

Sensitivity analysis of tropospheric ozone to modified biogenic emissions for the Mid-Atlantic region

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Abstract

Biogenic sources contribute a large portion of emissions of volatile organic compounds (VOCs), a precursor to tropospheric ozone (O₃). These emissions are difficult to control and are affected by land-use and climate. A sensitivity analysis was performed using an emissions scenario with a 100% increase in biogenic emissions and another scenario with an additional 100% increase in motor vehicle emissions. Meteorological and air pollution models were used to generate hourly ozone estimates for a case study high ozone episode. Resulting concentration estimates correspond to the total effect of changes from emissions, incorporating the interaction between anthropogenic and biogenic emissions.

Biogenic VOCs had a greater impact than a comparable percent increase in motor vehicle emissions of ozone precursors, in this case study. The 100% increase in biogenic VOC emissions raised ozone levels, with an estimated maximum 1-h concentration 30% higher than that of the baseline scenario. The additional emissions of ozone precursors from motor vehicles raised the maximum 1-h concentration 40% over that of the baseline. The largest increases in ozone concentrations occurred near peak values. Urban areas had larger increases in ozone levels than rural regions. Both adjusted emissions scenarios resulted in ozone concentrations lower than that of the baseline for some estimates. These reductions occurred near low ozone levels however and were generally small.

This research demonstrates the importance of biogenic VOC emissions in ozone formation for this region and of biogenic emissions inventories. Results also imply that climate change-induced increases in biogenic VOC emissions could significantly impact ozone concentrations.

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1. Introduction

Controlled human exposure, animal toxicology, and epidemiological studies have identified associations between tropospheric ozone (O₃) and several human health endpoints including increased respiratory symptoms and decreased lung function (EPA, 1996). The

Clean Air Act and associated regulations have substantially improved air quality, yet ozone remains an important health concern.

Ozone is formed through complex reactions involving sunlight, nitrogen oxides (NO_x), and volatile organic compounds (VOCs). The concentration of O₃ in a given area depends on many factors including temperature, meteorology, and the presence of precursors. High levels of ozone are associated with high temperatures as the chemical reactions are temperature dependent. Due to this complex chemistry, increases in either NO_x or VOCs could potentially result in decreased ozone levels,

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depending on the initial concentrations of precursors and the region's ozone isopleth plot (Seinfeld and Pandis, 1998).

Biogenic emissions of VOCs are important for several reasons. They are difficult to control and could be affected by global warming. Their true emission rates are difficult to estimate. Global warming could impact tropospheric ozone through: (1) increased temperature, which affects biogenic emissions and the reactions forming tropospheric ozone; (2) additional altered weather patterns such as wind speed and direction, precipitation, and clouds; and (3) increased anthropogenic emissions from increased energy demand (e.g., greater use of air conditioning) (Bernard et al., 2001; McCarthy et al., 2001). Increased temperatures could also alter emissions of biogenic VOCs through redistribution of vegetation from changed temperature and precipitation patterns (Constable et al., 1999). Elevated temperatures and other consequences of climate change could induce higher ozone levels ranging from about 25% to 82% (Constable et al., 1999; Kellomaki et al., 2001; Turner et al., 1991; Vizuete et al., 2002).

Previous modeling efforts have examined the contribution of biogenic emissions to ozone concentrations (e.g., Chameides et al., 1988; Chock et al., 1995; Hanna et al., 2001; Lurmann et al., 1983, 1984; Mendoza-Dominguez et al., 2000; Nowak et al., 2000; Pierce et al., 1998; Pun et al., 2002; Sillman et al., 1995; Tao et al., 2003; Xu et al., 2002). A large fraction of biogenic emissions' contribution to ozone levels can result from synergy between anthropogenic and biogenic emissions (Tao et al., 2003).

This research uses air pollution modeling to examine how a large increase in biogenic emissions affects ambient ozone levels for a case study in the Mid-Atlantic region from 27–29 June 1990, a representative high ozone episode for the region.

