

Power Plant Fuel Switching and Air Quality in a Tropical Forested Environment

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1 **Abstract**

2 How a changing energy matrix for **electricity production** affects air quality is considered
3 for an urban region in a tropical, forested environment. Manaus, the largest city in the central
4 Amazon basin of Brazil, is in the process of changing its energy matrix **for electricity production**
5 from fuel oil and diesel to natural gas across an approximately ten-year period, **with a minor**
6 **contribution by hydropower**. Three scenarios of urban air quality, specifically afternoon ozone
7 concentrations, were simulated using the Weather Research and Forecasting (WRF-Chem)
8 model. The first scenario used fuel oil and diesel for **electricity production**, which was the reality
9 in 2008. The second scenario was based on the fuel mix from 2014, the most current year for
10 which data were available. The third scenario considered nearly complete use of natural gas for
11 **electricity** production, which is the anticipated future, possibly for 2018. For each case,
12 inventories of anthropogenic emissions were based on **electricity** generation, refining operations,
13 and transportation. Transportation and refinery operations were held constant across the three
14 scenarios to focus on effects of power plant fuel switching in a tropical context. **The simulated**
15 **NO_x and CO emissions for the urban region decrease by 89% and 55%, respectively, after the**
16 **complete change in the energy matrix**. The results of the simulations indicate that a change to
17 natural gas significantly decreases maximum afternoon ozone concentrations over the population
18 center, **reducing ozone by >70% for the most polluted days**. The sensitivity of ozone
19 concentrations to the fuel switchover is consistent with a NO_x-limited regime, as expected for a
20 tropical forest having high emissions of biogenic volatile organic compounds, high water vapor
21 concentrations, and abundant solar radiation. **There are key differences in a shifting energy**
22 **matrix in a tropical, forested environment compared to other world environments. Policies**
23 favoring the burning of natural gas in place of fuel oil and diesel have great potential for ozone
24 reduction and **improved** air quality for growing urban regions located in tropical, forested
25 environments around the world.

26 1. Introduction

27 The evolution of modern civilization is closely associated with obtaining and distributing
28 energy at large scale (Price, 1995). Although electricity production for Brazil as a whole is
29 obtained mostly by hydroelectric plants (ANEEL, 2008), in today's Amazon region, constituting
30 the largest tropical forest in the world (Behling et al., 2001), electricity is largely produced by
31 fossil fuel power plants (ELETROBRAS, 2014a). Sulfur-laden oil and diesel are the historical
32 fuels. The Amazon region is of vital importance for the functioning of both regional ecosystems
33 and climate (Fisch et al., 1998;Nobre et al., 2016). Topics for research in recent years have
34 included the relationship between the biosphere and the atmosphere in the Amazon (Fan et al.,
35 1990;Stark et al., 2015), the impacts of land use change (Dickinson and Kennedy,
36 1992;Fearnside, 2003;Paula et al., 2014;Wertz-Kanounnikoff et al., 2016), and the consequences
37 of urbanization, population growth, and increased anthropogenic emissions to the composition of
38 the atmosphere (Shukla et al., 1990;Potter et al., 2001;Wright, 2005;Malhi et al., 2008;Martin et
39 al., 2016b).

40 The population of northern Brazil has grown rapidly in recent decades. In the last 50
41 years (1960-2010), the urban population of the region increased from about 1 to 11 million,
42 while the urban population of Brazil grew from 32 to 160 million in the same period (IBGE,
43 2010). This growth in the northern region is linked to public policies to increase development,
44 exemplified by the establishment in 1967 of a free trade zone in Manaus in central Amazonia. In
45 2014, this concession was extended until 2073 (Queiroz, 2014), suggesting continued rapid
46 population growth for the region in the coming decades. Continued growth related to electricity
47 production can be expected in support of the population and industry.

48 In this context is Manaus, Amazonas, the financial, corporate, and economic center of
49 northern Brazil. It has a population of two million and is the seventh largest city in Brazil (IBGE,
50 2015). The population in recent time has increased nearly every year by 50,000 persons due to
51 internal migration motivated by the large industrial district, an area that receives tax exemption
52 from the government. Population growth continually increases the demand for land, energy, and
53 power, leading to the loss of adjacent forest and the degradation of air quality in the region
54 (Cropper and Griffiths, 1994). The installed base for electricity production has increased by
55 around 10% annually in Manaus over the last two decades.

56 In 2009, a 650-km natural gas pipeline was inaugurated, linking a region of natural gas
57 production in Urucu, Amazonas, to Manaus (Soares et al., 2014). From an operational and cost
58 point of view, an uninterrupted fuel supply and the direct distribution from the source to the end
59 user, such as provided by the natural gas pipeline, significantly reduced both costs and related
60 emissions for the transport of fuels on trucks and ships (Neiva and Gama, 2010). With the supply
61 of natural gas, the power plants of Manaus have been adjusting to the economic conditions of the
62 changed fuel mix, replacing fuel oil and diesel with natural gas across approximately a ten-year
63 period. Although the historical change was not motivated at the policy level by environmental
64 drivers, the change nonetheless represents a unique opportunity to evaluate how fuel switching
65 can affect air quality, especially in regard to little-studied tropical forest environments.

66 Emission factors of pollutants and pollutant precursors differ greatly between fuel oil and
67 diesel on the one hand and natural gas on the other, and these emissions affect regional air
68 quality and human health (Vitousek et al., 1997; Holgate et al., 1999). Air pollution can lead to
69 arterial vasoconstriction (Brook et al., 2002), cytogenetic damage in lymphocytes (Holland et al.,
70 2015), and chronic obstructive pulmonary disease (COPD) (Schikowski et al., 2014), and asthma

71 immunopathogenesis (Alexis and Carlsten, 2014). The World Health Organization (WHO)
72 provides recommendations on the thresholds of pollutant concentrations, such as ozone,
73 particulate matter, nitrogen dioxide, and sulfuric dioxide, above which human health is adversely
74 affected (WHO, 2006).

75 Ozone is the criteria air quality pollutant considered herein. The interactions among
76 oxides of nitrogen (NO_x), volatile organic compounds (VOCs), water vapor, and sunlight
77 combine to produce ozone (Seinfeld and Pandis, 2006). It is a secondary pollutant whose
78 production depends on the prevailing chemistry and meteorological conditions. Daily surface
79 concentrations are maximum in the afternoon because the production rate depends on sunlight.
80 The ratio of NO_x to VOC concentrations is of fundamental importance for the production rate of
81 ozone. In tropical, forested Amazonia, biogenic volatile organic compounds are emitted in great
82 quantities from the forest and are naturally abundant while NO_x emissions are primarily from the
83 soil and atmospheric concentrations remain low (Fehsenfeld et al., 1992; Kesselmeier and Staudt,
84 1999; Karl et al., 2007; Jardine et al., 2015; Jokinen et al., 2015; Yáñez-Serrano et al., 2015; Liu et
85 al., 2016). The pristine forest environment produces maximum afternoon surface ozone
86 concentrations of 10 to 20 ppb in the wet season (Kirchhoff, 1988). Human activities can
87 significantly elevate NO_x concentrations above background concentrations (Delmas et al.,
88 1997; Lamarque et al., 2010; Daskalakis et al., 2016). For this reason, economic activities and
89 policy decisions that affect NO_x emissions deserve special attention in the context of Amazonia.
90 A quantitative understanding of how an anthropogenically perturbed VOC: NO_x ratio affects
91 ozone production in this region is, however, not trivial. Compared to temperate urban regions
92 that have been studied in greater detail for ozone production, the tropical region has more intense
93 solar radiation and higher water vapor concentrations (Kuhn et al., 2010). Regional modeling is

94 an important approach for understanding the linked effects (Potter et al., 2001;Isaksen et al.,
95 2009).

