

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, refinery 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, 2008a), in today's Amazon region,
30 constituting the largest tropical forest in the world (Behling et al., 2001), electricity is largely
31 produced by fossil fuel power plants (ELETROBRAS, 2014a). Sulfur-laden oil and diesel are the
32 historical fuels. The Amazon region is of vital importance for the functioning of both regional
33 ecosystems and climate (Fisch et al., 1998;Nobre et al., 2016). Topics for research in recent years
34 have included the relationship between the biosphere and the atmosphere in the Amazon (Fan et
35 al., 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., 2016).

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

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

118 **2. Model Description**

119 **2.1 WRF-Chem**

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

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

139 Meteorological fields were obtained from re-analysis data of the National Center for
140 Environmental Prediction (NCEP) at a spatial resolution of $0.5^\circ \times 0.5^\circ$ and a time resolution of 6
141 h from February 1 to 28, 2014. NCEP data are based on the Climate Forecast System Reanalysis
142 (Saha et al., 2011). Land cover was based on data from the Moderate Resolution Imaging
143 Spectroradiometer (MODIS) (Rafee et al., 2015). The climatology has differences between dry
144 and wet seasons, with minimum values of monthly precipitation reached in August (47 mm) and
145 maximum values found in March (335 mm) (Ramos et al., 2009). The month considered herein
146 (February) has a climatological average of 290 mm. For February 2014, there was a deficit of
147 21.5% for meteorological stations in Manaus (Figure S1), with high precipitation above 20 mm
148 on five days. The February deficit might correlate with a shifted position of the Bolivian high to
149 the west of its normal position. This anticyclonic circulation at high atmosphere is associated
150 with latent heat release during austral summer (Silva Dias et al., 1983; Jones and Horel, 1990).
151 By comparison, the Intertropical Convergence Zone (ITCZ) was at its climatological position in
152 February 2014, and exceptional events related to the South Atlantic Convergence Zone (SACZ)
153 or other frontal systems in the region were absent (CPTEC-INPE, 2014).

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

161

162 **2.2 Emissions**

163 Forest, vehicle, power plant, and refinery emissions were considered. Biogenic emissions
164 from the forest were based on the Model of Emissions of Gases and Aerosols from Nature
165 (MEGAN, version 2.1) (Guenther et al., 2012). MEGAN varies emissions taking into account the
166 type of vegetation, the seasonality based on temperature and leaf area index (LAI), the intensity
167 of incident light, and the soil moisture. It considers 150 different compounds. Approximate
168 biogenic emissions for Domain 2 were 50% as isoprene, 30% as methanol, ethanol,
169 acetaldehyde, acetone, α -pinene, β -pinene, t- β -ocimene, limonene, ethane, and propene, 17% as
170 another twenty compounds (mostly terpenoids), and 3% as another 100 compounds. During the
171 wet season, regional contributions by biomass burning to ozone precursors are considered
172 negligible (Martin et al., 2016).

173 For vehicle emissions, a vehicle count for Manaus of 600,000 was considered
174 (DENATRAN, 2014). The breakdown of vehicle by type, daily travel distances, and emission
175 factors is listed in Table 1 (ANP, 2014). The Manaus fleet has an average age of 5 years. This
176 relatively young age can be attributed to the timing of rapid urban growth coupled to a vast
177 increase in vehicle ownership during an explosive economic expansion period from 2009 to
178 2015. The methodology of Martins et al. (2010) was used to distribute the vehicle emissions
179 spatially based on night-time light intensity observations of the Defense Meteorological Satellite
180 Program - Operational Linescan System (DMSP-OLS). These observations were assumed to
181 correlate with overall daily patterns of vehicle traffic. Additional information about this
182 methodology is described in Andrade et al. (2015)

183 For stationary sources related to electricity production, a survey of the locations of power
184 plants in Manaus region was conducted. Although the city of Manaus has a large industrial park,

