FINAL REPORT

PROJECT

The Effect of Nitrogen Oxide Emissions from Automobiles on the Concentration of Tropospheric Ozone in the Great Smoky Mountains National Park

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ABSTRACT

The Great Smoky Mountains National Park (GSMNP) is the most visited national park in the United States, drawing over 9 million visitors per year. Emissions of nitrogen oxides (NO_x) from the exhaust of automobiles transporting those visitors into and through the park combine with biogenic emissions of volatile organic compounds (VOCs) from the extensive park forests to form tropospheric (i.e., ground level) ozone, (O_3) which is harmful to plants, animals and humans. In this project, the National Oceanic and Atmospheric Administration's Atmospheric Chemistry and Canopy Exchange Simulation System (ACCESS) model is being used to estimate the impact of automobile NO_x emissions on O_3 within and downwind of GSMNP. The one-dimensional column model ACCESS utilizes a current state-of-the-science, near explicit atmospheric chemistry mechanism to simulate tropospheric O_3 from ground level to the top of the planetary boundary layer (PBL) (~2 km) and accounts for turbulent vertical atmospheric transport of trace species from within the forest canopy and up throughout the full depth of the PBL. NO_x emissions from varying levels of automobile traffic in the park will be simulated with ACCESS and the impact of the traffic on O_3 concentrations will be evaluated. Data from air quality monitoring sites within and around GSMNP will be used to assess ACCESS results.

INTRODUCTION

The Earth's atmosphere is a highly-structured system of chemical and transport processes. Emissions from forests, cities, oceans, agriculture, and industry contribute, both beneficially and detrimentally to this chemistry, and have the ability to form chemical products in the lower atmosphere (referred to as the troposphere) that could either potentially be beneficial to living things, or be destructive to them. One such topographical area of concern would be the Great Smoky Mountains National Park (GSMNP), which is the most visited national park in the United States of America, attracting over 9 million visitors per year (http://en.wikipedia.org/wiki/Great_Smoky_Mountains_National_Park). GSMNP is largely covered by dense forested terrain, resulting in significant emissions of biogenic volatile organic compounds (BVOCs) such as isoprene.

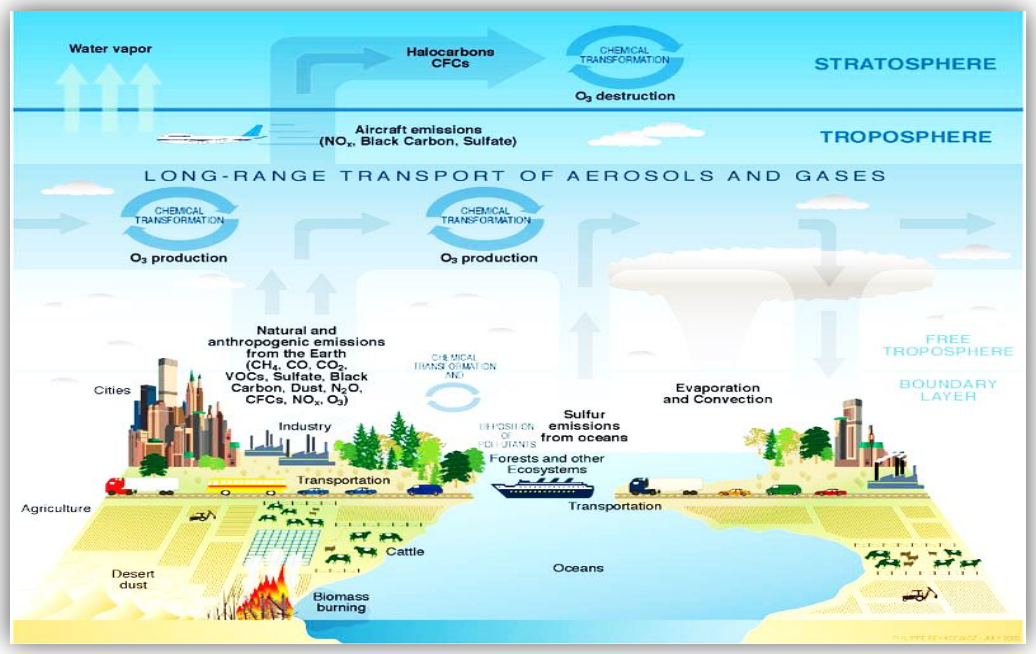


Figure A: The Chemistry of the Atmosphere[1]

[1] Image Source: ClimateScience.gov: "Schematic of chemical and transport processes related to atmospheric composition." (http://www.climatescience.gov/Library/stratplan2003/final/ccspstratplan2003-chap3.htm).

GSMNP tourists' automotive emissions directly affect the nitrogen oxide (NO_x)[2] levels in the area. These levels are important because research has shown that NO_x is an important precursor to tropospheric ozone (O_3) when mixed with BVOCs such as isoprene. Because of the interconnectivity of the atmospheric systems, studying and understanding how the different components fit together (e.g., automotive emissions, BVOCs) may help guide policy to better preserve the atmosphere by reducing ozone.

Ozone is a naturally occurring atmospheric gas that is benign when present in trace amounts; however, larger amounts can be harmful to animals and humans and potentially devastating to plant life. (Figure B schematically illustrates reactions that can lead to the production of ozone in the troposphere.)

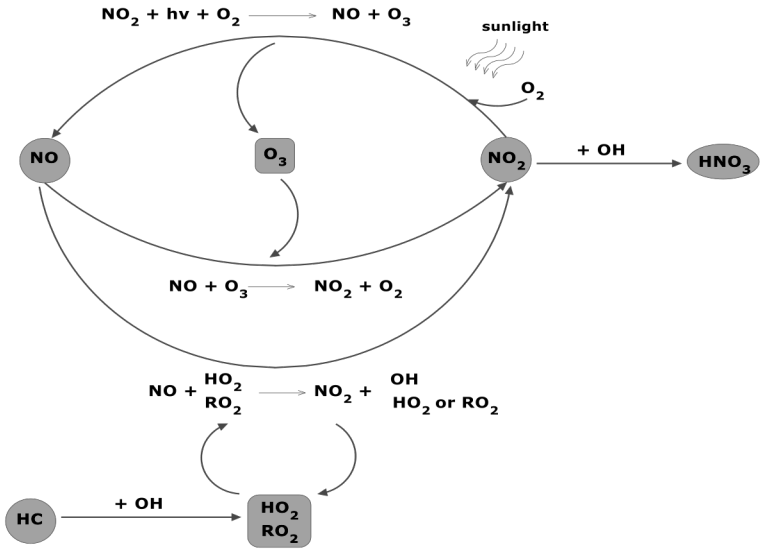


Figure B: Atmospheric photochemical production of tropospheric ozone, a component of smog. R denotes a generic organic moiety.[3]

The GSMNP, a large forested area in the Southeastern United States, naturally yields BVOCs (e.g., isoprene) that can contribute to the production of tropospheric ozone. GSMNP's scale makes the area susceptible to major problems with ground-level ozone (e.g., smog). In this

[2] Atmospheric chemists use the term NO_x to denote the sum of NO and NO_2 concentrations.
[3] Image Source: Dr. Rick D. Saylor, from atmospheric smog seminar given at James Madison University.

project, the NOAA-developed Atmospheric Chemistry and Canopy Exchange Simulation System (ACCESS) has been used to assess the impact of minimal, moderate, and extreme NO_x emissions on the park. ACCESS has been used to simulate how the concentrations, budgets (chemical production), and vertical fluxes of important species are affected by minimum, moderate, and high traffic NO_x emissions. Species studied include: isoprene (C_5H_8); ozone (O_3); nitric oxide (NO); nitrogen dioxide (NO_2); peroxyacetyl nitrate (PAN); and methacryloyl peroxy nitrate (MPAN).