96 The study herein evaluates how a changing energy matrix in a tropical, forested
97 environment affects urban pollutant concentrations. Ozone is chosen for detailed study because
98 of the concern for human health and the susceptibility of its secondary production to factors at
99 play in a forest environment. Manaus is chosen for study because of its location in the tropical
100 forest, its size, and its shifting energy matrix. A large international experiment, Observations and
101 Modeling of the Green Ocean Amazon (GoAmazon2014/5), was also carried out across two
102 years in 2014 and 2015 in the Manaus region (Martin et al., 2016b), including aircraft flights
103 (Martin et al., 2016a). A companion study by Rafee et al. (2017) compared simulated to
104 measured pollutant concentrations for GoAmazon2014/5. The present study, which investigates
105 how a shift in the energy matrix across a ten-year period affects regional air quality, provides
106 interpretative context for the two-year experiment of GoAmazon2014/5. For Case A of the
107 present study, fuel oil and diesel are used for electricity production, which was the reality in
108 2008. The Urucu pipeline began initial, albeit small, shipments of natural gas in 2010, with
109 increasing amounts every year thereafter. By 2014, natural gas had increased from 0% to 65% of
110 the energy matrix for electricity production. Case B corresponds to the energy matrix of 2014.
111 Case C considers the nearly complete use of natural gas for electricity production, which is the
112 planned future, possibly for 2018. For each case, inventories of anthropogenic emissions are
113 based on electricity generation, refining operations, and transportation. Transportation and
114 refinery operations are held constant across the three scenarios to focus on effects of power plant
115 fuel switching in a tropical context. The study herein focuses on the wet season because regional
116 anthropogenic activities of the urban environment are easily compared to background conditions.

117 The dry season is more complicated because of continental biomass burning that produce
118 additional ozone precursors (Martin et al., 2010).

119 2. Model Description

120 2.1 WRF-Chem

121 Simulations were carried out using the Weather Research and Forecasting model fully
122 coupled to a chemical module (WRF-Chem version 3.6.1) (Grell et al., 2005). The WRF
123 configuration included the treatment of Lin et al. (1983) for cloud microphysics, MM5 for
124 surface layer (Grell et al., 1994), Noah for land surface (Chen et al., 1997), Yonsei University for
125 boundary layer (Hong et al., 2006), Goddard for short-wave radiation (Chou and Suarez, 1999),
126 the Rapid Radiative Transfer Model for long-wave radiation (Mlawer et al., 1997), and Grell and
127 Freitas (2013) for cumulus clouds. The modeling approach with these parametrizations has been
128 studied (Ying et al., 2009; Misenis and Zhang, 2010; Gupta and Mohan, 2015), showing
129 sensitivity to capture the effects of a changing emissions inventory.

130 Two nested domains were employed (Figure 1). An outer domain (denoted as “Domain
131 1” in inset figure) had a resolution of 10 km and a dimension of 1050 km × 800 km. This domain
132 employed re-analysis data from the Climate Forecast System Reanalysis (CFSv2). An inner
133 domain (“Domain 2” represented in the full figure) had a resolution of 2 km and a dimension of
134 302 km × 232 km. This domain included the study area for which dynamic chemical transport
135 modeling was simulated. The urban region of Manaus is seen in white in the land cover image of
136 Domain 2. Domain 2 had initial and boundary conditions based on interpolation of Domain 1.
137 The grid center was the same for both domains (2.908° S and 60.319° W). The model spin-up
138 time was 24 h, followed by 72 h of simulation. In this way, ten simulations covered a one-month
139 period. This approach balanced between computational time and numerical diffusion.

140 Meteorological fields were obtained from re-analysis data of the National Center for
141 Environmental Prediction (NCEP) at a spatial resolution of $0.5^\circ \times 0.5^\circ$ and a time resolution of 6
142 h from February 1 to 28, 2014. NCEP data are based on the Climate Forecast System Reanalysis
143 (Saha et al., 2011). Land cover was based on data from the Moderate Resolution Imaging
144 Spectroradiometer (MODIS) (Rafee et al., 2015). For this region, the climatological rainfall in
145 February is 290 mm, which can be compared to a maximum of 335 mm in March and a
146 minimum of 47 mm in August (Ramos et al., 2009). For February 2014, observed precipitation
147 was 21.5% below the climatological value (Figure S1), as explained by the positioning of the
148 Bolivian High to the west of its usual location (CPTEC-INPE, 2014). During the period of
149 February in the wet season contributions by biomass burning to ozone production in central
150 Amazonia are most often negligible (Martin et al., 2016b).

151 For the chemical part of the model, anthropogenic and biogenic emissions of gases were
152 considered (described in section 2.2). For Domain 2, the widely used Regional Acid Deposition
153 Model Version 2 (RADM2) served as the chemical mechanism. It included 63 chemical species,
154 21 photolysis reactions, and 124 chemical reactions (Stockwell et al., 1990; Chang, 1991). Initial
155 and boundary conditions for trace gases in Domain 2 were obtained from MOZART-4, an offline
156 chemical transport model that has 85 chemical species, 12 aerosol compounds, 39 photolysis
157 reactions and 157 gas-phase reactions (Emmons et al., 2010).

158

159 2.2 Emissions

160 Forest, vehicle, power plant, and refinery emissions were considered. Biogenic emissions
161 were based on the Model of Emissions of Gases and Aerosols from Nature (MEGAN, version
162 2.1) (Guenther et al., 2012). MEGAN varies emissions taking into account the type of

163 vegetation, the seasonality based on temperature and leaf area index (LAI), the intensity of
164 incident light, and the soil moisture. It considers 150 different compounds. Approximate
165 biogenic emissions for Domain 2 are 50% as isoprene, 30% as methanol, ethanol, acetaldehyde,
166 acetone, α -pinene, β -pinene, t- β -ocimene, limonene, ethane, and propene, 17% as another twenty
167 compounds (mostly terpenoids), and 3% as another 100 compounds.

