

## Response to reviews

Reviewer comments are in **bold**. Author responses are in plain text. Modifications to the manuscript are in *italics*. Page and line numbers in the responses correspond to those in the ACPD paper.

### Review #2

**The manuscript brings an interesting contribution to the evaluation of the air pollution conditions associated with the production of thermoelectric energy in Manaus, Amazonas, Brazil. In particular, it presents modelling evidence based on an optimistic scenario of reducing the levels of atmospheric pollutants that participate in photochemical reactions to generate hazardous secondary pollutants. The effective variable considered in the scenarios is the change in the type of fuel used in the thermoelectric power plants of Manaus, a metropolis located in the Amazon forest. The results show a marked decrease in the O<sub>3</sub> level as a consequence of the fuel switching from diesel to natural gas mainly. Recommendations to the Atmos. Chem. Phys.: My recommendation to the journal ACP is the publication of the manuscript after a mandatory minor revision considering the following points:**

The authors thank the reviewer for reading the manuscript and for the specific comments and the technical corrections. The final version of the manuscript takes into account the aspects pointed out. Responses to the specific points follow below.

#### Specific Comments:

**1 - The authors could provide two additional explanatory paragraphs about the models "Regional Acid Deposition Model" Version 2 (RADM2) (Chang, 1991) and Model for Ozone and Related Tracers (MOZART-4) (Emmons et al., 2010).**

We agree with the reviewer on this comment. The following sentence was added to the manuscript.

Section 2.1, Line 152.

*For Domain 2, the widely used Regional Acid Deposition Model Version 2 (RADM2) served as the chemical mechanism. It included 63 chemical species, 21 photolysis reactions, and 124 chemical reactions (Stockwell et al., 1990; Chang, 1991). Initial and boundary conditions for trace gases in Domain 2 were obtained from MOZART-4, an offline chemical transport model that has 85 chemical species, 12 aerosol compounds, 39 photolysis reactions and 157 gas-phase reactions (Emmons et al., 2010).*

**2 - Would it be interesting to indicate if the emission rates of the thermoelectric plants refer to an uninterrupted operation?**

We agree with the reviewer on the importance of this detail, and the following sentence was inserted in the manuscript:

Section 2.3, Line 200:

*For the Manaus region, the power plants generate energy uninterruptedly at full load throughout the year, with contractual arrangements with industry to idle when residential demand increases.*

**3 - The inclusion of a graph for the observed annual cycle (e.g., with box plots) of the pollutants considered for Manaus, to permit a in depth discussion of the meteorological conditions which was related to the month period analysed.**

We thank the reviewer for this perspective. The authors are not aware of measured ozone annual cycle in Manaus urban zone. We do see the importance of characterize background ozone conditions in the wet season for the region, which was done in section 1. In this regard, please see response 7.

**4 - Characterizing the period of investigation from the meteorological point of view, in its synoptic and mesoscale aspects.**

The authors agree with the reviewer comment. The following sentence was added to the main text:

Section 2.1, Line 144:

*For this region, the climatological rainfall in February is 290 mm, which can be compared to a maximum of 335 mm in March and a minimum of 47 mm in August (Ramos et al., 2009). For February 2014, observed precipitation was 21.5% below the climatological value (Figure S1), as explained by the positioning of the Bolivian High to the west of its usual location (CPTEC-INPE, 2014).*

**5 - Explaining the perturbations observed in the concentrations of pollutants observed (time series) in relation to the observed precipitation and possibility of wet deposition on the surface. In relation to the days without precipitation characterizing the mechanism of dry removal of the pollutants, qualitatively.**

The authors agree with the reviewer comment. A new Figure S1 shows with observed daily rain amount, and a following sentence was added to the main text:

Section 3, Line 268:

*The observed daily rain amounts (Figure S1) show that the days having the highest ozone concentrations corresponded to days of low or no precipitation (<5 mm). Conversely, the days of highest precipitation (>20 mm) and cloudiness had nearly background ozone concentrations.*

**6 - Could the authors indicate that as a result of the wet removal process, the pollutants can be deposited/transferred on the surface, vegetation or indeed sent to the rivers. It could be indicated the superficial route when the meteorological conditions are of precipitation. It would be interesting to point out possible conservation routes rather than simply saying that the levels were decreasing. It could be explained this point better. Also the authors could also compare the concentration levels of sequential days in which the second day rains in Manaus. Or at least present a qualitative discussion.**

We thank the reviewer for that comment. Low ozone concentrations during the wet season are mostly linked to high cloudiness, leading to a lack of radiation and reduced rates of photochemical reactions and ozone production ( $\text{NO}_2 + h\nu = \text{NO} + \text{O}$  and  $\text{O} + \text{O}_2 + \text{M} = \text{O}_3 + \text{M}$ ). Ozone is a soluble gas, but the formation is dependent of radiation and the concentrations of VOC and  $\text{NO}_x$ . In Manaus atmosphere due to high humidity and probably the large availability of OH, others chemical reactions should be important (e.g.,  $\text{NO}_2 + \text{OH} + \text{M} = \text{HNO}_3 + \text{M}$ ), decreasing the ozone production. The chemical mechanism used in the simulations considered these reactions. However, this subject was not addressed in this work.