185 these industries mostly produce electronic products and burn little fuel directly. Instead, power
186 plants and a large refinery are major emitters. The data of installed capacity, generated
187 electricity, and fuel used were obtained for each plant (Table 2). The locations of these power
188 plants are shown in Figure 1. The emission factors for electricity production by fuel type were
189 based on the database of the USA Environmental Protection Agency (EPA) using the median
190 value of the emission factors (Table 3). The fuel consumption factor for electricity production is
191 also listed in Table 3 (ELETROBRAS, 2014b). Another major source of pollution in the region
192 was the refinery Isaac Sabbá, with the capacity to process 7.3×10^6 liters of oil per day
193 (PEROBRAS, 2016). The emission factors of refinery operations are listed in Table 3 (DeLuchi,
194 1993)

195 **2.3 Scenarios**

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

207 energy uninterruptedly at full load throughout the year, with contractual arrangements with
208 industry to idle when residential demand increases.

209 In order to compare only the effects of the change in the type of fuel used, the same
210 matrix of power plants was used for the three scenarios. Although the combined capacity of
211 electricity production increased in recent years following the population and energy demand
212 growth, this change was omitted so the comparative study of the effects of fuel type on air
213 quality could be isolated. Likewise, vehicle emissions were held constant for the three fuel
214 scenarios considered herein to focus on effects of power plant fuel switching in a tropical
215 context. In this regard, the intent of the analysis herein was to represent the effects of power
216 plant fuel switching on air quality in a tropical forested environment in a general yet realistic
217 sense by selection of a representative urban environment. The intent was not an actual simulation
218 of the city of Manaus, which would necessitate adjustment of transportation, industry, power,
219 land use, and other aspects of urban growth corresponding to the year of each case. The study
220 herein was also restricted to the wet season, again to focus on shifts in the energy matrix and
221 avoid the complicating effects of biomass burning prevalent in the dry season.

222 The emissions of CO and NO_x by source are listed in Table 4 for Cases A, B, and C.
223 Power plant emissions constitute 84%, 78%, and 64% of urban CO emissions for Cases A, B,
224 and C, respectively. For NO_x, they constitute 98%, 95%, and 82%, respectively. The high percent
225 contribution by power plant emissions arises from a combination of the (i) old technology used
226 in the plants (i.e., no pollution controls) and low-end fuels and (ii) the young age of the modern
227 vehicle fleet using high-end fuels. From Case A to B, total CO and NO_x emissions decrease by
228 25% and 60%, respectively. From Case A to C, the respective reductions are 55% and 89%.

229 **3. Results and Discussion**

230 Figure 2 shows a box-whisker plot of ozone concentrations for all afternoons for each
231 case. The time period of 12:00 to 16:00 (local time) was selected for analysis because it
232 represents the maximum ozone concentration, which is fundamentally linked to photochemistry.
233 For the statistical analysis of Figure 2, an area of 10 km × 10 km centered on Manaus was taken
234 to assess ozone concentrations in the populated urban area. The black box in Figure 3 represents
235 this region. The analysis represented in Figure 2 shows that within a single case ozone
236 concentrations had large differences throughout the simulated month. These day-to-day
237 differences arose largely because of variability in cloudiness and other meteorological
238 components of the simulation. Some days were sunny, favoring the photochemical process of
239 ozone formation, whereas other days were overcast or rainy.

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

248 A comparison between measurements of NO_x and O₃ onboard the G-1 aircraft over and
249 downwind of Manaus during GoAmazon2014/5 and simulation results is presented in Figure S2
250 for Case B. Figure S2a shows agreement between median and interquartile ranges of observed
251 and simulated NO_x concentrations. These concentrations above the natural regional background

252 arise as primary pollutant in Manaus emissions. Likewise, simulated O₃ concentrations also show
253 good agreement with aircraft data (Figure S2b). Ozone is a secondary pollutant, and the
254 agreement supports the validity of the emission inventory of ozone precursors and the chemical
255 mechanisms used in the simulation. Overall, the comparison shows that the simulations
256 satisfactorily represent average regional afternoon concentrations of NO_x and O₃. A companion
257 study by Rafee et al. (2017) focuses on the comparison of simulated and measured pollutant
258 concentrations for GoAmazon2014/5.