168 For vehicle emissions, a vehicle count for Manaus of 600,000 was considered
169 (DENATRAN, 2014). The breakdown of vehicle by type, daily travel distances, and emission
170 factors is listed in Table 1 (ANP, 2014). The Manaus fleet has an average age of 5 years. This
171 relatively young age can be attributed to the timing of rapid urban growth coupled to a vast
172 increase in vehicle ownership during an explosive economic expansion period from 2009 to
173 2015. The methodology of Martins et al. (2010) was used to distribute the vehicle emissions
174 spatially based on night-time light intensity observations of the Defense Meteorological Satellite
175 Program - Operational Linescan System (DMSP-OLS). These observations were assumed to
176 correlate with overall daily patterns of vehicle traffic. Additional information about this
177 methodology is described in Andrade et al. (2015)

178 For stationary sources related to electricity production, a survey of the locations of power
179 plants in Manaus region was conducted. Although the city of Manaus has a large industrial park,
180 these industries mostly produce electronic products and burn little fuel directly. Instead, power
181 plants and a large refinery are major emitters. The data of installed capacity, generated
182 electricity, and fuel used were obtained for each plant (Table 2). The locations of these power
183 plants are shown in Figure 1. The emission factors for electricity production by fuel type were
184 based on the database of the USA Environmental Protection Agency (EPA) using the median
185 value of the emission factors (Table 3). The fuel consumption factor for electricity production is

186 also listed in Table 3 (ELETROBRAS, 2014b). Another major source of pollution in the region
187 is the refinery Isaac Sabbá, with the capacity to process 7.3×10^6 liters of oil per day
188 (PETROBRAS, 2016). The emission factors of refinery operations are listed in Table 3
189 (DeLuchi, 1993)

190 2.3 Scenarios

191 Simulations were performed to evaluate ozone concentrations for three different
192 scenarios. The first scenario (Case A) was based on emissions of historical Manaus before the
193 gradual process of fuel switching began in 2010. It corresponded to an energy matrix of 100% oil
194 or diesel for electricity production. Because a gradual change in the energy matrix took place, the
195 second scenario (Case B) considered the mix of oil, diesel, and natural gas used in 2014 for
196 electricity production. In 2014, 65% of the power was generated by natural gas and the
197 remaining 35% by oil or diesel (ELETROBRAS, 2014b). The third scenario (Case C) used an
198 energy matrix of 100% natural gas, removing all oil and diesel from electricity production in
199 Manaus. This scenario represents the anticipated situation for the Manaus region within the next
200 several years. Table 2 lists the fuel mix of each case. All three scenarios also include a baseline
201 contribution of 24% by regional hydropower. For the Manaus region, the power plants generate
202 energy uninterruptedly at full load throughout the year, with contractual arrangements with
203 industry to idle when residential demand increases.

204 In order to compare only the effects of the change in the type of fuel used, the same
205 matrix of power plants was used for the three scenarios. Although the combined capacity of
206 electricity production increased in recent years following the population and energy demand
207 growth, this change was omitted so the comparative study of the effects of fuel type on air
208 quality could be isolated. Likewise, vehicle emissions were held constant for the three fuel

209 scenarios considered herein to focus on effects of power plant fuel switching in a tropical
210 context. In this regard, the intent of the analysis herein was to represent the effects of power
211 plant fuel switching on air quality in a tropical forested environment in a general yet realistic
212 sense by selection of a representative urban environment. The intent was not an actual simulation
213 of the city of Manaus, which would necessitate adjustment of transportation, industry, power,
214 land use, and other aspects of urban growth corresponding to the year of each case. The study
215 herein was also restricted to the wet season, again to focus on shifts in the energy matrix and
216 avoid the complicating effects of biomass burning prevalent in the dry season.

217 The emissions of CO and NO_x by source are listed in Table 4 for Cases A, B, and C.
218 Power plant emissions constitute 84%, 78%, and 64% of urban CO emissions for Cases A, B,
219 and C, respectively. For NO_x, they constitute 98%, 95%, and 82%, respectively. The high percent
220 contribution by power plant emissions arises from a combination of the (i) old technology used
221 in the plants (i.e., no pollution controls) and low-end fuels and (ii) the young age of the modern
222 vehicle fleet using high-end fuels. From Case A to B, total CO and NO_x emissions decrease by
223 25% and 60%, respectively. From Case A to C, the respective reductions are 55% and 89%.

224 3. Results and Discussion

225 Figure 2 shows a box-whisker plot for all days and afternoon times of the simulations for
226 each case. The time period of 12:00 to 16:00 (local time) was selected for analysis because it
227 represents the maximum ozone concentration, which is fundamentally linked to photochemistry.
228 As a check on the model output, a comparison between aircraft measurements of ozone
229 concentrations and model predictions for Case B is presented in Figure S2. For the statistical
230 analysis of Figure 2, an area of 10 km × 10 km centered on Manaus was taken to assess ozone
231 concentrations in the populated urban area. The black box in Figure 3 represents this region. The

232 analysis represented in Figure 2 shows that within a single case ozone concentrations had large
233 day-to-day differences throughout the simulated month. The differences among days was largely
234 due to variability in cloudiness and other meteorological components of the simulation. Some
235 days were sunny, favoring the photochemical process of ozone formation, whereas other days
236 were overcast or rainy.

237 The inter-case variability in ozone concentration across Cases A, B, and C in Figure 2
238 arose from differences in the energy matrix for electricity production. A partial shift from diesel
239 and oil to natural gas (i.e., Cases A and B) did not greatly shift ozone concentrations, on either
240 polluted or clean days. However, a complete shift to natural gas (i.e., Case C) considerably
241 reduced ozone concentrations in the urban region. Maximum afternoon ozone concentrations on
242 fair weather days decreased by >70% (e.g., 110 to 30 ppb) for the three most polluted days of the
243 simulated month, which occurred on fair weather days. On poor weather days, the additional
244 pollution from Manaus contributed to small or negligible additional ozone production.

245 Figure 3 shows examples of the spatial distribution of ozone concentration for each of
246 Cases A, B, and C for the single afternoon of February 1, 2014. Spatial distributions of the mean
247 of afternoon values and their standard deviation across the full month of simulation are shown in
248 Figure S3 of the Supplement. The ozone plume spreads downwind from Manaus carried by the
249 easterlies of the equatorial trade winds, in agreement with observations reported by Kuhn et al.
250 (2010) and Martin et al. (2016b). The map shows that the pollution associated with Manaus
251 emissions not only affects local air quality of the urban population but also reaches other
252 regional downwind population centers, such as Careiro, Iranduba, and Manacapuru. The
253 qualitative spatial pattern of the ozone plume is similar among Cases A, B, and C, as explained
254 by the use of identical meteorology. The concentrations, however, have strong differences. From

255 Case A to B, the concentrations inside the plume do not differ greatly, in agreement with the
256 box-whisker representation in Figure 2. For Case C, the ozone footprint and concentrations
257 decrease greatly, both for the Manaus urban region and even more so for downwind populations,
258 reinforcing the important impact of the fuel switch.

259 Figure 4 presents a difference analysis between historical practices (i.e., Case A) and
260 future plans (i.e., Case C) to finalize the foregoing points related to Figures 2 and 3. The
261 difference analysis represents a shift in the entire energy matrix for electricity production from
262 oil and diesel to that of natural gas. The left panel of Figure 4 shows the difference map for a
263 single day corresponding to the plots of Figure 3. Ozone concentrations decrease by
264 approximately 50 ppb in the center of the plume. The right panel shows a box-whisker plot of
265 difference values in the afternoon period across the month, corresponding to the plots of Figure
266 2. Days 1, 5, 8, 12, 15, and 16 had the highest differences between the two scenarios, indicating
267 that these days were the sunniest and most polluted. For the other days of the month, the median
268 difference was very close to zero, indicating that these days were overcast or had high levels of
269 convection that brought in clean air. The observed daily rain amounts (Figure S1) show that the
270 days having the highest ozone concentrations corresponded to days of low or no precipitation (<5
271 mm). Conversely, the days of highest precipitation (>20 mm) and cloudiness had nearly
272 background ozone concentrations.