METHODOLOGY

The ACCESS program was used to generate all of the data for our research simulations of the chemistry within the planetary boundary layer (PBL) around the GSMNP. Variables included: meteorological data; chemical species emission data; initial conditions data; and the forest canopy profile of leaf area indices (LAIs). (Each condition variable was specified in an ACCESS control file.)

The processes in ACCESS are governed by the equation below:

$$\frac{\partial C_i(z,t)}{\partial t} = E_i(z,t) + A_i(z,t) + D_i(z,t) + R_i(z,t) + \frac{\partial F_i(z,t)}{\partial z}$$

These variables for species *i* [*i(z,t)*] are:

- $C_i(z,t)$ is the vertical gas-phase concentration profile of species *i*.
- $E_i(z,t)$ is the emission rate of species *i*.
- $A_i(z,t)$ is the rate of mixing of species *i* with a defined background concentration.
- $D_i(z,t)$ is the deposition rate of species *i*.
- $R_i(z,t)$ is the rate of chemical transformation of species *i*.

$\frac{\partial F_i(z,t)}{\partial z}$ is the rate of vertical turbulent mixing of species ***i***.[4]

Figure C: Physical and chemical processes included in ACCESS.v1.2.0.[5]

These simulations attempt to identify: the source of atmospheric pollutants; the sites where the reactions occur most predominately; and the impact the products of these reactions have on the atmospheric environment (the latter will primarily be an interpretation done by the research team).

To prepare for our simulations, we tested a simpliflied version of ACCESS to see how it ran on an HPC platform. The results were unimpressive as the program ran slightly more slowly on Oak Ridge National Laboratories' Kraken-XT5 than it did on the CSURE-REU student, James Herndon's, personal laptop. This led to our decision to run all of our simulations on the University of Tennessee's Star1 (no time limit) rather than ORNLs Kraken-XT5 HPC (24-hour time limit). While our simplified version of ACCESS had 77 reactions, the full ACCESS v1.2.0

[4] Saylor, R. D. (2012). The Atmospheric Chemistry and Canopy Exchange Simulation System (ACCESS): model description and application to a temperate deciduous forest canopy. *Atmospheric Chemistry and Physics*, *12*(9). Retrieved from http://www.atmos-chem-phys.net/13/693/2013/acp-13-693-2013.pdf.
[5] Image Source: Dr. Rick D. Saylor, Diagram of factors implemented in an ACCESS simulation.

contains 7,000 different reactions when using the truly full mechanism (one can also opt for a smaller ~3,400 reaction mechanism, to focus only on isoprene chemistry, which is what we did), so the likelihood of exceeding our time allotment and yet not completing the simulation framed our decision. This graph shows the time required to run a simulation on Kraken and on a laptop computer. (It is important to note that ACCESS is currently a serial (i.e., non-parallel) code when looking at this graph.)

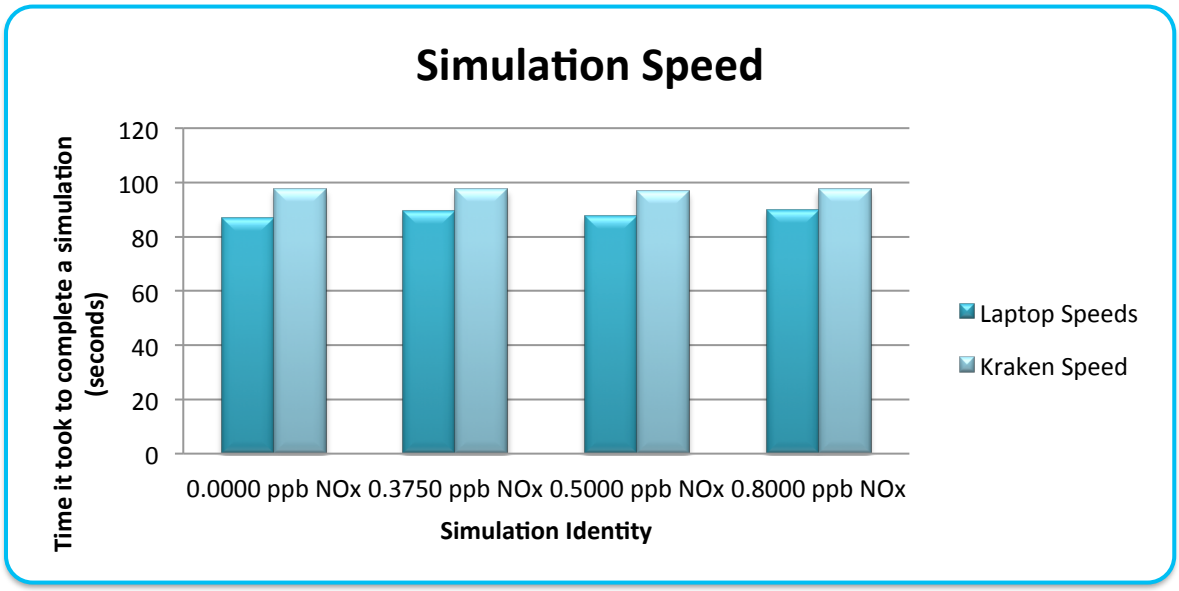


Figure D: Time requirements to run simulation on the Kraken-XT5 and laptop.

We created control files for each simulation specifying the unique conditions of the canopy for each of the five simulations. Variables included the level of NO_x emission, introduced in model layer 1 at the surface to simulate emissions from automobile traffic within the park. When NO_x is created via automobile exhaust, the ratio of NO to NO_2 is typically near 90:10. For example, the gsmnp13u3 simulation has 0.9 nmol m^{-2} s^{-1} NO and 0.1 nmol m^{-2} $s^{-1}NO_2$. The table shows NO_x concentrations for each simulation that was performed.

