-CHEM-SRC (Freitas et al., 2011) Version 1.2. Fire emissions were estimated from GOES, AVHRR and MODIS fire count data using the Brazilian Biomass Burning Emission Model (3BEM; Longo et al., 2009).

Anthropogenic emissions were estimated from the RETRO, GOCART and EDGAR v4.0 global databases updated with South American inventories (Alonso et al., 2010). Biogenic emissions were provided by a monthly climatology for the year 2000 produced with the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006). In WRF-Chem, the same Gaussian diurnal cycle with peak at 15:00 UTC (11:00 LT) is applied to both anthropogenic and biogenic emissions, while in CCATT-BRAMS the diurnal cycle of biogenic emissions follows the solar radiation cycle. In both models, the biomass burning daily cycle peaks at 18:00 UTC (15:00 LT). In both CCATT-BRAMS and WRF-Chem, the Regional Atmospheric Chemistry Mechanism (RACM) was used (Stockwell et al., 1997). In WRF-Chem, the Goddard Chemistry Aerosol Radiation and Transport (GOCART; Chin et al., 2002) aerosol scheme was used with aerosol direct radiative effects. CCATT-BRAMS has a smoke aerosol scheme with intensive optical properties (extinction efficiency, single scattering albedo and asymmetry parameter) calculated in an offline Mie code based on observations of climatological size distribution and complex refractive index from AERONET sites in the southern Amazon (Rosario et al., 2011, 2013). CCATT-BRAMS includes scavenging of soluble species in the convective scheme following Berge (1993), as described in Freitas et al. (2005), where the wet removal rates are a function of the precipitation rate, liquid water content and precipitable water. In the cloud microphysics scheme the wet deposition follows Barth et al. (2001), whereby low solubility species partition into the liquid phase according to Henry's Law and high solubility species by diffusion-limited mass transfer. In WRF-Chem, at the convective-parameterizing scale, a constant fraction of gas and aerosol species in convective updrafts are removed (complete removal for sulfur dioxide – SO_2, sulfate – H_2SO_4, ammonium – NH_3, nitric acid – HNO_3 and sea salt; no removal for hydrophobic organic (OC) and black carbon (BC) and dimethyl sulfide (DMS); and 50% removal for all other aerosol species). On the other hand, no wet scavenging is included for cloud water and precipitation resolved by the microphysics scheme, because this option is not currently available in WRF-Chem for the RACM chemical mechanism.

The CCATT-BRAMS simulations also employ a lightning NO_x parameterization based on convective cloud top height (Stockwell et al., 1999). In WRF-Chem, wet deposition and lightning production of NO_x were not considered, because these parameterizations have not yet been evaluated for the Amazon region. Uncertainties remain about the scavenging efficiencies of soluble species by deep convective storms. Simulations of an idealized thunderstorm by several cloud-resolving models yielded varying results for CH_2O, H_2O_2 and HNO_3 in convective outflow due to differing microphysics and assumptions about retention of chemical species during cloud drop freezing (Barth et

al., 2007). In the tropics, over continents, lightning production is comparable to other sources of NO_x, including biomass burning and soil release, and it is the primary source over oceans (Bond et al. 2002). Since lightning NO_x production peaks in the upper troposphere, it could be an important contributor to ozone production. The roles of wet deposition and lightning NO_x production will be more closely examined in future modeling studies of tropospheric chemistry in the Amazon.

For model results evaluation, the mean vertical O_3 profiles for observations, CCATT-BRAMS and WRF-Chem were calculated for the regions to the west, north, south, east, and around Manaus. Horizontal flight legs were excluded from analysis to eliminate the influence of plumes in the boundary layer. To calculate the mean simulated profiles, the four grid points closest in latitude and longitude to each observation were determined at the two model hours that bracket the observations. At each of these grid points and hours, vertical profiles were extracted from the model output and then linearly interpolated to the observed GPS height. The four points from each time were averaged, weighting by the inverse distance to the observed longitude and latitude. Finally, the prior and posterior hour values were averaged with appropriate weights. Thus, 16 model points were used with spatial and temporal weights to obtain each model value for comparison to observations. The observed and model time series were then separated into five regions to the west, north, east, and south of Manaus, and in the region of Manaus itself. The mean value and standard deviation were calculated for each region and 500 m vertical bin.