2. Emissions of ozone precursors

Biogenic emissions provide a natural background ozone level of approximately 25–45 ppb (MARAMA, 1997). NO_x results from biological processes in soil, forest fires, and lightning; however, electric utilities and motor vehicles are much larger sources. In 1990, electrical utilities emitted 44% of NO_x emissions in the Mid-Atlantic region, on-road vehicles were responsible for 26%, and off-road vehicles accounted for 11% (MARAMA, 1997). Biogenic emissions of NO_x constitute <10% of total NO_x emissions in the US (EPA, 2000).

Anthropogenic sources of VOCs include transportation and industrial processes such as oil and natural gas production, solvent use, and the paper industry (Piccot et al., 1992). Motor vehicles contributed 10% of total

VOC emissions for the Mid-Atlantic region in 1990 (MARAMA, 1997). Biogenic emissions of VOCs are affected by many factors including the type of vegetation, stage of leaf development, light, humidity, stress, and injury. Higher temperatures generally result in higher emissions (Fuentes et al., 2000; Kesselmeier and Staudt, 1999). In many areas, the vegetative sources of VOCs far exceed anthropogenic sources (Fuentes et al., 2000) and play a significant role in ozone formation (Chameides et al., 1988; McCarthy et al., 2001). In 1990, 77% of VOC emissions in the Mid-Atlantic region were biogenic, whereas the second highest category, on-road vehicles, only contributed 7% (MARAMA, 1997).

Human activity can alter biogenic emissions through land-use patterns and potentially through climate. Anthropogenic VOC emissions in the US decreased by 20% from 1989 to 1998 while total emissions of NO_x have increased 2%. Nevertheless many areas are out of compliance with the National Ambient Air Quality Standard (NAAQS) for ozone (EPA, 2000).

Biogenic emissions inventories used as input to photochemical modeling systems have significant influence on predicted ozone concentrations (Hanna et al., 2001). Further, there are large uncertainties in estimates of biogenic emissions from inventories and emission algorithms (EPA, 1996; Geron et al., 1995; Guenther et al., 2000, 1995; Kesselmeier and Staudt, 1999; Pierce et al., 1998; Potter et al., 2001; Wiedinmyer et al., 2001). Potential sources of uncertainty include (Emission Inventory Improvement Program, 1996): the use of the category "other VOCs" in some inventories; error in measurement studies (e.g., impact of the sampling process on vegetation); incorrect emission rates; oversimplified representation of the canopy; omission of feedback mechanisms in models; and different estimates for the percentage of vegetation coverage and land-use type.

3. Methods

3.1. Overview

Estimated ambient concentration fields for tropospheric ozone were generated for two emissions scenarios to explore the effect of biogenic emissions for a high ozone case study in the Mid-Atlantic. The time frame of the simulations spanned 27 June (hour 00) to 30 June (hour 00) 1990 (Greenwich Mean Time, GMT). For additional information on tropospheric ozone formation in this area, including some detail about the specific episode modeled (see Deuel and Douglas, 1996; Ryan, 1995; Ryan et al., 2000; Vukovich, 1995, 1998). The domain consists of 69 columns and 42 rows, generating 2898 gridcells that are 12 km \times 12 km in the horizontal. Pollutant concentration estimates were generated for

each gridcell for each hour of the simulations. Concentrations were estimated for a baseline scenario, which did not use adjusted emissions, and two scenarios of adjusted emissions.

3.2. Meteorological and air pollution modeling

The Penn State/National Center for Atmospheric Research (NCAR) 5th generation Mesoscale Model (MM5) Version 3–4 was used to generate meteorological fields, which were inputs for the air pollution modeling system (NCAR, 2000). Meteorological simulations were performed for three spatial domains, employing square gridcells with horizontal dimensions of 108, 36, and 12 km. The model was modified to allow one-way nesting and four-dimensional data assimilation (FDDA) (Otte, 1999, 2000). One-way nesting was used to allow initial and boundary conditions for higher resolution domains to be calculated from the results of coarser domains. FDDA nudges analyses toward three-dimensional analyzed fields of observational data. All scenarios use the same meteorological fields, such as wind speed and direction, to isolate the impact of increased biogenic emissions. This excludes the effects of altered weather patterns, and increased ozone formation reaction rates from higher temperatures.