SIM NAME	NO_x EMISSION
gsmnp03u3	0 nmol m^{-2} s^{-1}
gsmnp13u3	1 nmol m^{-2} s^{-1}
gsmnp23u3	10 nmol m^{-2} s^{-1}
gsmnp33u3	100 nmol m^{-2} s^{-1}
gsmnp43u3	0.1 nmol m^{-2} s^{-1}

RESULTS AND DISCUSSION

The results from our simulations are intriguing. We did not see as much ozone formed above the canopy as we'd initially expected, and we also saw a fair amount of destruction of ozone below the canopy (i.e., near ground level) due to the direct titration reaction between nitric oxide and ozone:

$$NO + O_3 \rightarrow NO_2 + O_2$$

We also noted a significant increase in concentrations of peroxyacetyl nitrate (PAN) and methacryloyl peroxy nitrate (MPAN) above the canopy. PAN and MPAN can be transported downwind from where they are created and if transported back down to the surface can thermally decompose to regenerate NO_x in areas with less direct anthropogenic production of NO_x:

$$RO_2NO_2 \rightarrow RO_2 + NO_2$$

$$RO_2NO_2 = \text{PAN or MPAN}$$

The regenerated NO_2 may then lead to the formation of O_3 via

$$NO_2 + \text{sunlight} + O_2 \rightarrow O_3 + NO$$

and in the presence of volatile organic compounds (denoted as R and being either anthropogenic or biogenic in source), a radical chain propagation sequence regenerates NO_2 so that many molecules of O_3 can be generated from each PAN or MPAN molecule transported downwind:

$$R + OH + O_2 \rightarrow RO_2$$

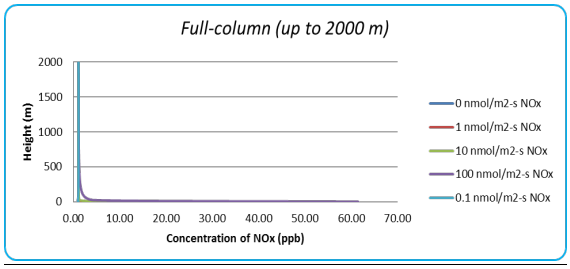
$$RO_2 + NO \rightarrow RO + NO_2$$

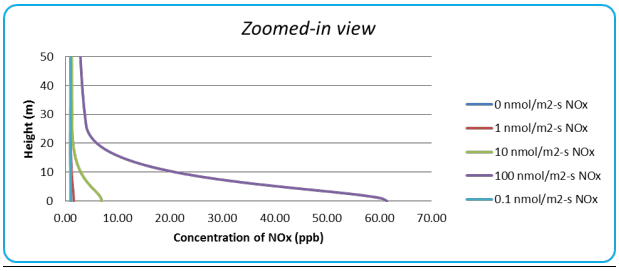
Under these conditions, NOx emitted within GSNMP from visitors' automobile traffic may potentially be transported to more remote areas of the Southern Appalachians and thereby lead to enhanced O_3 concentrations far downwind of the point of original NOx emission.

SPECIES GRAPHS

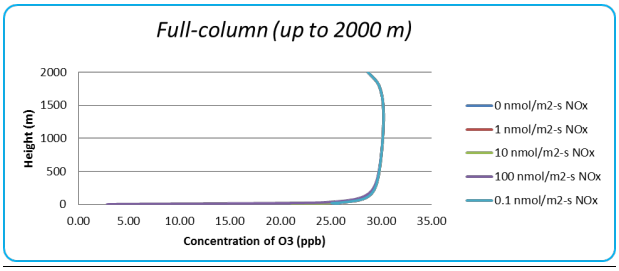
The species graphs contain data on the concentration of each individual species of concert at different heights within the planetary boundary layer.