259 Figure 3 shows examples of the spatial distribution of ozone concentration for each of
260 Cases A, B, and C for the single afternoon of February 1, 2014. Spatial distributions of the mean
261 of afternoon values and their standard deviation across the full month of simulation are shown in
262 Figure S3 of the Supplement. The ozone plume spreads downwind from Manaus carried by the
263 easterlies of the equatorial trade winds, in agreement with observations reported by Kuhn et al.
264 (2010), Martin et al. (2016), and Martin et al. (2017). The map shows that the pollution associated
265 with Manaus emissions not only affects local air quality of the urban population but also reaches
266 other regional downwind population centers, such as Careiro, Iranduba, and Manacapuru. The
267 qualitative spatial pattern of the ozone plume is similar among Cases A, B, and C, as explained
268 by the use of identical meteorology. The concentrations, however, have strong differences. From
269 Case A to B, the concentrations inside the plume do not differ greatly, in agreement with the
270 box-whisker representation in Figure 2. For Case C, the ozone footprint and concentrations
271 decrease greatly, both for the Manaus urban region and even more so for downwind populations,
272 reinforcing the important impact of the fuel switch.

273 Figure 4 presents a difference analysis between historical practices (i.e., Case A) and
274 future plans (i.e., Case C) to finalize the foregoing points related to Figures 2 and 3. The

275 difference analysis represents a shift in the entire energy matrix for electricity production from
276 oil and diesel to that of natural gas. The left panel of Figure 4 shows the difference map for a
277 single day corresponding to the plots of Figure 3. Ozone concentrations decrease by
278 approximately 50 ppb in the center of the plume. The right panel shows a box-whisker plot of
279 difference values in the afternoon period across the month, corresponding to the plots of Figure
280 2. Days 1, 5, 8, 12, 15, and 16 had the highest differences between the two scenarios, indicating
281 that these days were the sunniest and most polluted. For the other days of the month, the median
282 difference approached zero, indicating that these days were overcast or had high levels of
283 convection that brought in clean air. The observed daily rain amounts (Figure S1) show that the
284 days of highest ozone concentrations corresponded to days of low or no precipitation (<5 mm).
285 Conversely, the days of highest precipitation (>20 mm) and cloudiness had nearly background
286 ozone concentrations.

287 For comparative studies, Collins et al. (1997) investigated the effects of a decrease in
288 NO_x emissions on ozone concentrations over Europe. The study reported that in summer a
289 decrease of 50% in NO_x emissions resulted in a reduction of ozone by 10 to 20%. A reduction in
290 NO_x emissions in the winter, however, had an opposite effect, increasing the ozone by over 40%.
291 These differing results are explained by the dominance of NO₂ as a source of ozone production
292 in the summer but the dominance of NO as sink to ozone in the winter. Frost et al. (2006)
293 performed evaluated the effects of NO_x emissions from power plants on ozone concentrations in
294 the eastern United States. The relationship between emissions reduction and ozone
295 concentrations was complex, depending on upwind NO_x concentrations. For low upwind
296 concentrations, a decrease in NO_x emissions reduced ozone whereas for high upwind
297 concentrations an equal decrease in NO_x emissions resulted in smaller reductions in ozone or

298 even at times increases in O₃. Mena-Carrasco et al. (2012) studied the effects of using natural gas
299 instead of diesel with respect to air quality and human health. The study, carried out for
300 Santiago, Chile, a region of Mediterranean climate, showed that substitution of natural gas for
301 diesel could reduce drastically the emissions and concentrations of particulate matter, which like
302 ozone is another important metric of air quality.