The Models-3 framework, an air pollution modeling system, was used to generate ambient air concentration fields (EPA, 1998a–c). Models-3 consists of separate processors for land-use, the interface of meteorology and chemistry, emissions projection and processing, the interface of emissions and chemistry, generation of initial and boundary conditions, estimation of photolysis rates, and chemistry and transport. The CMAQ (Community Multi-Scale Air Quality) Chemical Transport Model (CCTM) is a three-dimensional Eulerian air quality model for the chemistry and transport of pollutants. The Regional Acid Deposition Model (RADM2) chemical mechanisms and 1990 National Emissions Trends (NET) inventory were used. The air pollution modeling simulations used two domains (the meteorological domains minus a peripheral buffer) with horizontal gridcell resolutions of 36 and 12 km. One-way nesting was used to provide initial and boundary conditions to nested domains. Final analysis used estimates from the highest resolution domain.

3.3. Emissions processing and modeling

Area, point, biogenic, and mobile emissions were estimated using the Models-3 Emission Processing and Projection System (MEPPS), which incorporates data on land-use, land-cover, meteorology, population, political boundaries, road networks, and raw emission inventories. Hourly emissions of VOCs from vegetation and NO_x from soil were estimated using the Biogenic

Emissions Inventory System (BEIS2), which is the Environmental Protection Agency (EPA)-preferred method (Emission Inventory Improvement Program, 1996). County-level vegetation data were categorized into 75 tree genera, 17 agricultural crop categories, and grasses. Estimates of NO_x from soil were based on the type of crop and fertilization rate. BEIS2 receives meteorological input from the Models-3 Meteorology–Chemistry Interface Processor (MCIP).

Day-specific, gridded, hourly estimates of motor vehicle emissions were generated using Mobile5, a vehicle emissions model. Mobile5 estimates emissions of hydrocarbons, carbon monoxide, and NO_x (EPA, 1994a). These emissions are a function of ambient temperature, average travel speed, operating mode, fuel volatility, mileage accrual rates, and vehicle type.

3.4. Emissions scenarios

A baseline episode and two modified emissions scenarios were used to estimate ozone concentrations for the case study. Hourly gridded estimates of ozone concentrations were generated using the following emissions scenarios:

- Scenario A—Baseline, unadjusted emissions using the 1990 NET emissions inventory.
- Scenario B—Biogenic emissions increased by 100% for isoprene, terpene, and other VOCs.
- Scenario C—Biogenic emissions increased by 100% for VOCs, as in Scenario B, and mobile source emissions of VOCs and NO_x increased by 100%.

Estimated ambient ozone levels for each of the scenarios were compared according to several metrics, such as the maximum hourly value and the percent of the modeling domain with ozone levels above a prescribed value. The impacts on urban versus rural areas was examined by combining census data with ozone levels.

This work is related to research by Tao et al. (2003), in which the 1995 summer was modeled for the US using 90-km gridcells for various levels of biogenic and anthropogenic emissions. A factor separation technique was used to examine the effect of biogenic or anthropogenic emissions alone, as well as the interaction between these emissions. What is generally referred to as the total biogenic contribution also includes an anthropogenic influence, as anthropogenic emissions can alter the impact of biogenic emissions due to the complex nonlinear process of tropospheric ozone formation (Tao et al., 2003).

In this study, each of the scenarios includes both biogenic and anthropogenic emissions; thus, the resulting ozone concentrations include the synergistic combination of those emissions. For example, Scenarios A and B differ by the 100% increase in biogenic VOC

emissions, so the difference between their ozone levels represents the effect of the elevated VOC emissions as well as the interaction between the biogenic emissions and baseline anthropogenic emissions. This is the total biogenic contribution, rather than the pure biogenic contribution, as defined by Tao et al. (2003).

4. Results

4.1. Model performance for base case simulation

Successful use of models to estimate the impact of human behavior on natural systems depends on some effort to establish what is commonly called validity of those models. Evaluations of air quality models often involve comparisons of measurements to estimated concentrations for the gridcells corresponding to the monitor locations. Peak ozone concentrations receive special attention, as they are important from a regulatory and public health standpoint. Model evaluation statistics are often calculated using only the hourly observation–prediction pairs for which the observed concentration is greater than a specific value to remove influence of low concentrations, such as nighttime values. Various cutoff values have been used for this purpose; however, 60 ppb is frequently employed and is in accordance with EPA practice (EPA, 1991; Russell and Dennis, 2000). Evaluation measures are often normalized by the measured concentrations.