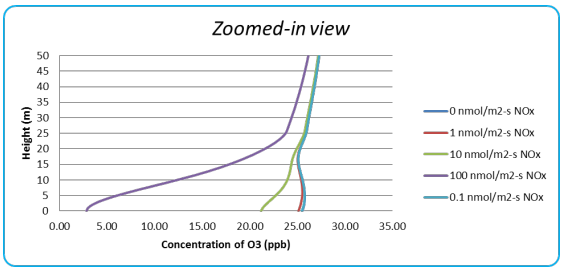
NOx Concentrations



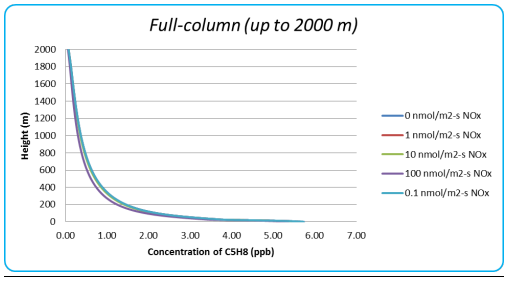


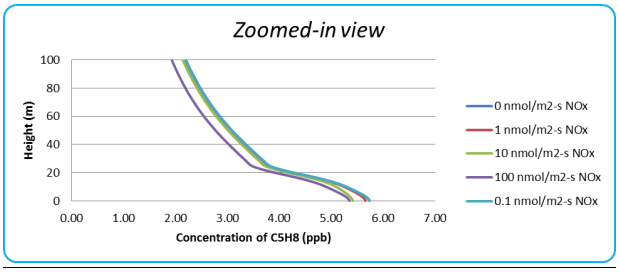
Ozone (O_3) Concentrations



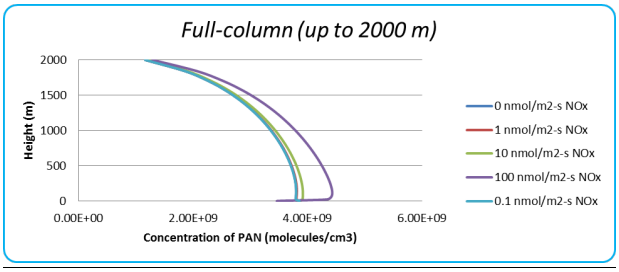


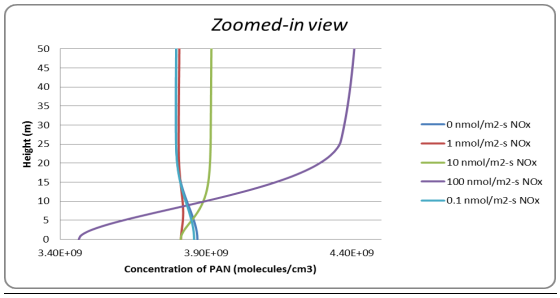
Isoprene Concentrations



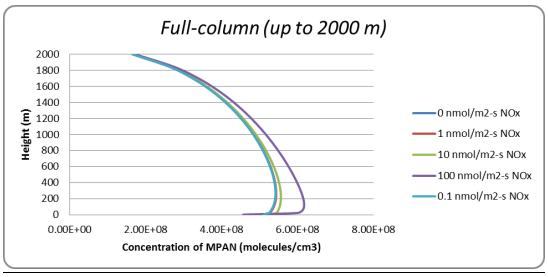


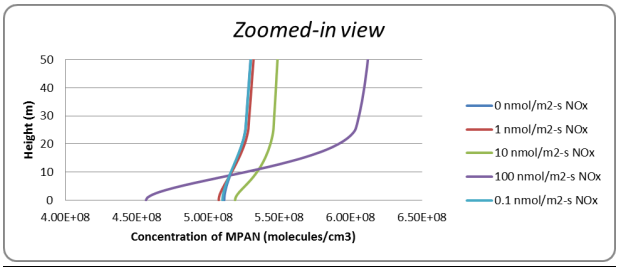
PAN Concentrations





MPAN Concentrations

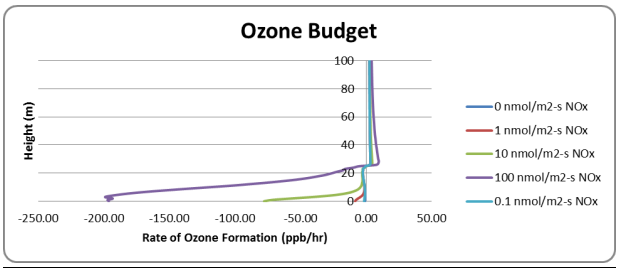


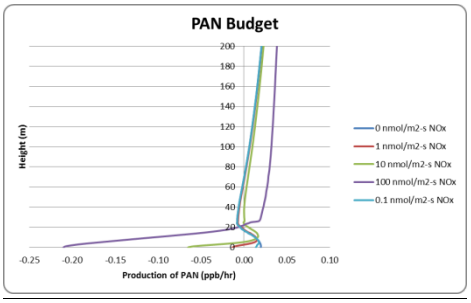


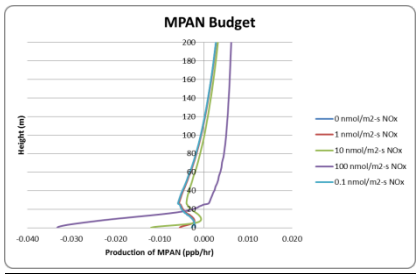
BUDGET GRAPHS

The budget graphs show the rate of chemical production of each species (in ppb/hr). It is important to note that a positive value implies production on these graphs while a negative value implies destruction. We saw a fair amount of ozone destroyed below the canopy (height of canopy is around 26 m) caused by the direct titration reaction with NO. We also saw a lot of production of PAN and MPAN, an important finding; we shall mention why in our conclusion.

Chemical Production / Budget





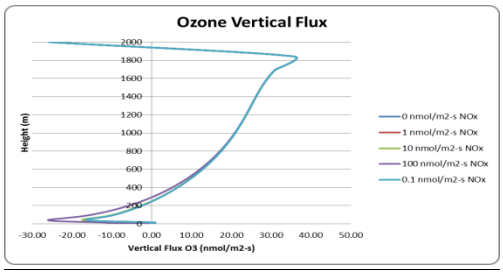


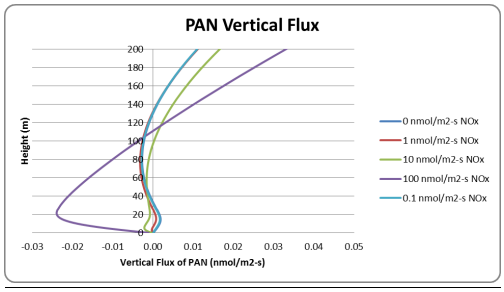
There is no chemical production of isoprene, nor is there chemical production of NO_x, so neither of these species profiles is pictured here.

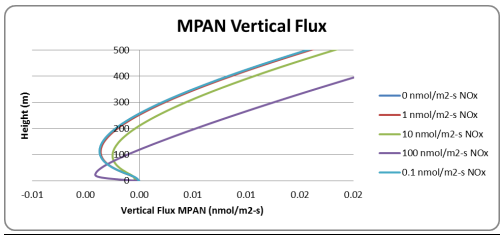
VERTICAL FLUX GRAPHS

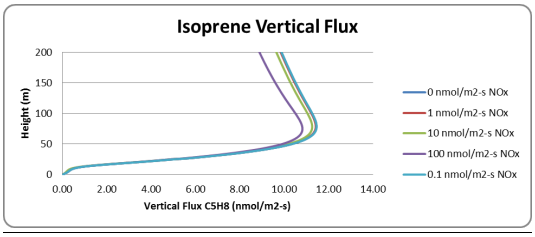
The vertical flux graphs show us generally which direction the chemical flux is within the planetary boundary layer. A positive value implies upward flux, a negative value implies downward flux. In some situations, a negative flux can be taken to imply destruction of a chemical species at a certain level; this implication appears to concur with our simulation results on ozone below 26 meters.

Vertical Flux Profiles









The vertical flux of NO_x is not so critical here, so it is not pictured. The only thing that we are using NO_x for is as a catalyst for potential reactions; that being said, we can reasonably look at the graphs of the above species and tell what we need to know about the vertical flux of NO_x just by looking at those.

Conclusions and Future Work

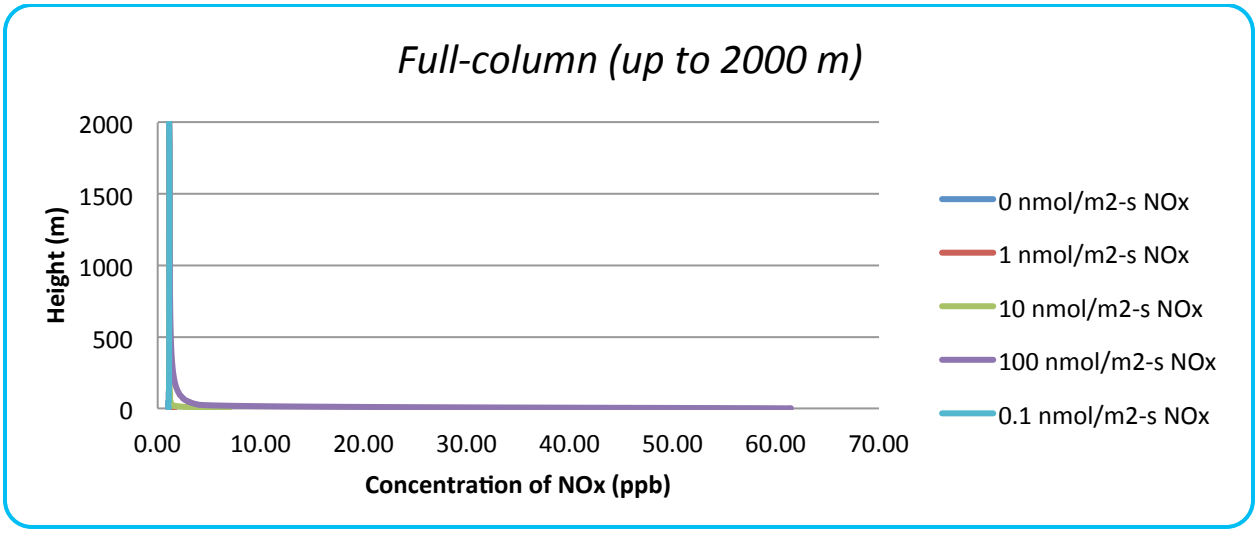
Under the conditions of the simulations performed we have observed that increased NO_x emissions from vehicular traffic result in reduced concentrations of ozone within the canopy from the titration reaction of NO with O_3. We also saw, somewhat to our surprise, that only small enhancements in ozone production occur above the forest canopy. However, the most notable result of our research was that increased NO_x emissions result in enhanced production and vertical fluxes of PAN and MPAN above the canopy, potentially resulting in enhanced ozone concentrations downwind in areas with little or no local NO_x emissions. These results are similar