273 For comparative studies, Collins et al. (1997) investigated the effects of NO_x emissions
274 decrease on ozone concentrations over Europe. They found that in summer, a decrease of 50% in
275 NO_x emissions result in a reduction on ozone over Europe by 10-20%, but that NO_x emission
276 reduction showed opposite effect in the winter, increasing the ozone in the same area by over
277 40%. Frost et al. (2006) performed a modelling study using WRF-Chem to evaluate the effects of

278 power plant NO_x emissions on ozone concentrations in the eastern United states. They show that
279 the relationship between NO_x emission reduction and ozone concentrations is complex, and
280 depends on previous levels of NO_x in the air around the emissions site. At low NO_x environment,
281 a decrease in new NO_x emissions reduces O₃, while at higher NO_x levels, the same NO_x
282 decreases results in a smaller O₃ decrease or even O₃ increase. Mena-Carrasco et al. (2012)
283 studied the benefits of using natural gas instead of diesel with respect to air quality and human
284 health. The study carried out in for Santiago, located in the central region of Chile with
285 Mediterranean climate, showed that the use of natural gas instead of diesel in urban buses could
286 reduce drastically the emissions and concentrations of particulate matter.

287 In summary, the results show that the altered energy matrix significantly influences air
288 quality, as gauged by the maximum afternoon ozone concentration. The relationship between the
289 Manaus emissions and the vast biogenic emissions constitutes an important scenario to study the
290 atmospheric chemistry feedbacks. The large differences between Cases A and C show that the
291 burning of fuel oil and diesel have enormous potential for regional ozone production.
292 Conversely, substitution with natural gas has an excellent effect for comparative air quality and
293 human health. In this context, even though anthropogenic emissions in Amazon region are low
294 compared to other regions of the world, such as Mexico City (Molina et al., 2010), São Paulo
295 (Silva Junior and Andrade, 2013), and Los Angeles (Haagen-Smit, 1952), the study results of
296 Figure 4 demonstrate the significant sensitivity of Amazonia to anthropogenic emissions. The
297 results emphasize the high sensitivity over the tropical forest to even small amounts of pollution,
298 as amplified by the high solar irradiance and water vapor concentrations in an environment of
299 plentiful biogenic VOC emissions. Specifically, the significant decrease in NO_x emissions from
300 Case A to B resulted in no strong differences in ozone concentrations whereas, conversely, the

301 smaller increase from Case C to B resulted in large ozone production. This nonlinear behavior of
302 ozone concentration with respect to pollution is linked to the chemical cycles of the ozone
303 production, most specifically related to the NO_x limitation or not (Lin et al., 1988). The results
304 herein suggest that the anticipated coming complete conversion to natural gas for electricity
305 production should significantly reduce ozone concentration in the Manaus urban region. The
306 GoAmazon2014/5 experiment occurred during two years of this ten-year transition in the energy
307 matrix. Smaller municipalities throughout the Amazon basin, which is two-thirds the size of the
308 continental USA, continue to burn sulfur-laden oil and diesel for electricity production. Further
309 changes in the energy matrix of Amazonia are dependent on continued development of
310 infrastructure for use of natural gas or making connections to the national grid and continued
311 developments in the use of hydropower, even as the population of Amazonia continues to grow
312 rapidly (Domingues, 2003;Tundisi, 2007;ANEEL, 2008).

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References

- Alexis, N. E., and Carlsten, C.: Interplay of air pollution and asthma immunopathogenesis: a focused review of diesel exhaust and ozone, *Int Immunopharmacol*, 23, 347-355, 10.1016/j.intimp.2014.08.009, 2014.
- Andrade, M. D. F., Freitas, E. D., Ynoue, R. Y., Todesco, E., Vara, A. V., Ibarra, S., Martins, L. D., Martins, J., and Carvalho, V. S.: Air quality forecasting system for southeastern Brazil, *Frontiers in Environmental Science*, 3, 10.3389/fenvs.2015.00009, 2015.
- ANEEL: Brazilian electricity atlas, Brasília, 2008.
- ANEEL: Normative Resolution N° 586, of November 19, 2013. Edited by Brazilian National Agency of Electric Energy, in, 2013.
- ANP: National Inventory of Atmospheric Emissions from vehicles of 2013, in, National Agency of Petroleum, Department of Environment, 2014.
- Behling, H., Keim, G., Irion, G., Junk, W., and De Mello, J. N.: Holocene environmental changes in the central Amazon Basin inferred from Lago Calado (Brazil), *Palaeogeography, Palaeoclimatology, Palaeoecology*, 173, 87-101, 2001.
- Brook, R. D., Brook, J. R., Urch, B., Vincent, R., Rajagopalan, S., and Silverman, F.: Inhalation of Fine Particulate Air Pollution and Ozone Causes Acute Arterial Vasoconstriction in Healthy Adults, *Circulation*, 105, 1534-1536, 10.1161/01.cir.0000013838.94747.64, 2002.
- Chang, J. S.: The regional acid deposition model and engineering model, National Acid Precipitation Assessment Program, Office of the Director, 1991.
- Chen, F., Janjić, Z., and Mitchell, K.: Impact of Atmospheric Surface-layer Parameterizations in the new Land-surface Scheme of the NCEP Mesoscale Eta Model, *Boundary-Layer Meteorology*, 85, 391-421, 10.1023/a:1000531001463, 1997.
- Chou, M.-D., and Suarez, M. J.: A solar radiation parameterization for atmospheric studies, *NASA Tech. Memo*, 104606, 40, 1999.
- Collins, W., Stevenson, D. S., Johnson, C., and Derwent, R.: Tropospheric ozone in a global-scale three-dimensional Lagrangian model and its response to NO_x emission controls, *Journal of Atmospheric Chemistry*, 26, 223-274, 1997.
- 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.
- Cropper, M., and Griffiths, C.: The interaction of population growth and environmental quality, *The American Economic Review*, 84, 250-254, 1994.
- Daskalakis, N., Tsigaridis, K., Myriokefalitakis, S., Fanourgakis, G. S., and Kanakidou, M.: Large gain in air quality compared to an alternative anthropogenic emissions scenario, *Atmospheric Chemistry and Physics*, 16, 9771-9784, 2016.
- Delmas, R., Serca, D., and Jambert, C.: Global inventory of NO_x sources, *Nutrient cycling in agroecosystems*, 48, 51-60, 1997.
- DeLuchi, M. A.: Emissions from the Production, Storage, and Transport of Crude Oil and Gasoline, *Air & Waste*, 43, 1486-1495, 10.1080/1073161X.1993.10467222, 1993.
- DENATRAN: Brazilian Vehicles Fleet of 2014: <http://www.denatran.gov.br/frota2014.htm>, access: 20 jan, 2014.
- Dickinson, R. E., and Kennedy, P.: Impacts on regional climate of Amazon deforestation, *Geophysical Research Letters*, 19, 1947-1950, 1992.
- Domingues, P. C. M.: A interconexão Elétrica dos Sistemas Isolados da Amazônia ao Sistema Interligado Nacional, 2003.
- ELETROBRAS: Relatory of Administration and Finances: <http://www.eletronbras.com/elb/ri/demonstracoesfinanceiras/main.asp?Team={BC80BD9D-8497-49C8-BD52-61B9626EA294}>, access: 28 sep, 2014a.
- ELETROBRAS: Relatory of energy generation., Personal Communication, Environment Department of Eletrobras Amazonas Energia., 2014b.
- 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.
- EPA: Compilation of air pollutant emission factors, volume 1: Stationary point and area source, in, AP 42, fifth edition ed., 1998.
- Fan, S.-M., Wofsy, S. C., Bakwin, P. S., Jacob, D. J., and Fitzjarrald, D. R.: Atmosphere-biosphere exchange of CO₂ and O₃ in the central Amazon Forest, *Journal of Geophysical Research: Atmospheres*, 95, 16851-16864, 10.1029/JD095iD10p16851, 1990.