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Mean precipitation during the dry-to-wet (November 2008) and wet-to-dry (May 2009) transition seasons was calculated for the TRMM 3B43 data and the CCATT-BRAMS and WRF-Chem models for three regions: the Amazon (15°S – 10°N, 50°W – 80°W), northeast Brazil (15°S – 0°N, 35°W – 50°W), and southeast South America (15°S – 35°S, 35°W – 65°W). The values are listed in Table 2. The mean precipitation on the 35-km resolution domain for the two months is shown in Figs. 3 and 4, respectively, as well as the delineations of the subregion boxes. The signs of NE-SE differences are correctly modeled by both models during both seasons, i.e., the NE is drier than the SE during November, and vice-versa during May. For the Amazon, CCATT-BRAMS slightly underestimates the precipitation rates in both seasons, but the rate in WRF-Chem is about twice that of TRMM 3B43. The models were also evaluated against TRMM 3B42 3-hourly precipitation rates at the 78 surface station locations in the Amazon (see Table 3). Both models had a positive bias in both seasons, but WRF-Chem had a higher bias and RMSE than CCATT-BRAMS.

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, although the mean precipitation rates are slightly lower (CCATT-BRAMS) and substantially higher (WRF-Chem) than the TRMM retrievals in the Amazon region.

Página 35: [8] Excluído **mbela** **12/10/2014 15:49:00**

Peak shortwave radiation is slightly overestimated by both models, which may be related to low cloudiness (convection is triggering too early) or AOD (too much aerosol wet removal). This will increase O_3 production from photolysis, as well as increase surface temperature and evaporation. Although biogenic emissions are not coupled with meteorology in these simulations, this may increase biogenic emissions in future studies that include online biogenic emissions. WRF-Chem predicts a nearly constant Bowen ratio at forest and pasture sites. This indicates that the Noah land surface model is not properly representing the impact of conversion of forest to pasture and the resulting increase in sensible heat flux.

In the dry-to-wet transition season, for both CCATT-BRAMS and WRF-Chem, the mean daily cycle of surface incident shortwave radiation calculated for the Manaus AERONET site for October–November 2008, falls within one standard deviation of the mean AERONET observations (Fig. 6), but is closer to the upper limit, possibly due to underestimated cloudiness or AOD in the models. For the forest and pasture sites, both models represent the daily cycles of incident shortwave and ingoing and outgoing longwave radiation, although incident shortwave is slightly overestimated (by 50 100 W m^{-2}) at peak (Fig. 7). During the wet-to-dry transition season, both models overestimate peak incident shortwave radiation by about 100 W m^{-2} (Fig. 8), suggesting that they underestimate cloudiness.Both models represent the daily cycles of incident shortwave and ingoing and outgoing longwave radiation, although incident shortwave is slightly overestimated (by 50-100 W m^{-2}) at peak. For both models, CCATT-BRAMS and WRF-Chem, the mean daily cycle of surface incident shortwave radiation calculated for the Manaus AERONET site for Oct.-Nov. 2008, falls within one standard deviation of the mean AERONET observations (Fig. 7), but is closer to the upper limit, possibly due to underestimated cloudiness or AOD in the models.

Página 35: [9] Excluído **mbela** **12/10/2014 15:43:00**

peak latent heat flux at 13:00 LT is higher at the forest site than at the pasture site (460 W m^{-2} vs. 268 W m^{-2}) whereas the sensible heat flux shows an opposite difference (180 vs. 215 W m^{-2}), due to lower evapotranspiration and higher surface temperatures in the pasture. As a result, the

Página 35: [10] Movido para a página 35 (Mover #7) **mbela**
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Both models represent the daily cycles of incident shortwave and ingoing and outgoing longwave radiation, although incident shortwave is slightly overestimated (by 50-100 W m^{-2}) at peak. For both models, CCATT-BRAMS and WRF-Chem, the mean daily cycle of surface incident shortwave radiation calculated for the Manaus AERONET site for Oct.-Nov. 2008, falls within one standard deviation of the mean AERONET observations (Fig. 7), but is closer to the upper limit, possibly due to underestimated cloudiness or AOD in the models.