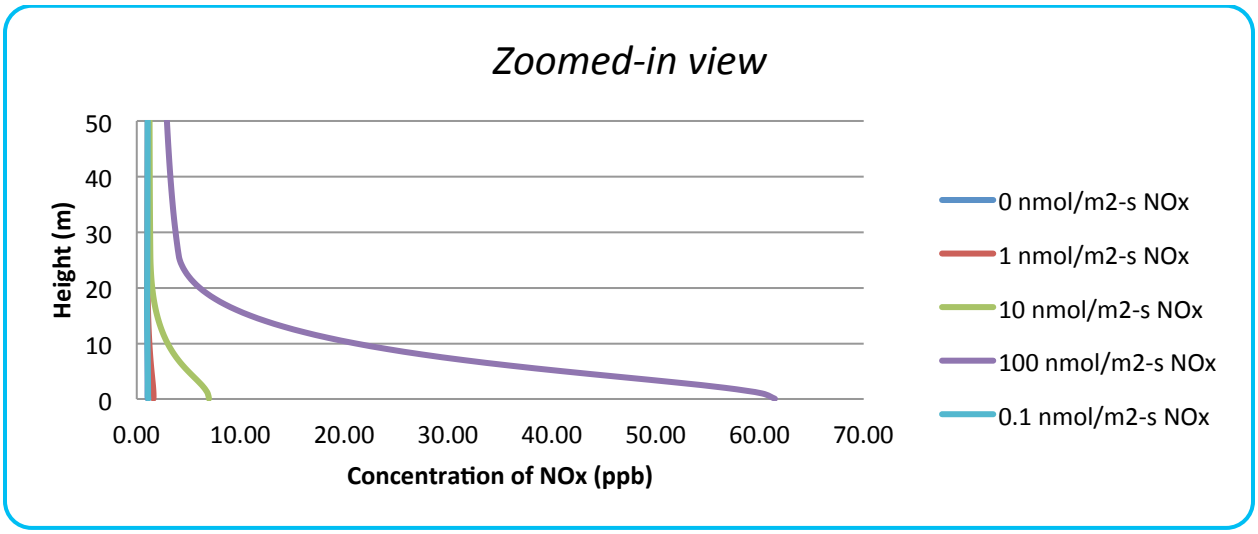
to what is typically seen in large cities, where NO emissions from traffic suppress ozone concentrations in the city but lead to enhanced ozone concentrations downwind.

Future work on this research will include additional simulations confirming results with different within canopy turbulent mixing parameterizations. It will also include an analysis of ozone data within and downwind of GSMNP. Final results from the investigation will be documented in a peer-reviewed journal publication.