Model developers, policy-makers, and EPA generally do not promote fixed criteria for accepting or rejecting model results for estimates of tropospheric ozone concentrations (EPA, 1991, 1994b; Russell and Dennis, 2000). However, EPA recommends some measures to help evaluate model performance (EPA, 1991, 1994b). The modeling system was evaluated using several graphical and statistical measures for several ozone episodes in 1990 and 1995 and geographic regions (the Mid-Atlantic, the Baltimore/Washington, DC area, and northern Georgia) (Bell, 2002). Samples of these measures are described below and in Appendix A.

Bias measures whether the model systematically under- or over-estimates the observed concentrations. The mean bias (D), also called the mean bias error, is the average of the difference between the estimated and observed values for all observation–prediction pairs. A value of zero would denote no average bias. This considers only the estimated concentrations for gridcells in which a monitor is located, rather than estimates from the entire simulation domain. Gross error (E_d) measures the model's precision and is similar to the mean bias; however, it does not allow positive and negative bias to offset each other.

The unpaired highest-prediction accuracy (A_u), also called the unpaired peak accuracy test or unpaired peak

prediction accuracy, compares the maximum observed value across all monitors and time periods and the maximum predicted value across the entire simulation. This measure is unpaired because the peak observed and estimated concentrations may have different locations and/or time periods. A positive A_u indicates that the model under-predicts, whereas a negative value indicates over-prediction. It is very dependent on the location and density of the monitoring network. If a monitor is not placed in the position where the highest ozone concentration occurs and the model predicts accurately, the A_u may be deceptively poor.

Table 1 provides several statistics of model performance for the baseline simulation for this case study. The modeling system employing a modified MM5 and Models-3 generally performs as well or better (closer to zero) than EPA's benchmarks and other modeling performance studies (EPA, 1991; Barickman and Swart, 1997; Hanna et al., 1996; Hogrefe et al., 2001; Jiang et al., 1998; Kumar et al., 1994; Kumar and Lurmann, 1997; Myers, 1990; N.C. Department of Environment and Natural Resources, 2000; Sistla et al., 1996, 2001; Tesche and McNally, 1991, 1992; Wang and Georgopoulos, 2001) for this and other case studies (Bell, 2002).

4.2. Emissions

Biogenic emissions of VOCs depend on land-use and vegetation (EPA, 2000; Kesselmeier and Staudt, 1999), which creates regional differences in biogenic VOC emissions. For the case study, biogenic terpene emissions were higher in Virginia, central and eastern Maryland, and New Jersey. Isoprene emissions were higher in Virginia, western and central Maryland, New Jersey, and central Pennsylvania. Both biogenic VOCs follow a diurnal pattern. Terpene emissions peak at 3–5 pm each day, and isoprene emissions peak at 2–3 pm.

Table 1
Model evaluation statistics for hourly ozone concentrations for the case study

	Model performance statistic	EPA suggested reasonable value
Mean bias, D (ppb)	6.7	
Mean bias, D_{60} (ppb)	8.2	
Normalized bias, D^* (%)	18.0	5–15 (±)
Gross error, E_d (ppb)	15.8	
Normalized gross error, E_d^* (%)	28.7	30–35
Unpaired highest-prediction accuracy, A_u (%)	7.7	15–20 (±)

4.3. Effects of emissions on tropospheric ozone concentrations

Estimated ambient air concentration fields for ozone for the adjusted emissions scenarios were compared to those for the baseline, Scenario A. In general, ozone levels were highest for Scenario C, second highest for Scenario B, and lowest for the baseline scenario (Table 2). Changes in ozone levels were not uniformly distributed geographically. The maximum hourly domain-wide average was increased only 4.4% for Scenario B and 11% for Scenario C, as compared with the baseline, Scenario A. The maximum hourly average concentration for an individual gridcell increased by 30% for Scenario B and 40% for Scenario C. The adjusted emissions scenarios also generated higher estimates for the simulation average, which is the average value across the entire domain and all time periods. Scenarios B and C had a higher percent of the domain that exceeds the 1-h NAAQS.