Página 35: [11] Excluído **mbela** **12/10/2014 19:04:00**

as for the dry-to-wet transition, peak latent heat flux at 13:00 LT is higher at the forest site than at the pasture site (401 W m^{-2} vs. 324 W m^{-2}). However, the sensible heat flux is also higher at the pasture site (119 W m^{-2} vs. 168 W m^{-2}) and

Página 35: [12] Excluído **mbela** **12/10/2014 15:43:00**

Mean vertical profiles at Manaus from radiosoundings, CCATT-BRAMS and WRF-Chem for October - November 2008 at 0, 12 and 18Z and April - May 2009 at 0 and 12Z are shown in Figs. 9 and 10. For BARCA A, while the temperature profile is well represented by the models, the dew point temperature in CCATT-BRAMS is approximately 10 K too high above 500 hPa and 5 K too low below 500 hPa. The wind speed is overestimated by both models above 500 hPa and underestimated below 500 hPa. For BARCA B, dew point temperature is about 5 K too high in CCATT-BRAMS above 500 hPa. Wind speed is about 2 m s^{-1} too low above 600 hPa in both models.
The models were evaluated against data from 26 METAR (airports) and 52 Synop (INPE) surface meteorological stations, whose locations are depicted in Fig. 11. Values of Root Mean Squared Error (RMSE) and bias for various meteorological parameters for CCATT-BRAMS and WRF-Chem simulations for BARCA A (October - November 2008) and BARCA B (April - May 2009) are shown in Table 3.

Página 35: [13] Excluído **mbela** **12/10/2014 15:40:00**

surface pressure is underestimated by 1 - 2 hPa. Wind speed is underestimated by CCATT-BRAMS and overestimated by WRF-Chem by 0.1 - 0.6 m s^{-1}, and

Página 35: [14] Movido para a página 34 (Mover #8) **mbela**
12/10/2014 15:46:00

Now we summarize the key findings of the model-data meteorological comparison and their implications for the chemistry simulations. The models capture the seasonal spatial distribution of precipitation over northern South America, although the mean

precipitation rates are slightly lower (CCATT-BRAMS) and substantially higher (WRF-Chem) than the TRMM retrievals in the Amazon region. This may indicate errors in the strength and vertical distribution of convective transport and the amount of convective wet removal. Peak shortwave radiation is slightly overestimated by both models, which may be related to low cloudiness (convection is triggering too early) or AOD (too much aerosol wet removal). This will increase O_3 production from photolysis, as well as increase surface temperature and evaporation. Although biogenic emissions are not coupled with meteorology in these simulations, this may increase biogenic emissions in future studies that include online biogenic emissions. WRF-Chem predicts a nearly constant Bowen ratio at forest and pasture sites. This indicates that the Noah land surface model is not properly representing the impact of conversion of forest to pasture and the resulting increase in sensible heat flux.

Página 35: [15] Movido para a página 35 (Mover #6) **mbela**
12/10/2014 15:42:00

The models generally show good agreement with soundings, but excess moisture in CCATT-BRAMS above 500 hPa may stimulate excess O_3 production.

Página 39: [16] Movido para a página 39 (Mover #3) **mbela**
12/10/2014 15:22:00

The mean tropospheric and total tropospheric column O_3 from OMI/MLS, CCATT-BRAMS and WRF-Chem for November 2008 and May 2009 are shown in Figs. 15 and 16, respectively. The models significantly underestimate the total columns from satellite and middle altitudes from BARCA. For both BARCA A and B, the models represent the pattern of lower O_3 over the Amazon and higher values over northeast Brazil (BARCA A only) and at 30°S, although the values are strongly underestimated. In November 2008, OMI/MLS mean tropospheric O_3 concentrations show an inflow of elevated O_3 (mean ca. 55 ppb, total 40-45 DU) on the northeast Brazilian coast due to cross-Atlantic transport from biomass burning in southern and sub-Saharan Africa. Additionally, a band of elevated O_3 (mean 55-60 ppb, total 35-40 DU) passes over the South American continent at around 30°S, also from cross-Atlantic transport. During this month, Northern Hemisphere O_3 levels to the north of South America are relatively low (mean 35-40 ppb, total 25-30 DU). On the other hand, the tropospheric ozone distribution in May 2009 (Fig. 16) is characterized by a band of low ozone extending over the Amazon Basin and northeast Brazil between 10°S and 10°N (mean 25-35 ppb, total 20-25 DU). In addition, lightly elevated values at around 30°S,

primarily over the oceans (40-55 ppb, 30-35 DU) and higher ozone in the Northern Hemisphere (mean 50-55 ppb, total 35-40 DU north of 10°N). Both models capture the overall distribution (inflow in NE Brazil in Nov. 2008, lower values over the Amazon Basin, elevated at 30°S) but values are underestimated relative to OMI/MLS.