303 In summary, the results presented herein show that an altered energy matrix significantly
304 influences air quality, as gauged by the maximum afternoon ozone concentration. The
305 relationship between the Manaus emissions and the vast biogenic emissions of the surrounding
306 forest constitutes an important scenario to study feedback connections in atmospheric chemistry.
307 The large differences between Cases A and C show that the burning of fuel oil and diesel has a
308 dominant role in regional ozone production. Conversely, substitution by natural gas greatly
309 improves the outlook for regional air quality and human health. In this context, even though
310 anthropogenic emissions in Amazon region are low compared to other regions of the world, such
311 as Mexico City (Molina et al., 2010), São Paulo (Silva Junior and Andrade, 2013), and Los
312 Angeles (Hassler et al., 2016), the study results of Figure 4 demonstrate the significant
313 sensitivity of Amazonia to anthropogenic emissions. The results emphasize the high sensitivity
314 of the atmospheric chemistry over the tropical forest to pollution, as amplified by the high solar
315 irradiance and water vapor concentrations in an environment of plentiful biogenic VOC
316 emissions. Specifically, the significant decrease in NO_x emissions from Case A to B resulted in
317 no strong differences in ozone concentrations whereas, conversely, the smaller increase from
318 Case C to B resulted in large ozone production. This nonlinear behavior of ozone concentration
319 with respect to pollution is linked to the chemical cycles of the ozone production, more
320 specifically to the domain of NO_x limitation or not (Lin et al., 1988). The results herein suggest

321 that the anticipated coming complete conversion to natural gas for electricity production should
322 significantly reduce ozone concentration in the Manaus urban region. The GoAmazon2014/5
323 experiment occurred during two years of this ten-year transition in the energy matrix (Martin et
324 al., 2016). Smaller municipalities throughout the Amazon basin, which is two-thirds the size of
325 the continental USA, continue to burn sulfur-laden oil and diesel for electricity production.
326 Further changes in the energy matrix of Amazonia are dependent on continued development of
327 infrastructure for use of natural gas or making connections to the national grid and continued
328 developments in the use of hydropower, even as the population of Amazonia continues to grow
329 rapidly (Domingues, 2003;Tundisi, 2007;ANEEL, 2008b).

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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) (ELETROBRAS, 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	D	D (5%) / G (95%)	G	11.80	200.0	0.68	{3.13° S, 60.03° W}
2	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	D	D	G	3.63	94.6	0.44	{3.07° S, 60.02° W}
4	D	D	G	0.75	22.8	0.38	{3.03° S, 59.97° W}
5	D	D	G	1.58	60.9	0.30	{3.06° S, 59.95° W}
6	Iranubua	D	G	1.92	54.7	0.40	{3.20° S, 60.17° W}
7	Breitener Tambiqui	F	G	5.42	60.0	1.03	{3.11° S, 59.94° W}
8	Breitener Jaraguí	F	G	5.39	60.0	1.03	{2.99° S, 60.03° W}
9	Ponta Negra	F	G	5.70	60.0	1.09	{3.09° S, 60.07° W}
10	Manauara	F	F (10.9%) / G (89.1%)	G	60.0	1.07	{2.95° S, 60.02° W}
11	Cristiano Rocha Refinery	F	F (10.5%) / G (89.5%)	G	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%)