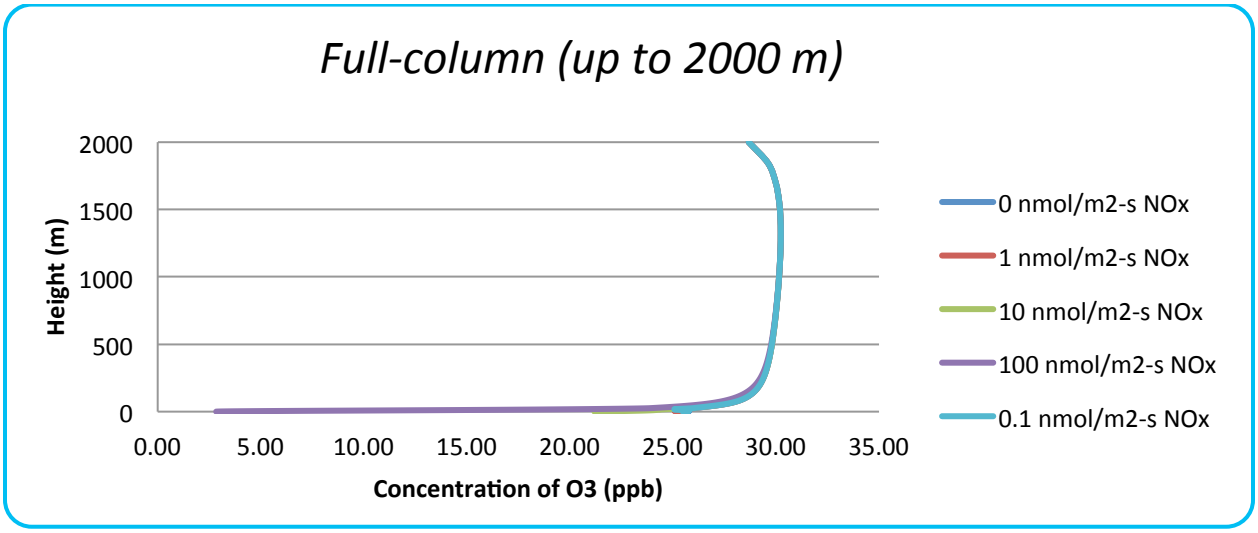
Appendix A: Charts and Supporting Data

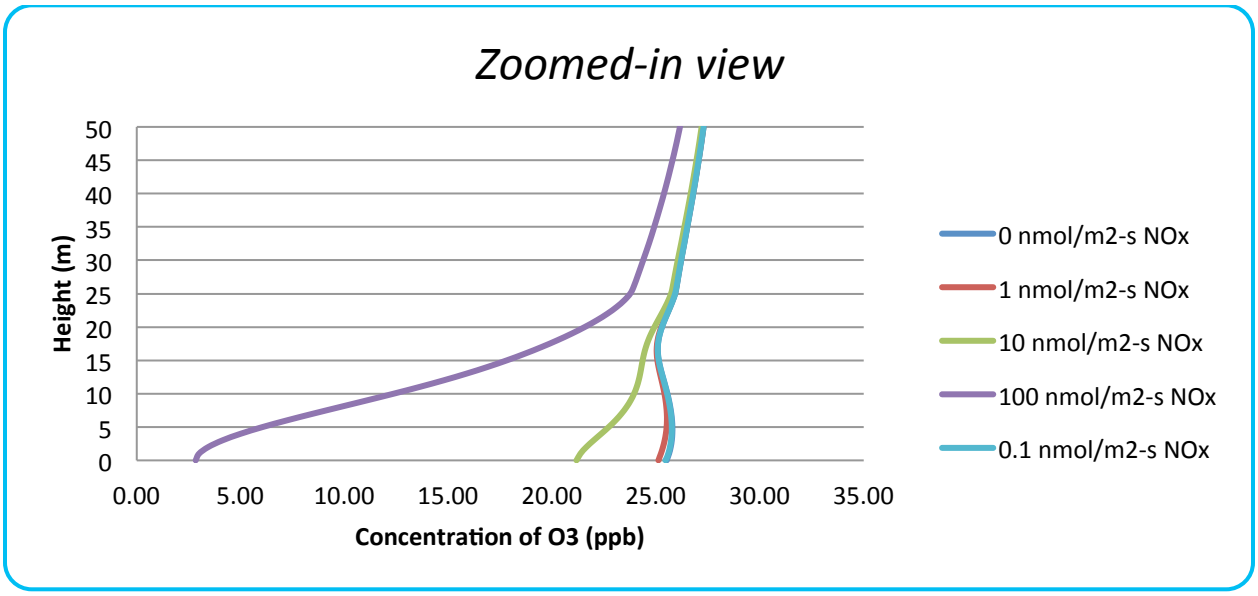
NOx Concentrations



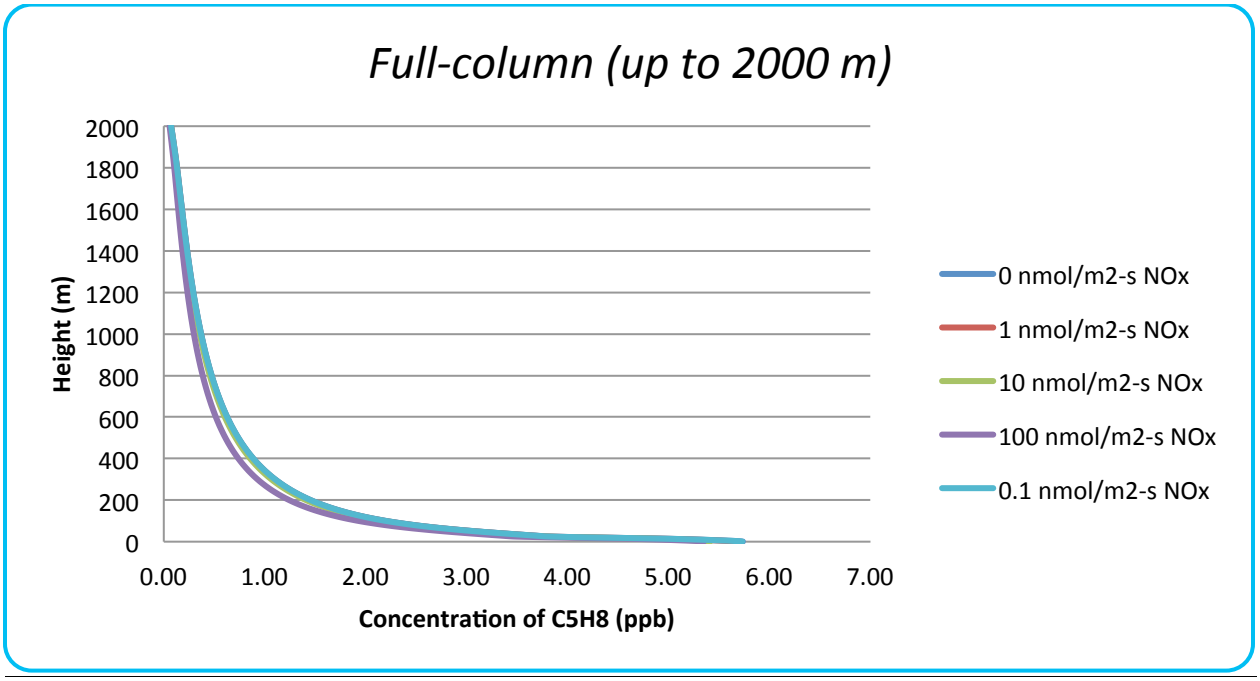