Página 39: [17] Movido para a página 36 (Mover #4) mbela 12/10/2014 15:29:00

However, the BARCA observations are generally lower than the models in the boundary layer, indicating that the satellites appear here to be dominated by the middle troposphere and long-range transport. An example of observed and simulated O_3 during the flight legs between Manaus and Belém in BARCA A and B is shown in Fig. 17. While the models capture the pattern of increasing O_3 values with height, the models underestimate elevated O_3 values from 2.5-4.5 km, and overestimate low values near the surface (1-1.5 km). The models also do not reproduce the variability in the high values, likely due to the aircraft intersection of biomass burning plumes. This is expected given the coarse horizontal grid resolution. Thus, mean profiles are analyzed in order to study differences among the regions and seasons and to assess the models' abilities to capture the impacts of such small-scale processes on regional O_3 distributions.

The mean vertical O_3 profiles for observations, CCATT-BRAMS and WRF-Chem for the regions to the west, north, south, east and around Manaus are shown for BARCA A and B in Figs. 18 and 20, respectively, and NO profiles corresponding to the aircraft tracks are depicted in Figs. 19 and 21, respectively. Mean profiles from longitudinal surveys over Amazônia of O_3 during ABLE-2A (Browell et al., 1988) and ABLE-2B (Harriss et al., 1990) and NO during ABLE-2A (Torres and Buchan, 1988) are included for comparison. In BARCA B, O_3 values were at or near background values in all regions, ranging from 8 - 15 ppb at the surface to 2 - 15 ppb at 4-4.5 km, and the models are generally within 5-10 ppb of the observations. During BARCA A, while the W region still had low O_3 values (5 ppb at the surface to 20 ppb at 4-4.5 km), the N, S and M regions ranged from 15-20 ppb at the surface to 30-35 ppb at 4-4.5 km, and the E region presented the most elevated values, from 25-55 ppb. ABLE-2A O_3 profiles are similar in all regions, ranging from 15-20 ppb near the surface to 30-40 ppb from 4-6 km, so that the BARCA values are higher in the fire-influenced east and south regions, lower in

the north and west regions, and very similar around Manaus. The profiles from ABLE-2B are within one standard deviation of the BARCA B measurements, except for the north region, where they are lower (5-15 ppb). These results suggest an increasing influence of fire emissions to the east and south of Manaus, but that O_3 in clean regions has not changed much.

Both models generally overestimate O_3 from 1-2 km and underestimate O_3 from 3-4.5 km. As seen in the CO results shown in Andreae et al. (2012), the model profiles have steeper slopes than the observations, except in the polluted south, possibly due to excessive vertical mixing of precursors. In addition, the models may be missing sources of O_3 and/or precursors at 3-4.5 km in the model inflow boundary conditions. In general the models overestimate O_3 in the PBL compared to aircraft measurements, but underestimate the total column values relative to the OMI/MLS satellite product. This suggests that the total column values in Amazonia are dominated by global pollution from Africa, rather than local O_3 production from biomass burning.

4.3.2

Página 39: [18] Movido para a página 40 (Mover #2) mbela 12/10/2014 15:19:00

The excess O_3 in the PBL in the models could be due to either a low deposition sink, as O_3 dry deposition velocities in the models are about half of observed values, or excessive model sensitivity to NO_x emissions, or both. Two additional simulations were conducted with WRF-Chem to evaluate the model sensitivity to these processes: (1) doubling the calculated deposition velocity for O_3 only (2DEPVEL) and (2) halving the NO_x surface emission rates (0.5ENOx). The O_3 profiles corresponding to BARCA flights for these two simulations are also included in Figs. 18 and 20. The corresponding NO profiles from all model simulations as well as a mean profile over Amazônia from ABLE-2A are depicted in Figs. 19 and 21. The 0.5ENOx simulation reduces O_3 more than 2DEPVEL throughout the entire profile. In the dry-to-wet transition, 2DEPVEL reduces O_3 in the lower PBL by about 25%, while 0.5ENOx decreases O_3 by around 40%, and in the wet-to-dry-transition the reductions are about 10% and 30%, respectively. In general the 0.5ENOx O_3 profiles are lower than observed in the first 500 m above the surface, but they provide the best representation of the data for the north and west regions in the dry-to-wet transition. They also provide a similarly good fit as 2DEPVEL for the east, Manaus and south regions, while in the wet-to-dry transition 0.5ENOx is closer to the observed value from 0-500 m in all regions except the north. During BARCA A, NO in all WRF-Chem simulations in the north, west, and Manaus