The additional 100% increase in emissions of mobile VOCs and NO_x in Scenario C further raised ozone concentrations above those of Scenario B; however, a larger difference was observed between Scenarios A and B than between Scenarios B and C, which concurs with the large proportion of biogenic VOCs. Scenario C

generates a larger or similar incremental increase in ozone levels than Scenario B for many ozone metrics, including the simulation-wide average; however, the maximum hourly concentration increased by 30% (54 ppb) between Scenarios A and B and only 7% (16.7 ppb) between Scenarios B and C. The relative impacts of Scenarios B and C on the hourly maximum is shown in Fig. 1, which depicts the highest 1-h average estimated concentrations for any 12-km × 12-km gridcell in the domain.

Scenarios B and C always have comparable or higher ozone levels than the baseline for all time periods for the domain-wide averages and maximum at any gridcell in the domain. The modified emissions did not affect temporal patterns of ozone levels. The daily peak domain-wide concentrations and hourly maximums for any gridcell for Scenarios B and C occurred within an hour of that for Scenario A for all days, usually at the same exact hour.

The lowest hourly maximum concentrations at any gridcell are similar for all three episodes at 53.1, 52.0, and 55.0 ppb for Scenarios A, B, and C, respectively. The largest increases occur at times of high ozone levels. The largest hourly maximum concentrations were 178.4, 232.4, and 249.1 ppb for Scenarios A, B, and C, respectively. Fig. 1 shows the large increases above

Table 2
Ozone levels for baseline and adjusted emissions scenarios

	Scenario A	Scenario B	Scenario C
Max 1-h average	178.4 ppb	232.4 ppb	249.1 ppb
Max 1-h domain-wide average	81.8 ppb	85.4 ppb	90.5 ppb
Simulation-wide average	52.3 ppb	55.4 ppb	58.6 ppb
% of domain with max 1-h concentration > 124 ppb	5.8%	17.7%	33.5%
Largest increase in 1-h ozone	—	120.4 ppb	113.1 ppb

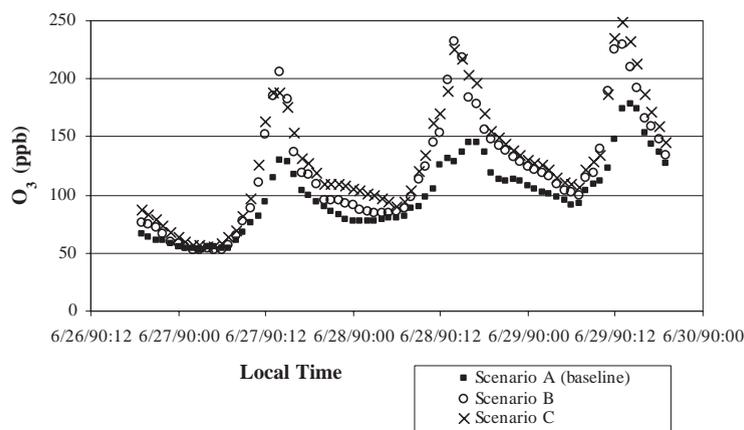


Fig. 1. Maximum hourly estimated ozone concentrations for three emissions scenarios.

baseline resulting from the elevated biogenic emissions and the much smaller incremental increase resulting from the raised motor vehicle emissions.

Figs. 2a–c are tile plots depicting the maximum hourly estimated ozone concentrations for each gridcell of the domain for each scenario. Each of these figures does not represent a single time period, but rather the highest estimate for any time period for each gridcell. The