- Fearnside, P. M.: Deforestation Control in Mato Grosso: A New Model for Slowing the Loss of Brazil's Amazon Forest, *AMBIO: A Journal of the Human Environment*, 32, 343-345, 10.1579/0044-7447-32.5.343, 2003.
- Fearnside, P. M.: Brazil's Samuel Dam: Lessons for hydroelectric development policy and the environment in Amazonia, *Environmental Management*, 35, 1-19, 2005.
- 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.
- Fisch, G., Marengo, J. A., and Nobre, C. A.: The climate of Amazonia-a review, *Acta Amazonica*, 28, 101-101, 1998.
- Frost, G., McKeen, S., Trainer, M., Ryerson, T., Neuman, J., Roberts, J., Swanson, A., Holloway, J., Sueper, D., and Fortin, T.: Effects of changing power plant NO_x emissions on ozone in the eastern United States: Proof of concept, *Journal of Geophysical Research: Atmospheres*, 111, 2006.
- Grell, G. A., Dudhia, J., and Stauffer, D. R.: A description of the fifth-generation Penn State/NCAR mesoscale model (MM5), 1994.
- Grell, G. A., Peckham, S. E., Schmitz, R., McKeen, S. A., Frost, G., Skamarock, W. C., and Eder, B.: Fully coupled "online" chemistry within the WRF model, *Atmospheric Environment*, 39, 6957-6975, <http://dx.doi.org/10.1016/j.atmosenv.2005.04.027>, 2005.
- Grell, G. A., and Freitas, S. R.: A scale and aerosol aware stochastic convective parameterization for weather and air quality modeling, *Atmos. Chem. Phys. Discuss*, 13, 23845-23893, 2013.
- Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.
- Gupta, M., and Mohan, M.: Validation of WRF/Chem model and sensitivity of chemical mechanisms to ozone simulation over megacity Delhi, *Atmospheric Environment*, 122, 220-229, 2015.

- Haagen-Smit, A. J.: Chemistry and physiology of Los Angeles smog, *Industrial & Engineering Chemistry*, 44, 1342-1346, 1952.
- Holgate, S. T., Koren, H. S., Samet, J. M., and Maynard, R. L.: *Air pollution and health*, Academic Press, 1999.
- Holland, N., Davé, V., Venkat, S., Wong, H., Donde, A., Balmes, J. R., and Arjomandi, M.: Ozone inhalation leads to a dose-dependent increase of cytogenetic damage in human lymphocytes, *Environmental and Molecular Mutagenesis*, 56, 378-387, 10.1002/em.21921, 2015.
- Hong, S.-Y., Noh, Y., and Dudhia, J.: A new vertical diffusion package with an explicit treatment of entrainment processes, *Monthly Weather Review*, 134, 2318-2341, 2006.
- IBGE: Demographic census 1960, 1970, 1980, 1991, 2000, and 2010., 2010.
- IBGE: Estimates of the resident population in Brazil and Federative Units from Brazilian Institute of Geography and Statistics., 2015.
- Isaksen, I. S., Granier, C., Myhre, G., Berntsen, T., Dalsøren, S. B., Gauss, M., Klimont, Z., Benestad, R., Bousquet, P., and Collins, W.: Atmospheric composition change: climate–chemistry interactions, *Atmospheric Environment*, 43, 5138-5192, 2009.
- 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.
- Kuhn, U., Ganzeveld, L., Thielmann, A., Dindorf, T., Schebeske, G., Welling, M., Sciare, J., Roberts, G., Meixner, F. X., Kesselmeier, J., Lelieveld, J., Kolle, O., Ciccioli, P., Lloyd, J., Trentmann, J., Artaxo, P., and Andreae, M. O.: Impact of Manaus City on the Amazon Green Ocean atmosphere: ozone production, precursor sensitivity and aerosol load, *Atmos. Chem. Phys.*, 10, 9251-9282, 10.5194/acp-10-9251-2010, 2010.
- Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., and Owen, B.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, *Atmospheric Chemistry and Physics*, 10, 7017-7039, 2010.
- Lin, X., Trainer, M., and Liu, S. C.: On the nonlinearity of the tropospheric ozone production, *Journal of Geophysical Research: Atmospheres*, 93, 15879-15888, 10.1029/JD093iD12p15879, 1988.
- Lin, Y.-L., Farley, R. D., and Orville, H. D.: Bulk parameterization of the snow field in a cloud model, *Journal of Climate and Applied Meteorology*, 22, 1065-1092, 1983.
- 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.
- Malhi, Y., Roberts, J. T., Betts, R. A., Killeen, T. J., Li, W., and Nobre, C. A.: Climate change, deforestation, and the fate of the Amazon, *science*, 319, 169-172, 2008.
- Martin, S., Andreae, M., Althausen, D., Artaxo, P., Baars, H., Borrmann, S., Chen, Q., Farmer, D., Guenther, A., and Gunthe, S.: An overview of the Amazonian Aerosol Characterization Experiment 2008 (AMAZE-08), *Atmos. Chem. Phys.*, 10, 415-438, 2010.
- Martin, S., Artaxo, P., Machado, L., Manzi, A., Souza, R., Schumacher, C., Wang, J., Biscaro, T., Brito, J., and Calheiros, A.: The Green Ocean Amazon Experiment

- (GoAmazon2014/5) Observes Pollution Affecting Gases, Aerosols, Clouds, and Rainfall over the Rain Forest, *Bulletin of the American Meteorological Society*, 2016a.
- Martin, S. T., Artaxo, P., Machado, L. A. T., Manzi, A. O., Souza, R. A. F., Schumacher, C., Wang, J., Andreae, M. O., Barbosa, H. M. J., Fan, J., Fisch, G., Goldstein, A. H., Guenther, A., Jimenez, J. L., Pöschl, U., Silva Dias, M. A., Smith, J. N., and Wendisch, M.: Introduction: Observations and Modeling of the Green Ocean Amazon (GoAmazon2014/5), *Atmos. Chem. Phys.*, 16, 4785-4797, 10.5194/acp-16-4785-2016, 2016b.
- Martins, J. A., Rocha, C. R. M., Oliveira, M. G. L., Ynoue, R. Y., Andrade, M. F., Freitas, E. D., and Martins, L. D.: Desenvolvimento de inventários de emissão de alta resolução: Intensidades de luzes noturnas e distribuição espacial de veículos., XVI CBMET, 2010.
- Mena-Carrasco, M., Oliva, E., Saide, P., Spak, S. N., de la Maza, C., Osses, M., Tolvett, S., Campbell, J. E., Tsao, T. e. C.-C., and Molina, L. T.: Estimating the health benefits from natural gas use in transport and heating in Santiago, Chile, *Science of The Total Environment*, 429, 257-265, <http://dx.doi.org/10.1016/j.scitotenv.2012.04.037>, 2012.
- Misenis, C., and Zhang, Y.: An examination of sensitivity of WRF/Chem predictions to physical parameterizations, horizontal grid spacing, and nesting options, *Atmospheric Research*, 97, 315-334, 2010.
- Mlawer, E. J., Taubman, S. J., Brown, P. D., Iacono, M. J., and Clough, S. A.: Radiative transfer for inhomogeneous atmospheres: RRTM, a validated correlated-k model for the longwave, *Journal of Geophysical Research: Atmospheres* (1984–2012), 102, 16663-16682, 1997.
- Molina, L. T., Madronich, S., Gaffney, J., Apel, E., Foy, B. d., Fast, J., Ferrare, R., Herndon, S., Jimenez, J. L., and Lamb, B.: An overview of the MILAGRO 2006 Campaign: Mexico City emissions and their transport and transformation, *Atmospheric Chemistry and Physics*, 10, 8697-8760, 2010.
- Neiva, L., and Gama, L.: The importance of natural gas reforming, INTECH Open Access Publisher, 2010.
- Nobre, C. A., Sampaio, G., Borma, L. S., Castilla-Rubio, J. C., Silva, J. S., and Cardoso, M.: Land-use and climate change risks in the Amazon and the need of a novel sustainable