regions is 10-15 ppt from 0-500 m above the surface, increasing to a maximum of 20-50 ppt at 2 km agl, and is generally lower than the ABLE-2A observations in the PBL. In the east and south, where biomass burning influence was seen, NO in 0-500 m agl increased from 20-50 ppt in the base simulation to 35-60 ppt in 2DEPVEL due to decreased O_3 and conversion of NO to NO_2, and was generally within one standard deviation of the ABLE-2A measurements in the PBL. In BARCA B, NO simulated by WRF-Chem is very low, 5-10 ppt in the entire profile, except for the west region, where a mean NO of 30 ppt is seen from 0-500 m a.g.l. This is again due to very low O_3, and for the Manaus region, where anthropogenic NO_x sources may have contributed to NO values of 20 ppt. These results suggest that adjustment of dry deposition parameterizations are needed to increase O_3 deposition velocities by about a factor of two in agreement with ground observations. Future research will compare simulated NO_x fields with observations from more recent field campaigns, as the results of these simulations also suggest that O_3 in WRF-Chem is very sensitive to NO_x emissions.

Página 70: [19] Excluído **mbela** **12/10/2014 14:53:00**

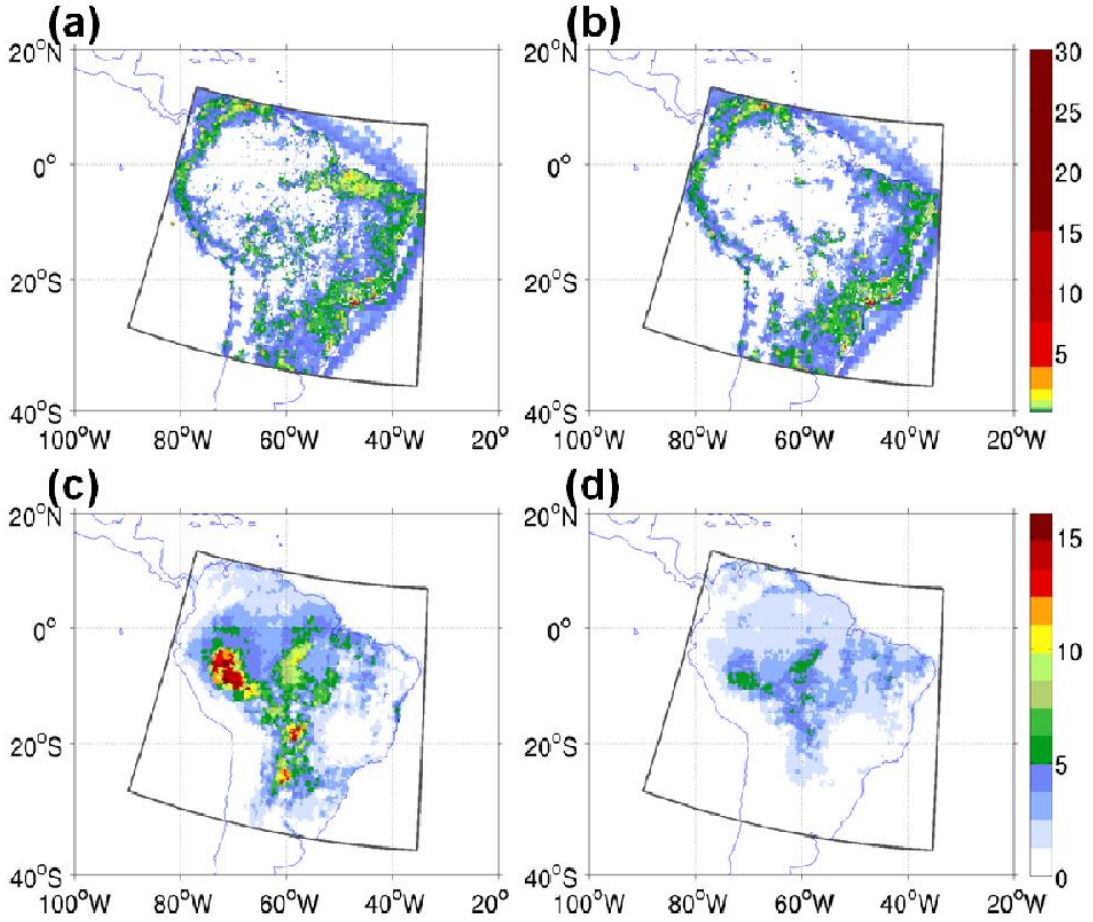

Figure 12. Mean emission rates (10^{-5} kg m^{-2} day^{-1}) from PREP-CHEM-SRC for the 35 km domain (dark gray outline) for NO_x for (a) BARCA A (November 2008) and (b) BARCA B (May 2009) and isoprene for (c) BARCA A and (d) BARCA B periods.