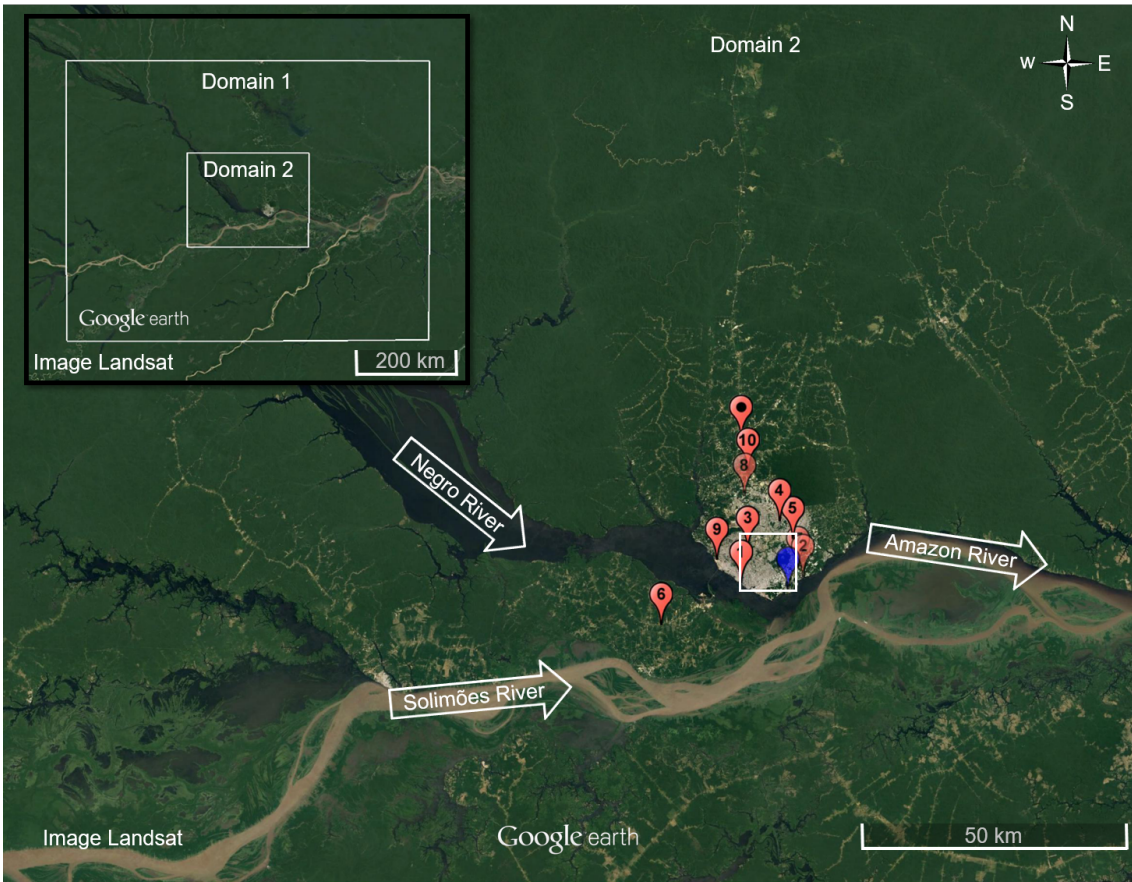


Figure 1

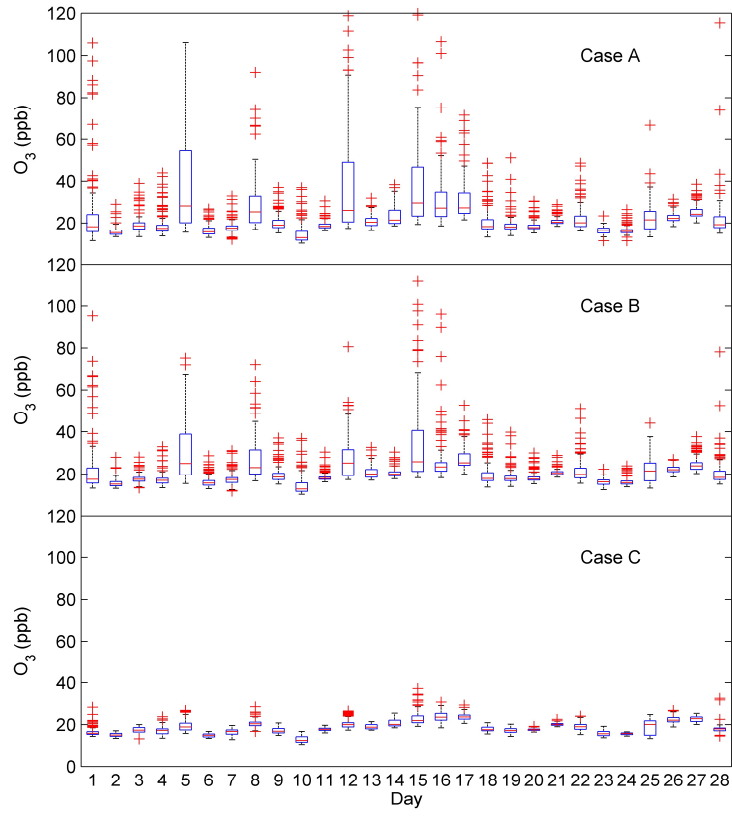


Figure 2