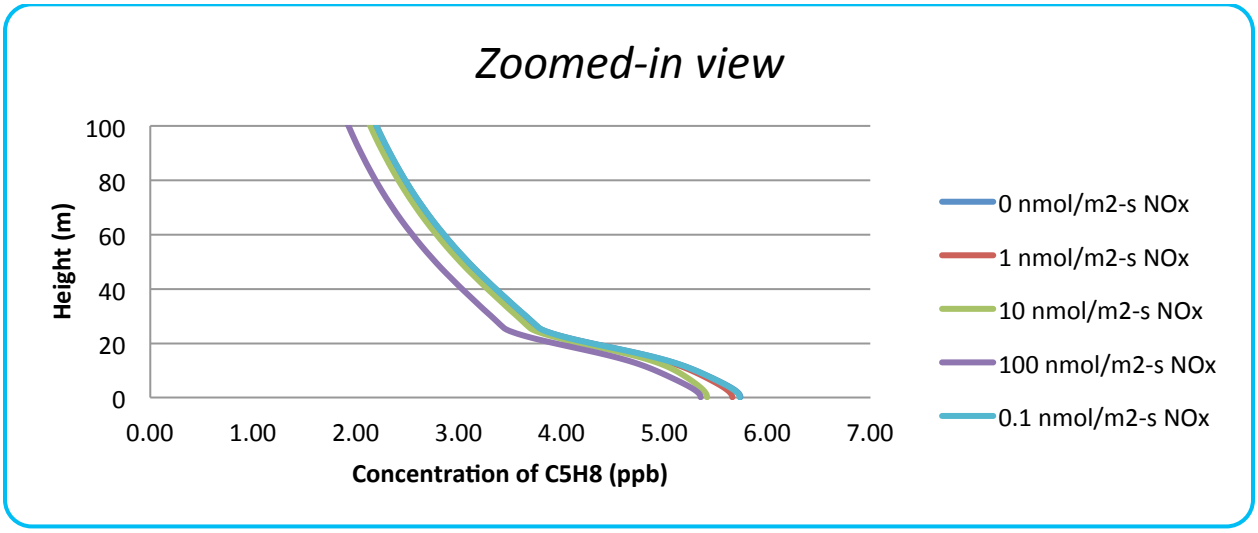
Ozone (O_3) Concentrations



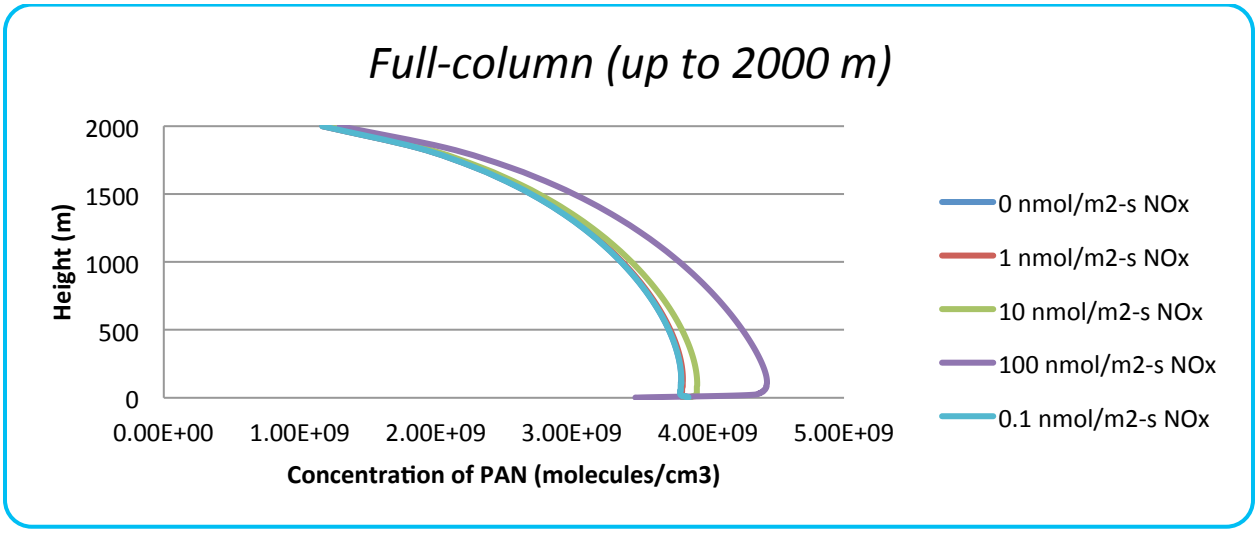


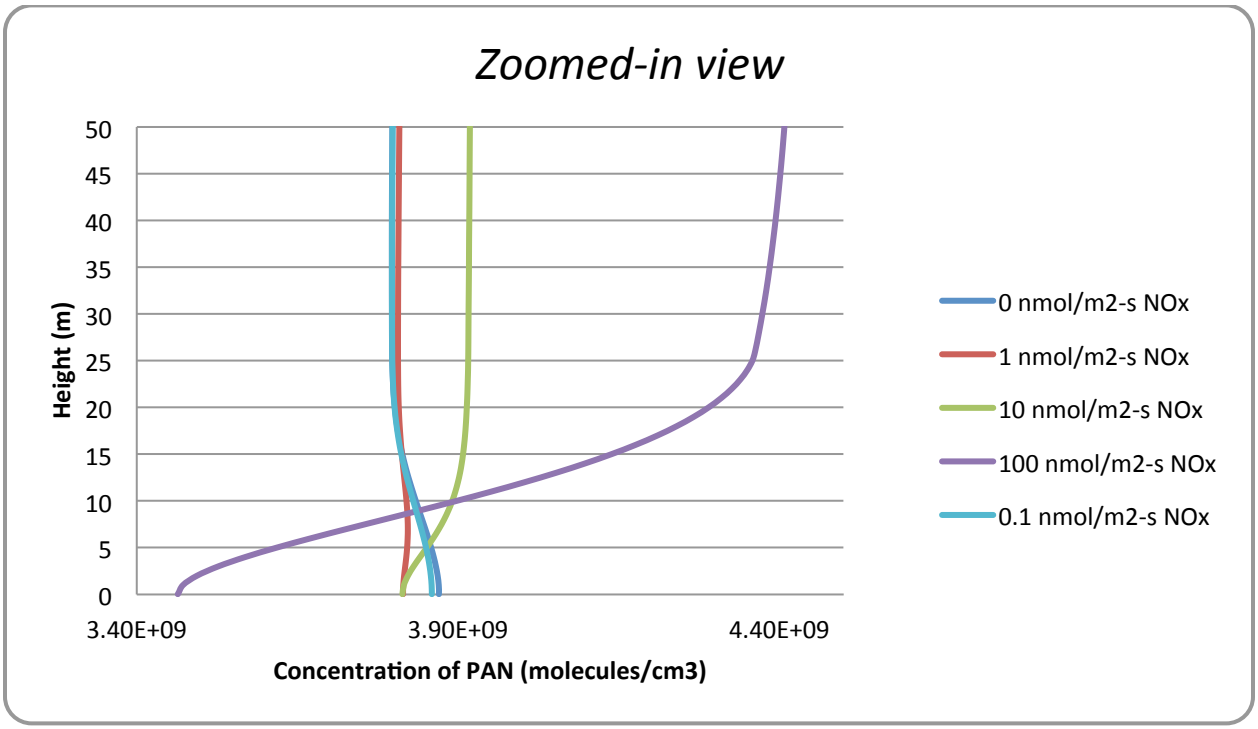
Isoprene Concentrations