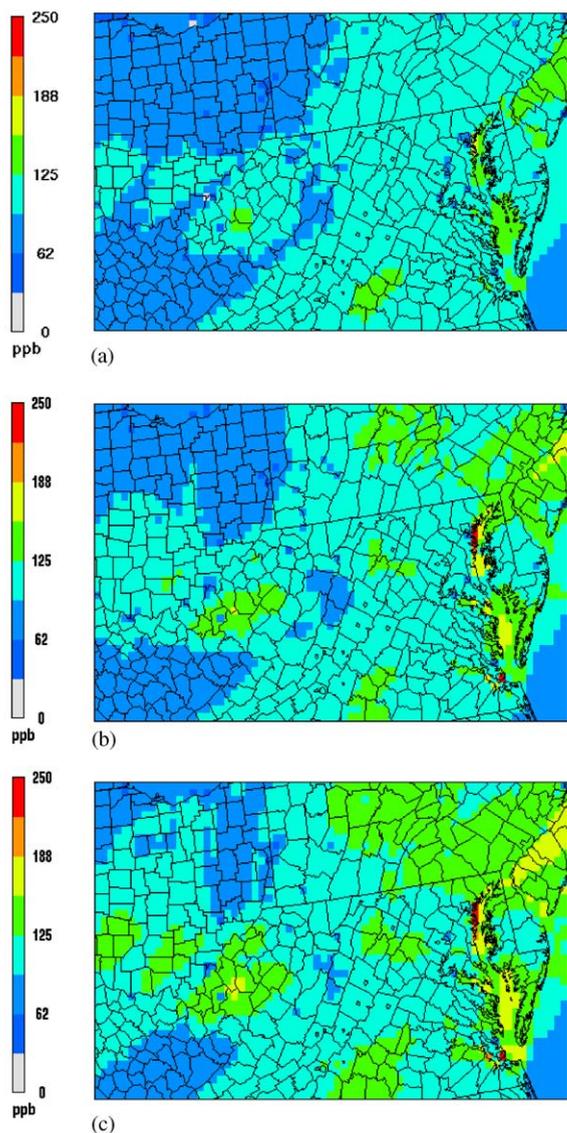


Fig. 2. (a) Maximum hourly estimated ozone concentrations for each gridcell, Scenario A (baseline emissions), (b) maximum hourly estimated ozone concentrations for each gridcell, Scenario B (100% increase in biogenic VOCs), (c) maximum hourly estimated ozone concentrations for each gridcell, Scenario C (biogenic VOCs and motor vehicle VOCs and NO_x increased 100%).

maximum concentration may occur at different times for different gridcells. The spatial extent of high ozone levels is larger for the scenarios with increased emissions.

High concentrations to the East of Baltimore, Maryland, which is generally downwind of the city, are estimated for all scenarios. This area had the highest hourly concentration for the baseline scenario and Scenario C. The largest increase in the hourly maximum occurred on the Virginia coast, for both adjusted emissions scenarios, as compared to Scenario A. The maximum 1-h average concentration for Scenario B also occurs on the Virginia coast. While this gridcell had a higher hourly maximum for Scenario B than C, the eight gridcells surrounding it generally showed similar, but slightly higher estimated ozone concentrations for Scenario C than for Scenario B. This demonstrates that while Scenario C, which has the highest emissions, generally results in higher ozone levels than Scenario B, some areas would have lower or comparable ozone concentrations with Scenario C than with Scenario B.

Both scenarios with increased precursor emissions lowered ozone concentrations for some gridcells and time periods, but these were generally minor and occurring at low baseline ozone levels. Such a decrease is possible due to the complex chemistry of ozone formation. For Scenario B, 68.1% of the hourly gridded estimates were higher than those of the baseline scenario. The additional emissions increases of Scenario C brought an additional 9.6% of the hourly gridded estimates above those of the baseline. Of the hourly gridded estimates for which Scenarios B or C were below those for Scenario A, the decrease from the baseline estimate was generally low, averaging 3.0 ppb for Scenario B and 3.3 ppb for Scenario C. The largest decrease for a single gridcell and time period was 25.1 ppb for Scenario C, occurring on 29 June 1990, hour 00, GMT, in a gridcell in northern Virginia. For Scenario B, the largest decrease was 17.0 ppb for the same hour in a gridcell in eastern Kentucky. All scenarios were near daily lows at this time period.

The increased emissions for both Scenarios B and C enhanced the extremes of ozone levels by raising peaks and slightly decreasing the lows. Ozone peaks were especially affected. The correlation between the 1-h domain-wide average for baseline Scenario A and the corresponding average increase from Scenario B is 0.80. For Scenario C this value is 0.89. The correlations between the hourly maximum for any gridcell of Scenario A and the corresponding increase from the adjusted emissions was 0.60 for Scenario B and 0.70 for Scenario C.