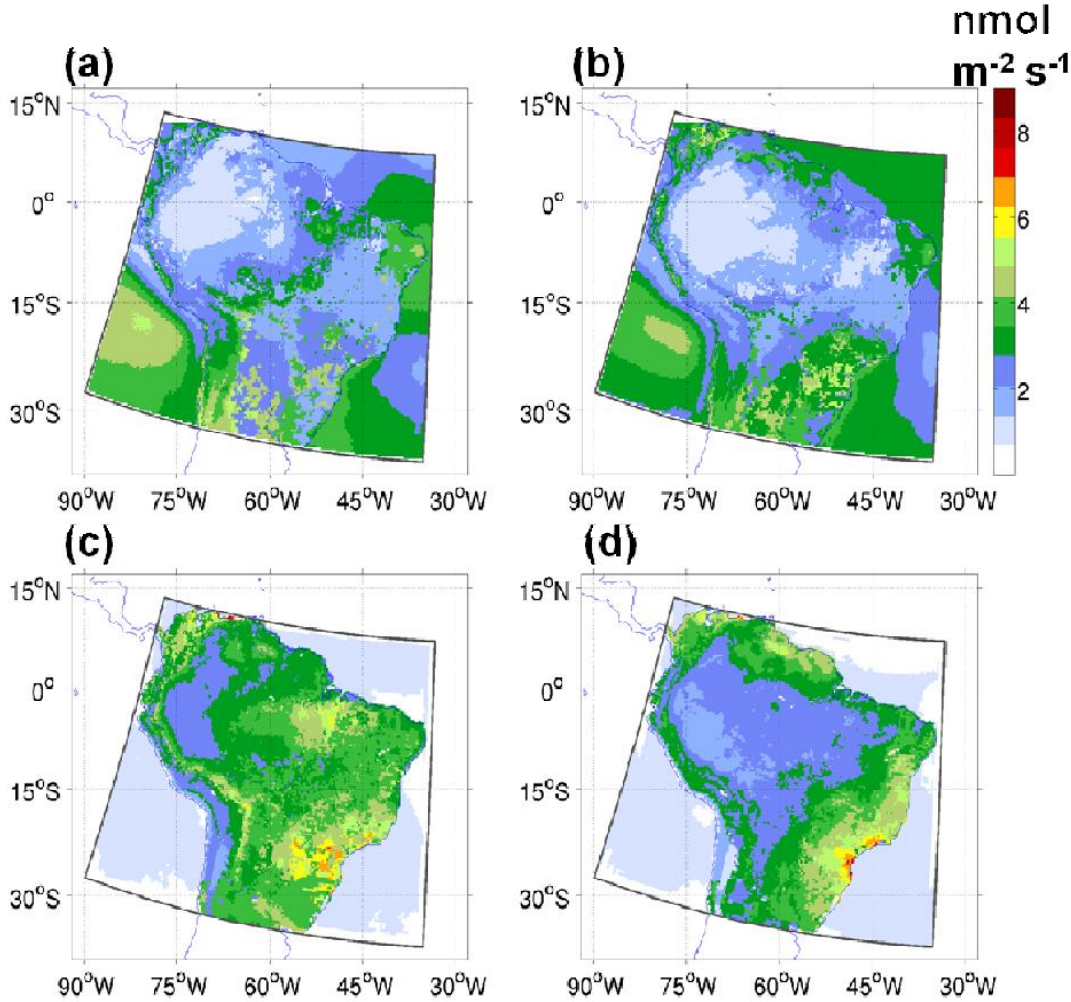

Figure 13. Average O_3 dry deposition flux (nmol m^{-2} s^{-1}) as simulated on the 35 km resolution domain (dark gray outline) by the CCATT-BRAMS model for (a) November 2008 and (b) May 2009 and by the WRF-Chem model for (c) November 2008 and (d) May 2009.