- development paradigm, *Proceedings of the National Academy of Sciences*, 113, 10759-10768, 2016.
- Paula, F. S., Rodrigues, J. L. M., Zhou, J., Wu, L., Mueller, R. C., Mirza, B. S., Bohannan, B. J. M., Nüsslein, K., Deng, Y., Tiedje, J. M., and Pellizari, V. H.: Land use change alters functional gene diversity, composition and abundance in Amazon forest soil microbial communities, *Molecular Ecology*, 23, 2988-2999, 10.1111/mec.12786, 2014.
- PETROBRAS: Operations of Isaac Sabba's Refinery: <http://www.petrobras.com.br/pt/nossas-atividades/principais-operacoes/refinarias/refinaria-isaac-sabba-reman.htm>, access: 07 dec, 2016.
- Potter, C., Klooster, S., Carvalho, C. R., Genovese, V. B., Torregrosa, A., Dungan, J., Bobo, M., and Coughlan, J.: Modeling seasonal and interannual variability in ecosystem carbon cycling for the Brazilian Amazon region, *Journal of Geophysical Research: Atmospheres*, 106, 10423-10446, 2001.
- Price, D.: Energy and human evolution, *Population and Environment*, 16, 301-319, 1995.
- Queiroz, D.: Zona Franca de Manaus está oficialmente prorrogada até 2073: <http://site.suframa.gov.br/noticias/zona-franca-de-manaus-esta-oficialmente-prorrogada-ate-2073>, access: 15 oct 2016, 2014.
- Rafee, S. A. A., Kawashima, A. B., de Moraes, M. V. B., Urbina, V., Martins, L. D., and Martins, J. A.: Assessing the Impact of Using Different Land Cover Classification in Regional Modeling Studies for the Manaus Area, Brazil, *Journal of Geoscience and Environment Protection*, 3, 77, 2015.
- Rafee, S. A. A., Kawashima, A. B., Almeida, D. S., Urbina, V., Moraes, M. V. B., Souza, R. V. A., Oliveira, M. B. L., Souza, R. A. F., Medeiros, A. S. S., Freitas, E. D., Martins, D. L., and Martins, J.: Mobile and stationary sources of air pollutants in the Amazon rainforest: a numerical study with WRF-Chem model, submitted, *Atmos. Chem. Phys*, 2017.
- Ramos, A. M., dos Santos, L. A. R., and Fortes, L. T. G.: Normais climatológicas do Brasil, 1961-1990, 2009.
- Saha, S., Moorthi, S., Wu, X., Wang, J., Nadiga, S., Tripp, P., Behringer, D., Hou, Y.-T., Chuang, H.-y., Iredell, M., Ek, M., Meng, J., Yang, R., Mendez, M. P., van den Dool, H., Zhang, Q., Wang, W., Chen, M., and Becker, E.: NCEP Climate Forecast System Version 2 (CFSv2) 6-hourly Products, in, *Research Data Archive at the National Center for*

- Atmospheric Research, Computational and Information Systems Laboratory, Boulder, CO, 2011.
- Schikowski, T., Mills, I. C., Anderson, H. R., Cohen, A., Hansell, A., Kauffmann, F., Krämer, U., Marcon, A., Perez, L., Sunyer, J., Probst-Hensch, N., and Künzli, N.: Ambient air pollution: a cause of COPD?, *European Respiratory Journal*, 43, 250-263, 10.1183/09031936.00100112, 2014.
- Seinfeld, J. H., and Pandis, S. N.: *Atmospheric Chemistry and Physics: From air pollution to Climate Change*, Second Edition ed., 2006.
- Shukla, J., Nobre, C., and Sellers, P.: Amazon deforestation and climate change, *Science(Washington)*, 247, 1322-1325, 1990.
- Silva Junior, R. S. d., and Andrade, M. d. F.: Prediction of photochemical pollutants in metropolitan area of São Paulo using air quality model (WRF/CHEM) and the CETESP pollutants emission inventory, *Revista Brasileira de Meteorologia*, 28, 105-121, 2013.
- Soares, P. M., Berni, M. D., and Manduca, P. C.: O petróleo é nosso: avaliação do potencial região do Urucu-AM e principais desafios, *RIT-REVISTA INOVAÇÃO TECNOLÓGICA*, 4, 64-77, 2014.
- Stark, S. C., Enquist, B. J., Saleska, S. R., Leitold, V., Schiatti, J., Longo, M., Alves, L. F., Camargo, P. B., and Oliveira, R. C.: Linking canopy leaf area and light environments with tree size distributions to explain Amazon forest demography, *Ecology Letters*, 18, 636-645, 10.1111/ele.12440, 2015.
- 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.
- Tundisi, J. G.: Exploração do potencial hidrelétrico da Amazônia, *Estudos avançados*, 21, 109-117, 2007.
- Vitousek, P. M., Mooney, H. A., Lubchenco, J., and Melillo, J. M.: Human domination of Earth's ecosystems, *Science*, 277, 494-499, 1997.
- Wertz-Kanounnikoff, S., Kongphan-Apirak, M., and Wunder, S.: Reducing forest emissions in the Amazon Basin: a review of drivers of land-use change and how payments for environmental services (PES) schemes can affect them, Bogor, Indonesia: Center for International Forestry Research (CIFOR), 2016.

- WHO: Air quality for particulate matter, ozone, nitrogen dioxide and sulphur dioxide: global update 2005, 2006.
- Wright, S. J.: Tropical forests in a changing environment, *Trends in Ecology & Evolution*, 20, 553-560, <http://dx.doi.org/10.1016/j.tree.2005.07.009>, 2005.
- 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.
- Ying, Z., Tie, X., and Li, G.: Sensitivity of ozone concentrations to diurnal variations of surface emissions in Mexico City: A WRF/Chem modeling study, *Atmospheric Environment*, 43, 851-859, 2009.

List of Figures

Figure 1. Satellite image of the land cover of the study region. Manaus, located at 3.1° S and 60.0° W, is visible in the center. Power plants (red markers) and an oil refinery (blue marker) are indicated (cf. Table 2). The white box represents the region of $10\text{ km} \times 10\text{ km}$ that is used for the analyses in Figures 2, 3 (black box), and 4. The Solimões River, running from the west to the east, is visible in brown. This river has turbid waters laden with sediment. The Rio Negro River is a main tributary. It is visible in black, running from the northwest to southeast. The named Amazon River (Portuguese) is the confluence of these two flows nearby Manaus. In the top left of the figure, the two grids used in the modeling are shown. The outer grid has corners of $\{5.10^{\circ}\text{ S}, 63.14^{\circ}\text{ W}\}$ and $\{0.73^{\circ}\text{ S}, 57.48^{\circ}\text{ W}\}$. The inner grid has corners of $\{3.63^{\circ}\text{ S}, 61.26^{\circ}\text{ W}\}$ and $\{2.16^{\circ}\text{ S}, 59.36^{\circ}\text{ W}\}$. The latitude-longitude corners of the main panel are the same as inner grid.