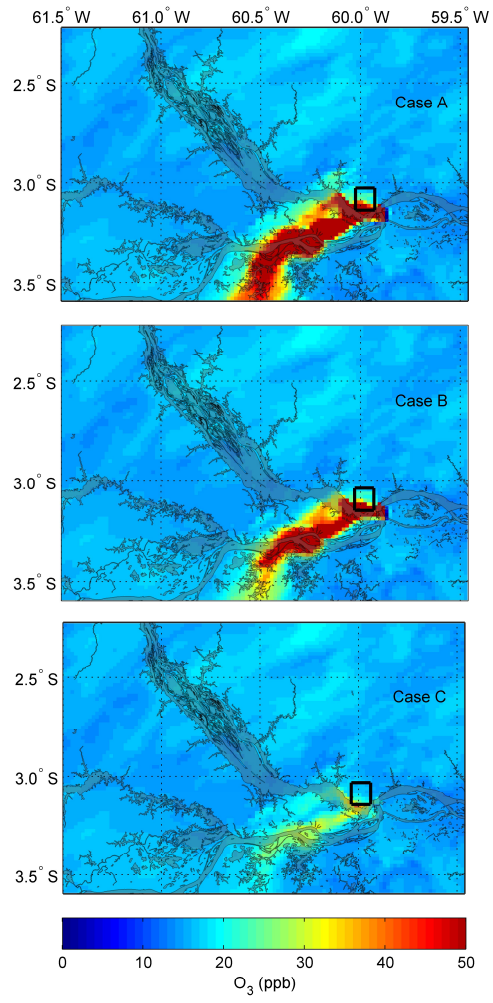


Figure 3

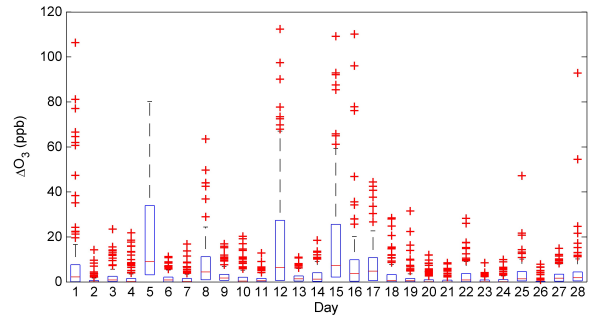
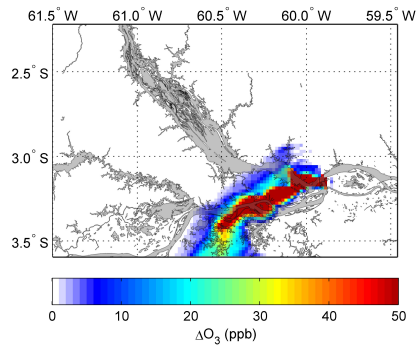


Figure 4