These relationships are shown in Fig. 3. Each time period of the simulation is represented as a single point. The x-axis reflects the maximum hourly average ozone concentration for a specific hour for the baseline.

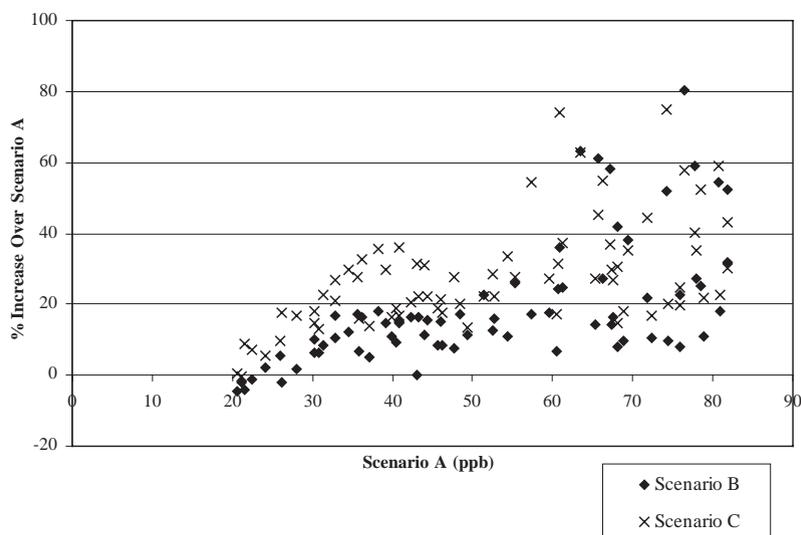


Fig. 3. Percent increase in maximum 1-h ozone concentrations for adjusted emissions scenarios compared to baseline scenario.

The y-axis is the percent difference between the hourly concentration of the adjusted scenario and that of the baseline scenario. Both scenarios with elevated emissions show an upward trend in the percent increase of ozone concentrations as the baseline ozone levels increase. In other words, the largest increases in ozone concentrations occur at times with high baseline levels.

4.4. Comparison of urban and rural areas

High ozone levels typically occur downwind of major sources, which often coincide with major urban areas. The estimated ozone concentrations of gridcells with high population density (at or above the 90th percentile) were compared to those with low population density (at or below the 10th percentile) in order to compare ozone levels in urban and rural areas. Population data at the census tract and block level were obtained from the 2000 US census data sets (US Census Bureau, 2000). The population of each census tract or block was allocated among the 12-km \times 12-km gridcells of the air pollution modeling domain according to the fraction of the census tract or block's area located within each gridcell. Although the case study time period was for 1990, the relative population density of different gridcells is likely to be similar to those of 2000.

For the baseline scenario, areas with the highest 10% and lowest 10% population had similar ozone levels. The highest hourly maximum value was 145 ppb in the rural areas and 147 ppb in the urban areas. The average hourly maximum for all gridcells was 103 and 100 ppb in the rural and urban designations, respectively. However, urban areas responded more dramatically to increased

emissions of ozone precursors, for both adjusted emissions scenarios (Fig. 4). Scenario B raised the maximum hourly value 5.6 ppb on average in rural areas and 11 ppb on average in urban regions, whereas Scenario C raised the maximum hourly value an average of 12 ppb in rural areas and 20 ppb in urban areas. This analysis implies urban areas would be more impacted by elevated emissions than rural areas.

5. Discussion

A 100% increase in biogenic VOC emissions raised ozone levels resulting in much higher ozone peaks, higher domain-wide hourly averages, and a greater fraction of estimates exceeding the 1-h NAAQS for ozone. An additional 100% increase in motor vehicle emissions of NO_x and VOCs further raised ozone levels. The incremental impact of increased motor vehicle emissions was generally less than the difference between the baseline scenario and that of a 100% increase in biogenic VOCs alone, which corresponds with the high proportion of VOCs of biogenic origin.

While a 100% increase in biogenic VOC emissions is likely conservatively high, emissions of ozone precursors can vary due to land-use and temperature. Increased temperatures from climate change would result in larger biogenic VOC emissions, which would subsequently affect ozone levels and thereby human health. This analysis demonstrates the important role of biogenic VOC emissions in ozone formation for this region, which has a greater impact than a comparable percentage increase in motor vehicle emissions of ozone precursors in this case study.