**7 - Presenting a better discussion on levels of background concentration associated with natural production by the forest and rivers.**

We agree with the reviewer on this. A paragraph is already in the main text (Section 1, Line 75) discussing precursor emissions and ozone production over the forest. In response to the reviewer's suggestion and to further clarify the manuscript, the following additional sentence was added to the.

Section 1, Line 75:

The interactions among oxides of nitrogen ( $\text{NO}_x$ ), volatile organic compounds (VOCs), water vapor, and sunlight combine to produce ozone (Seinfeld and Pandis, 2006). *It is a secondary pollutant whose production depends on the prevailing chemistry and meteorological conditions. Daily surface concentrations are maximum in the afternoon because the production rate depends on sunlight.* The ratio of  $\text{NO}_x$  to VOC concentrations is of fundamental importance for the production rate of ozone. In tropical, forested Amazonia, biogenic volatile organic compounds are emitted in great quantities from the forest and are naturally abundant while  $\text{NO}_x$  emissions are primarily from the soil and atmospheric concentrations remain low (Fehsenfeld et al., 1992; Kesselmeier and Staudt, 1999; Karl et al., 2007; Jardine et al., 2015; Jokinen et

al., 2015;Yáñez-Serrano et al., 2015;Liu et al., 2016). *The pristine forest environment produces maximum afternoon surface ozone concentrations of 10 to 20 ppb in the wet season (Kirchhoff, 1988).*

**Technical correction:**

**Page 11 / line 255**

**Fix the orthographic flaw:"... The large diffe7rences ..."**

The correction has been made

## References

- Chang, J. S.: The regional acid deposition model and engineering model, National Acid Precipitation Assessment Program, Office of the Director, 1991.
- CPTEC-INPE: Meteorological Bulletin of the Center for Weather Forecasting and Climatic Studies (CPTEC) of the Brazilian National Institute of Space Research (INPE):  
<http://climanalise.cptec.inpe.br/~rclimanl/boletim/index0214.shtml> accessed 04 Apr 2017, 14:37., 2014.
- Emmons, L., Walters, S., Hess, P., Lamarque, J.-F., Pfister, G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., and Laepple, T.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), *Geoscientific Model Development*, 3, 43-67, 2010.
- Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C. N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P.: Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, *Global Biogeochemical Cycles*, 6, 389-430, 10.1029/92GB02125, 1992.
- Jardine, K., Yañez-Serrano, A. M., Williams, J., Kunert, N., Jardine, A., Taylor, T., Abrell, L., Artaxo, P., Guenther, A., Hewitt, C. N., House, E., Florentino, A. P., Manzi, A., Higuchi, N., Kesselmeier, J., Behrendt, T., Veres, P. R., Derstroff, B., Fuentes, J. D., Martin, S. T., and Andreae, M. O.: Dimethyl sulfide in the Amazon rain forest, *Global Biogeochemical Cycles*, 29, 19-32, 10.1002/2014GB004969, 2015.
- Jokinen, T., Berndt, T., Makkonen, R., Kerminen, V.-M., Junninen, H., Paasonen, P., Stratmann, F., Herrmann, H., Guenther, A. B., Worsnop, D. R., Kulmala, M., Ehn, M., and Sipilä, M.: Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications, *Proceedings of the National Academy of Sciences*, 112, 7123-7128, 10.1073/pnas.1423977112, 2015.
- Karl, T., Guenther, A., Yokelson, R. J., Greenberg, J., Potosnak, M., Blake, D. R., and Artaxo, P.: The tropical forest and fire emissions experiment: Emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia, *Journal of Geophysical Research: Atmospheres*, 112, n/a-n/a, 10.1029/2007JD008539, 2007.
- Kesselmeier, J., and Staudt, M.: Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology and Ecology, *Journal of Atmospheric Chemistry*, 33, 23-88, 10.1023/A:1006127516791, 1999.
- Kirchhoff, V. W. J. H.: Surface ozone measurements in Amazonia, *Journal of Geophysical Research: Atmospheres*, 93, 1469-1476, 10.1029/JD093iD02p01469, 1988.
- Liu, Y., Brito, J., Dorris, M. R., Rivera-Rios, J. C., Seco, R., Bates, K. H., Artaxo, P., Duvoisin, S., Keutsch, F. N., and Kim, S.: Isoprene photochemistry over the Amazon rainforest, *Proceedings of the National Academy of Sciences*, 113,

6125-6130, 2016.

Ramos, A. M., dos Santos, L. A. R., and Fortes, L. T. G.: Normais climatológicas do Brasil, 1961-1990, 2009.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From air pollution to Climate Change, Second Edition ed., 2006.

Stockwell, W. R., Middleton, P., Chang, J. S., and Tang, X.: The second generation regional acid deposition model chemical mechanism for regional air quality modeling, *Journal of Geophysical Research: Atmospheres*, 95, 16343-16367, 1990.

Yáñez-Serrano, A. M., Nölscher, A. C., Williams, J., Wolff, S., Alves, E., Martins, G. A., Bourtsoukidis, E., Brito, J., Jardine, K., Artaxo, P., and Kesselmeier, J.: Diel and seasonal changes of biogenic volatile organic compounds within and above an Amazonian rainforest, *Atmos. Chem. Phys.*, 15, 3359-3378, 10.5194/acp-15-3359-2015, 2015.