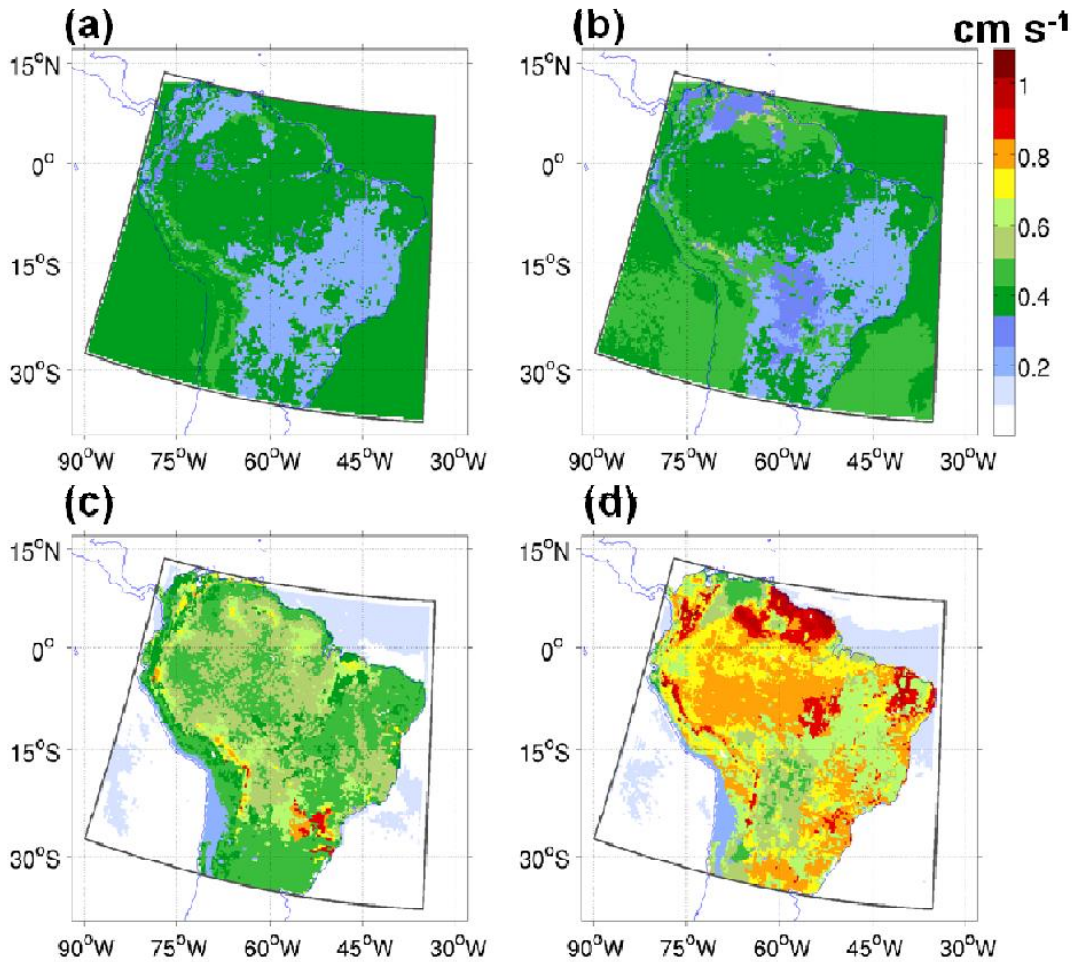

Figure 14. Same as Fig. 13, but daytime (11:00-21:00 UTC) median deposition velocity (cm s^{-1}).