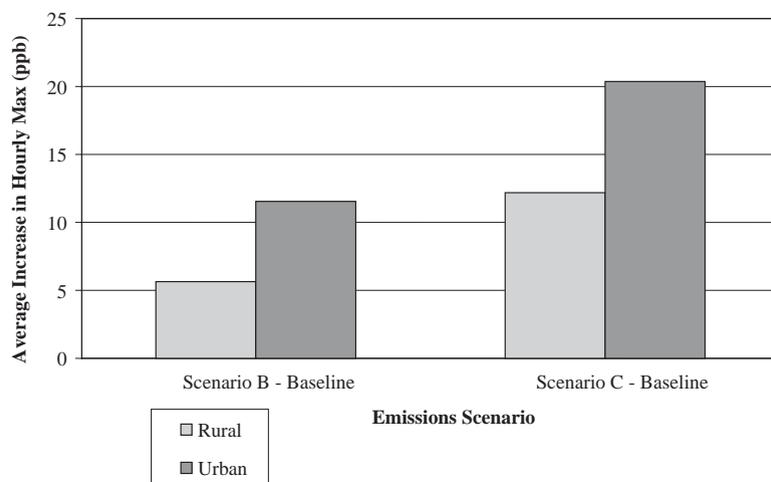


Fig. 4. Average increase in hourly maximum ozone levels for urban and rural areas.

Scenario concentrations include the total effects of elevated emissions, including the interaction of anthropogenic and biogenic emissions. Additional modeling simulations would be required to separate the pure biogenic and anthropogenic components from the total effects, which is an area of further research. Although biogenic emissions are difficult to control, a major portion of these emissions' impact on ozone levels often results from synergy between biogenic and anthropogenic emissions, and such synergism is likely to be large in areas where emissions of both categories are high (Tao et al., 2003). Thus, while biogenic emissions play a significant role in tropospheric ozone formation, control of anthropogenic emissions of ozone precursors can help lower pollution levels.

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Appendix A. Model evaluation measures

Mean bias:

$$D = \frac{1}{N_T} \sum_{i=1}^N \sum_{j=1}^{H_i} (c_o(i,j) - c_p(i,j))$$

Normalized bias (for hourly pairs with $c_o(i,j) > 60$ ppb):

$$D^* = \frac{1}{N_T} \sum_{i=1}^N \sum_{j=1}^{H_i} \frac{c_o(i,j) - c_p(i,j)}{c_o(i,j)} \times 100\%$$

Gross error (for hourly pairs with $c_o(i,j) > 60$ ppb):

$$E_d = \frac{1}{N_T} \sum_{i=1}^N \sum_{j=1}^{H_i} |c_o(i,j) - c_p(i,j)|$$

Normalized gross error (for hourly pairs with $c_o(i,j) > 60$ ppb):

$$E_d^* = \frac{1}{N_T} \sum_{i=1}^N \sum_{j=1}^{H_i} \frac{|c_o(i,j) - c_p(i,j)|}{c_o(i,j)} \times 100\%$$

Unpaired highest-prediction accuracy:

$$A_u = \frac{c_o(\hat{i}_o, \hat{j}_o) - c_p(\hat{i}_p, \hat{j}_p)}{c_o(\hat{i}_o, \hat{j}_o)} \times 100\%$$

$c_o(i,j)$ = observed concentration at location i (monitor location) at time j .

$c_p(i,j)$ = estimated concentration at location i (gridcell in which the monitor is located) at time j .

N = number of monitoring stations.

H_i = number of hourly prediction–observation pairs for location i (i.e., number of time periods for which observed data are available for monitor i).

$N_T = \sum_{i=1}^N H_i$ = total hours for all prediction–observation pairs across all monitors.

$c_o(\hat{i}_o, \hat{j}_o) = i, j \text{ MAX } c_o(i, j)$ = peak observed concentration.

$c_p(\hat{i}_p, \hat{j}_p) = i, j \text{ MAX } c_p(i, j)$ = peak estimated concentration.

$\hat{i}_o, \hat{j}_o, \hat{i}_p,$ and \hat{j}_p = the locations and times of the peak observed and estimated concentrations.

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