Figure 2. Box-whisker plot of near-surface ozone concentrations for historic emissions (Case A), present-day emissions (Case B), and planned future emissions (Case C). On each day of the simulated month, the time period for the statistical analysis corresponds to 12:00 and 16:00 of the afternoon. The region of areal averaging is $10\text{ km} \times 10\text{ km}$ centered on 3.1° S and 60.0° W (boxed regions of Figures 1 and 3). The bottom and top of the blue boxes correspond to the first and third quartiles, respectively. The red line inside the box is the median. The whiskers represent the full range of values

excluding outliers. The red crosses show outliers, as defined by more than 1.5 times the interquartile range.

Figure 3. Maps of near-surface ozone concentrations for historic emissions (Case A), present-day emissions (Case B), and planned future emissions (Case C). Ozone concentrations correspond to 15:00 (local time) near the surface for the meteorology of February 1, 2014. The local river system is shown in the background. The black box, centered over the population center of Manaus, represents the averaging area used in the **box-whisker plots of Figures 2 and 4.**

Figure 4. Difference analysis for historic compared to planned future emissions (i.e., Case A minus Case C). (left) Difference map of ozone concentrations (cf. Figure 3). (right) Box-whisker plot of differences in afternoon ozone concentrations during the one-month time series (cf. Figure 2).

Table 1. Manaus transportation fleet. Percent composition, daily travel distance, and emission factors are listed for different vehicle types in 2014 (ANP, 2014).

Type (fuel)	%	Daily travel distance (km)	CO (g km ⁻¹)	NO _x (g km ⁻¹)
Light vehicles (gasoline)	21.6	48.2	5.43	0.34
Light vehicles (ethanol)	2.5	48.2	12.0	1.12
Light vehicles (flex)	42.1	48.2	5.13	0.32
Urban bus (diesel)	1.9	208.3	4.95	9.81
Trucks (diesel)	3.2	304.7	4.95	9.81
Pickup trucks (diesel)	3.9	49.9	4.95	9.81
Motorcycles (gasoline)	24.8	27.9	9.15	0.13

Table 2. Power plant information in the study region in 2014. Numbered pins in Figure 1 correspond to the power plants listed here. Plant name, the fuel mix for Cases A, B, and C, the **annual electricity generated**, the **nameplate power capacity**, the **capacity factor**, and the plant location are listed. Fuel types are abbreviated as fuel oil (F), diesel (D), and natural Gas (G) (ELETTROBRAS, 2014b). In addition to these plants, there is a hydroelectric power plant (Balbina) that is 140 km north of Manaus {1.91° S, 59.57° W}. The **annual electricity generated was 2.19×10^9 kWh for a nameplate power capacity of 250 MW** (Fearnside, 2005). In 2013, Manaus became linked to the Brazilian national grid (ANEEL, 2013).

Power Plant	Case A	Case B	Case C	Electricity	Nameplate	Capacity	Location
				Generated (10^8 kWh)	Power Capacity (MW)	Factor	
1 Aparecida	D	D (5%) / G (95%)	G	11.80	200.0	0.68	{3.13° S, 60.03° W}
2 Mauá / Electron	F / D	F (7.8%) / G (35.6%) / D (56.6%)	G	22.40	728.9	0.35	{3.12° S, 59.93° W}
3 Flores	D	D	G	3.63	94.6	0.44	{3.07° S, 60.02° W}
4 Cidade Nova	D	D	G	0.75	22.8	0.38	{3.03° S, 59.97° W}
5 São José	D	D	G	1.58	60.9	0.30	{3.06° S, 59.95° W}
6 Iranduba		D	G	1.92	54.7	0.40	{3.20° S, 60.17° W}
7 Breitenr Tambaquí	F	G	G	5.42	60.0	1.03	{3.11° S, 59.94° W}
8 Breitenr Jaraguí	F	G	G	5.39	60.0	1.03	{2.99° S, 60.03° W}
9 Ponta Negra	F	G	G	5.70	60.0	1.09	{3.09° S, 60.07° W}
10 Manausara	F	F (10.9%) / G (89.1%)	G	5.63	60.0	1.07	{2.95° S, 60.02° W}
11 Cristiano Rocha Refinery	F	F (10.5%) / G (89.5%)	G	5.96	65.0	1.05	{2.89° S, 60.03° W}
Total				70.20	1,466.9		{3.14° S, 59.96° W}

Table 3. Emission factors of CO and NO_x for consumption of fuel oil, diesel, and natural gas in electricity production and refinery operations, obtained as median values from the US EPA (1998) (DeLuchi, 1993). The fuel consumption factor for electricity production is also listed (ELETROBRAS, 2014b).

	Fuel oil (g L ⁻¹)	Diesel (g L ⁻¹)	Natural gas (g m ⁻³)	Refinery (g L ⁻¹)
CO	0.60	3.65	0.97	0.45
NO _x	3.90	36.20	2.50	0.56
Fuel Consumption	0.29 (L kWh ⁻¹)	0.38 (L kWh ⁻¹)	0.25 (m ³ kWh ⁻¹)	

Table 4. Emissions of carbon monoxide (CO) and nitrogen oxides (NO_x) by vehicles, power plants, and refinery. Values are shown for historic emissions (Case A), present-day emissions (Case B), and planned future emissions (Case C). Values are based on pre-processing chemistry emissions as described in methodology. The percent reduction in total emissions relative to Case A is shown in parentheses for Cases B and C.

	Case A (kg day ⁻¹)	Case B (kg day ⁻¹)	Case C (kg day ⁻¹)
CO (vehicles)	800	800	800
CO (diesel power plants)	11,600	6,100	0
CO (fuel oil power plants)	1,700	200	0
CO (natural gas power plants)	0	3,100	4,600
CO (refinery)	1,800	1,800	1,800
Total CO	15,900	12,000 (-25%)	7,200 (-55%)
NO _x (vehicles)	400	400	400
NO _x (diesel power plants)	115,500	40,700	0
NO _x (fuel oil power plants)	11,400	1,200	0
NO _x (natural gas power plants)	0	7,800	12,000
NO _x (refinery)	2,100	2,100	2,100
Total NO_x	129,400	52,200 (-60%)	14,500 (-89%)