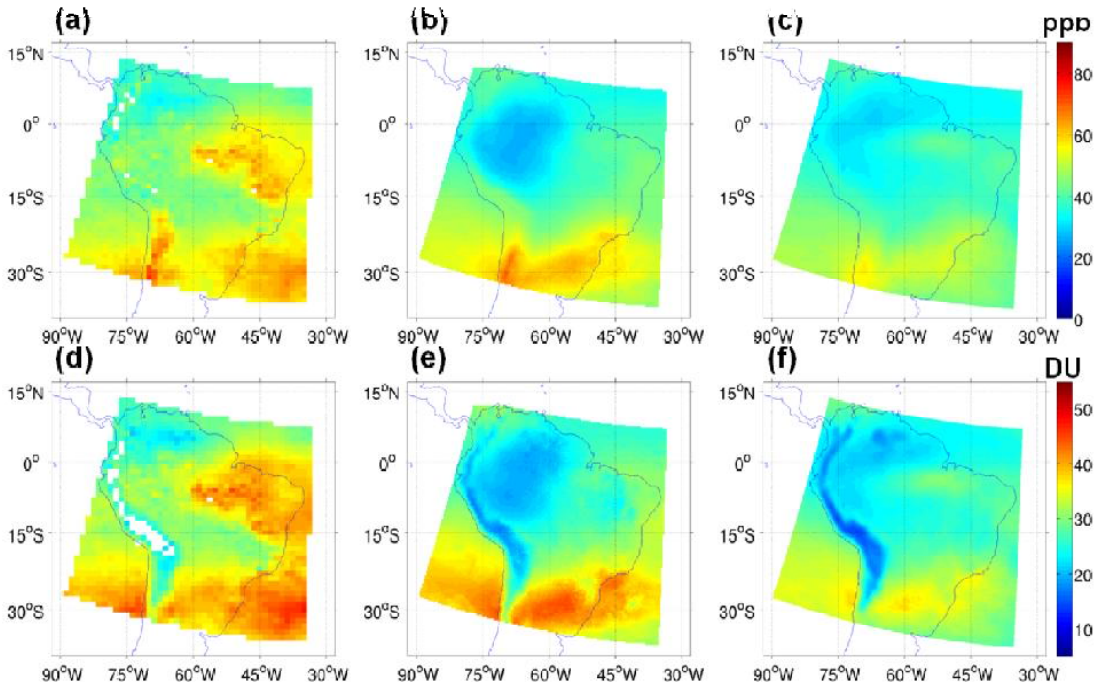

Figure 15. Mean tropospheric O_3 (ppb) on the 35 km domain from (a) OMI/MLS, (b) CCATT-BRAMS and (c) WRF-Chem and total tropospheric column O_3 (Dobson units) from (d) OMI/MLS, (e) CCATT-BRAMS and (f) WRF-Chem for November 2008.

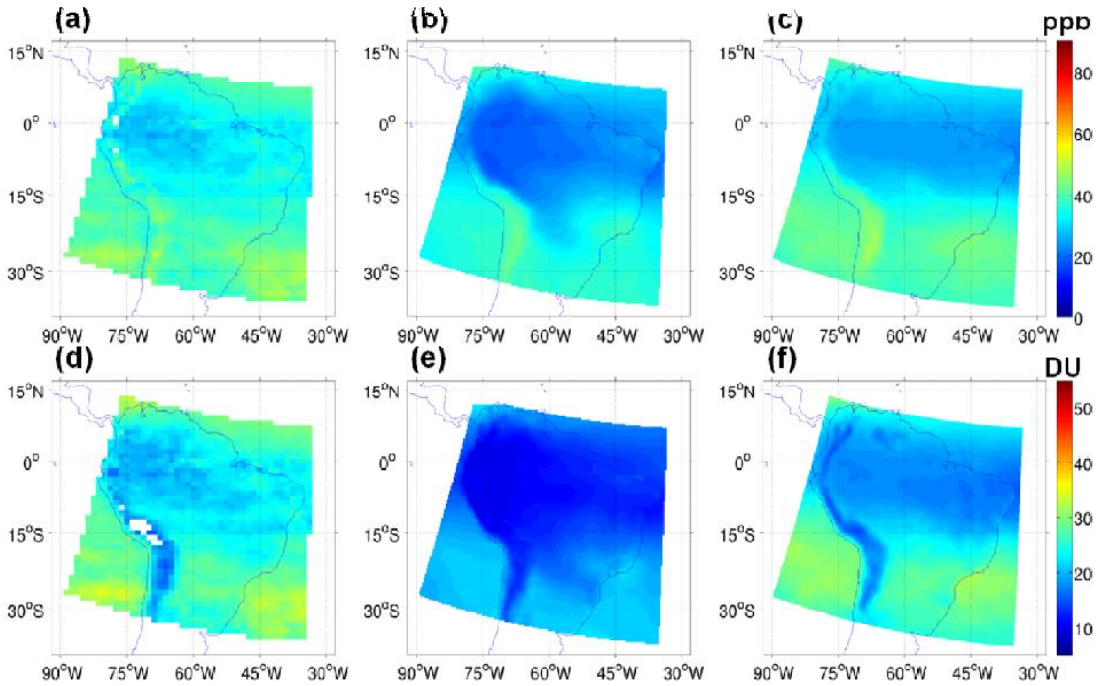

Figure 16. Same as Fig. 15, but for May 2009.