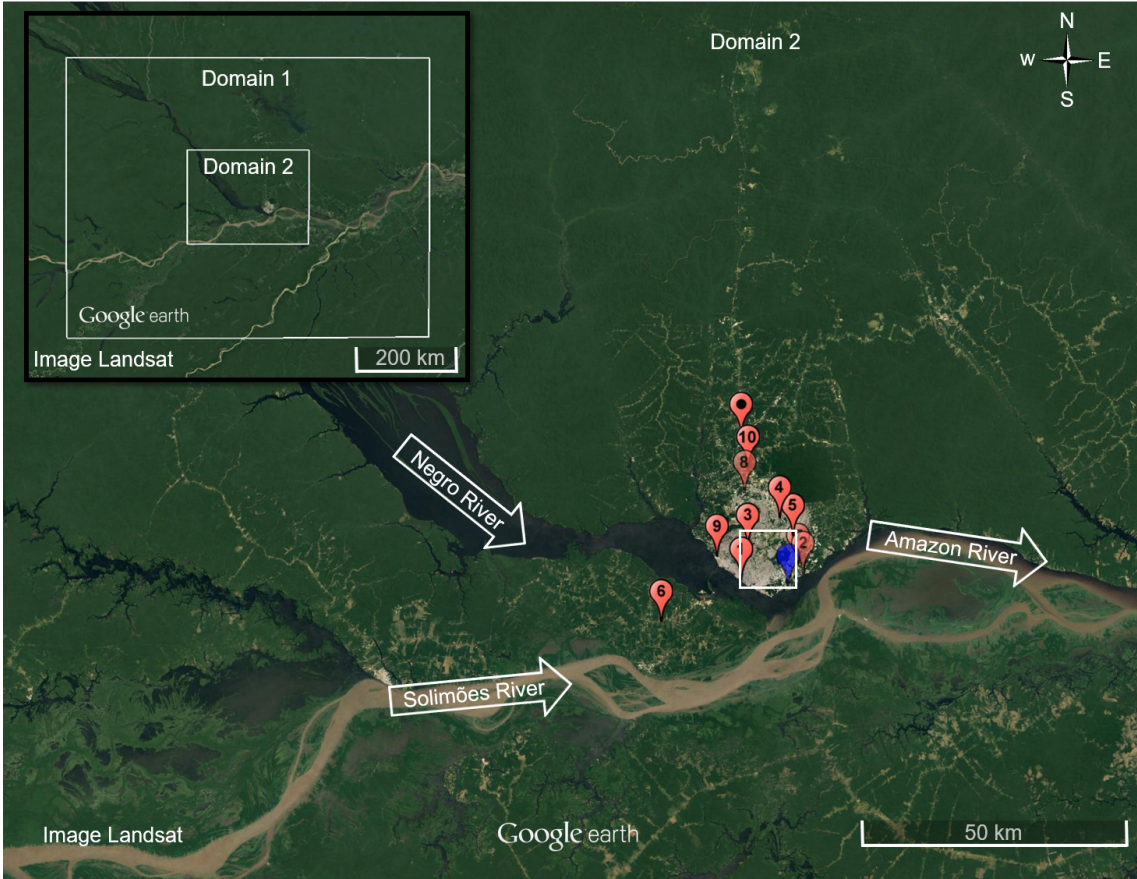


Figure 1

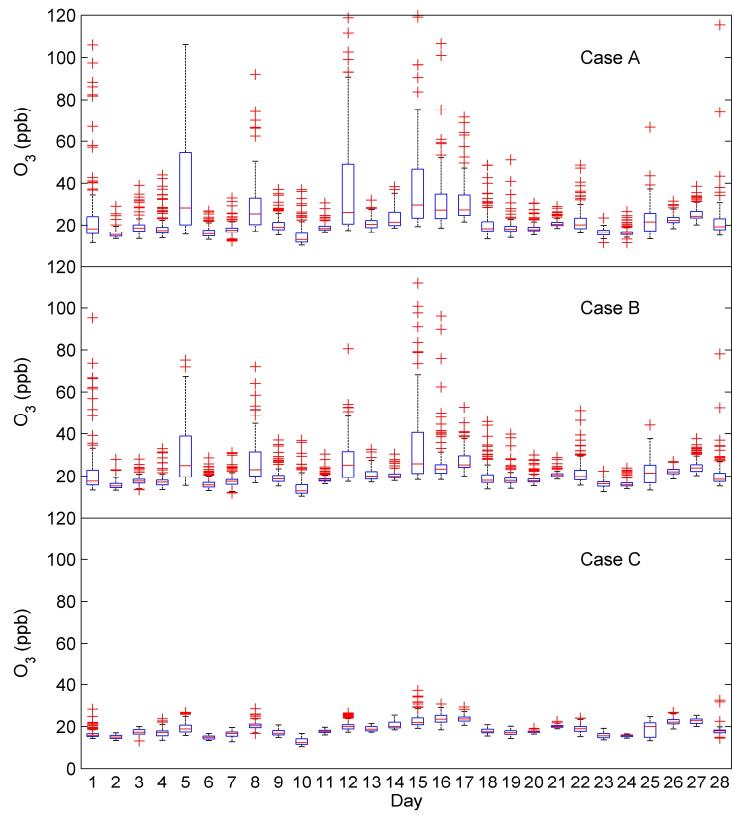


Figure 2

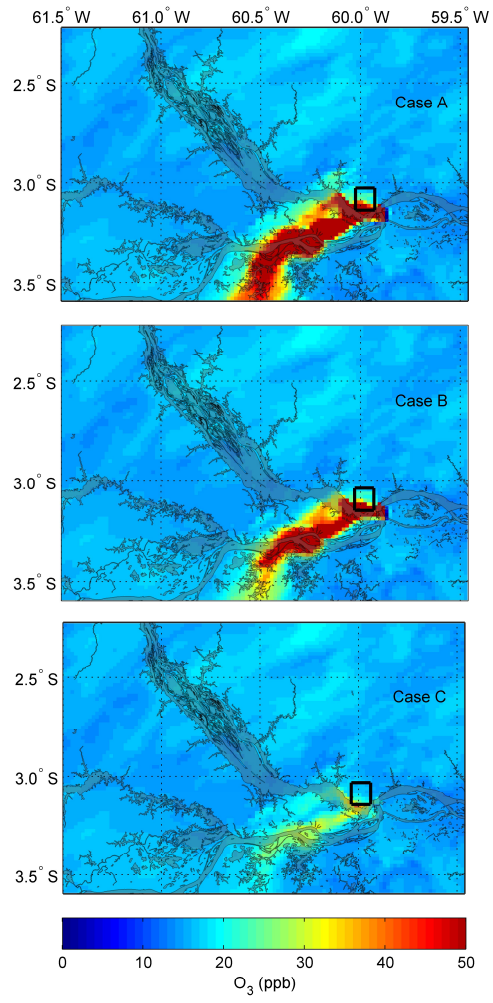


Figure 3

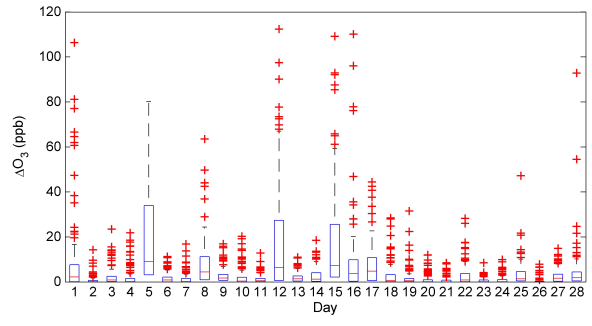
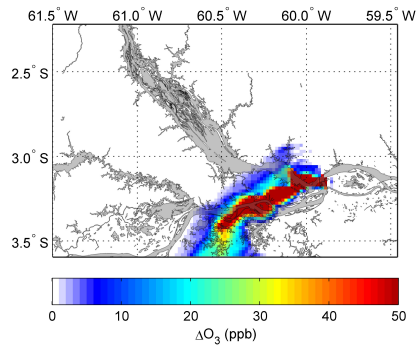


Figure 4