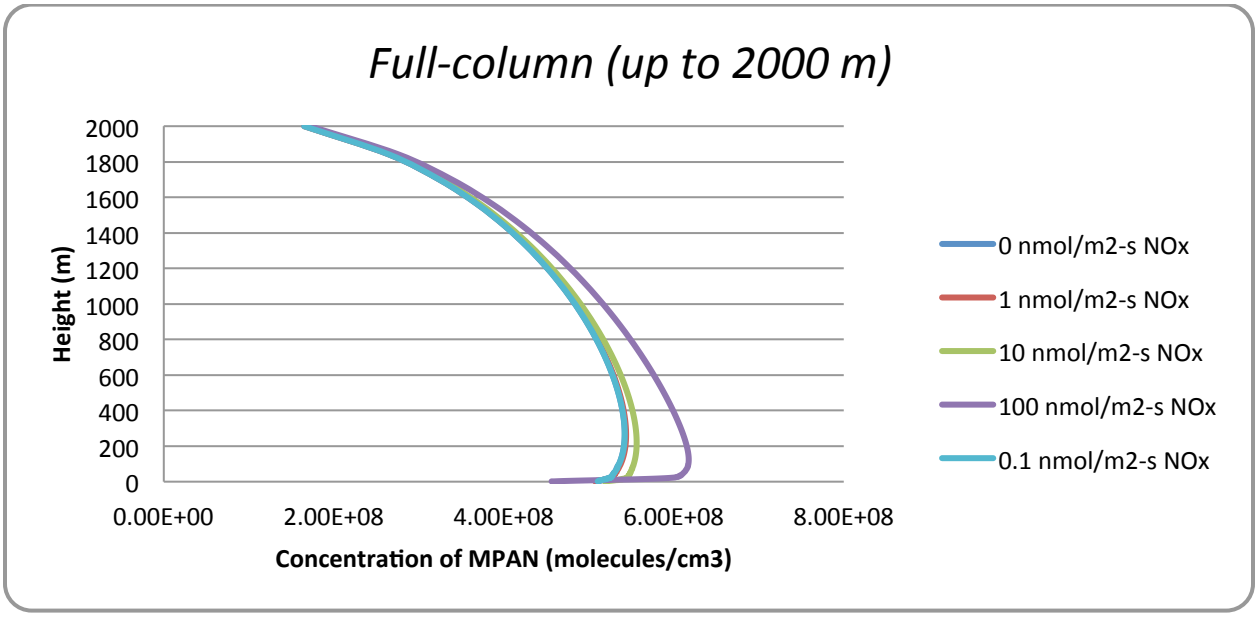


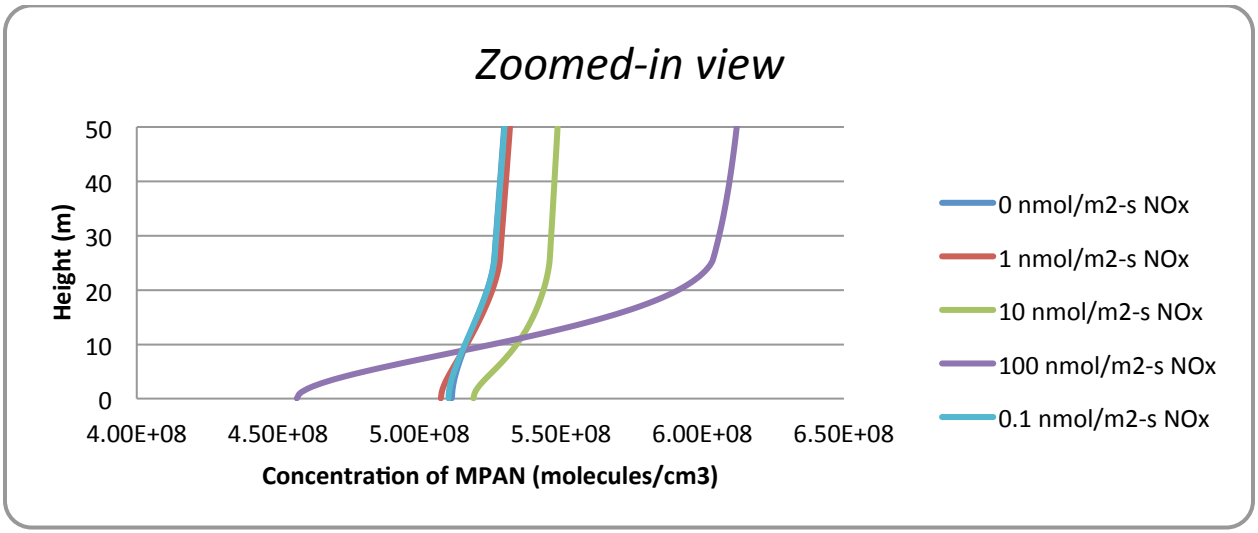
PAN Concentrations



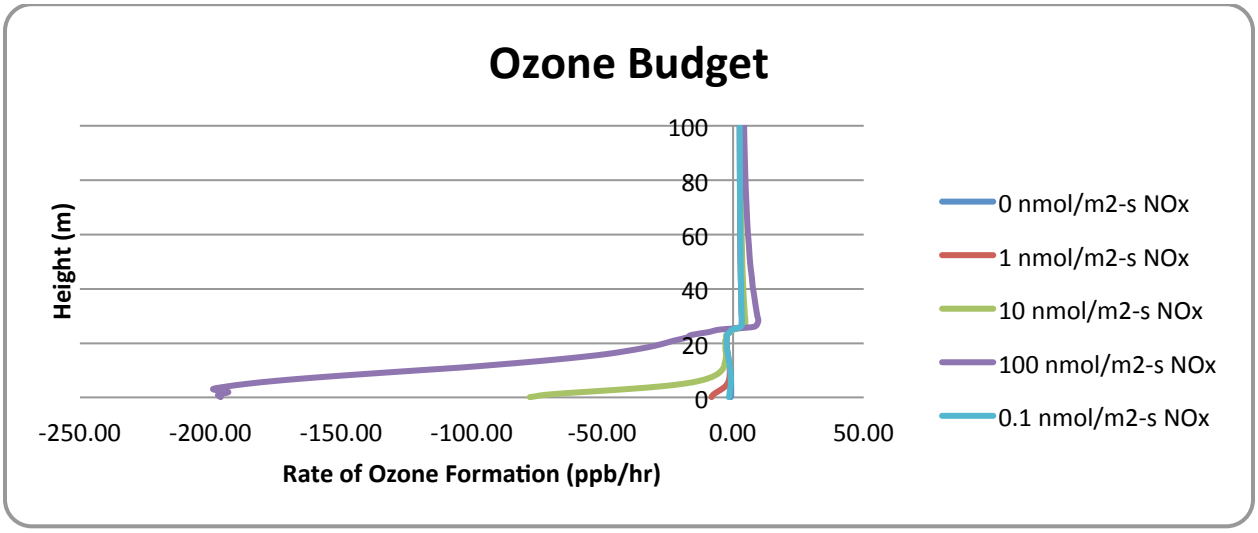


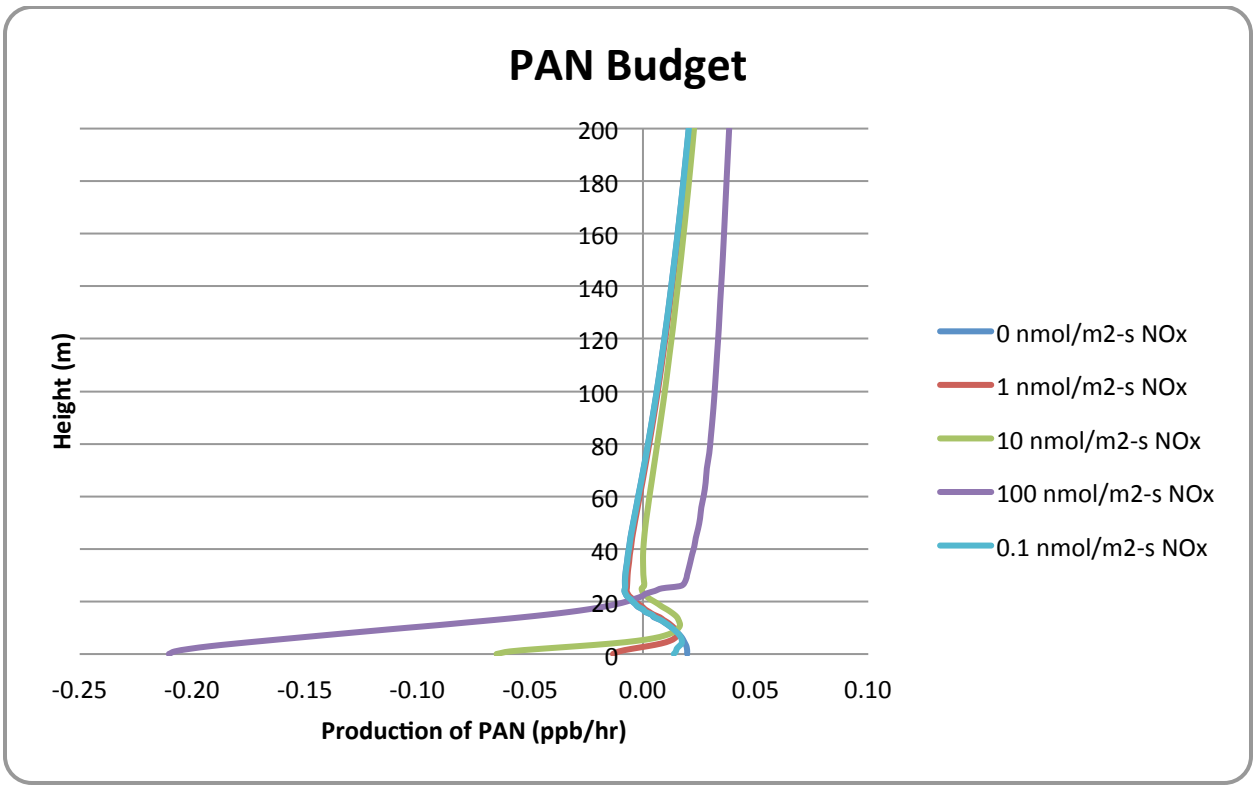
MPAN Concentrations

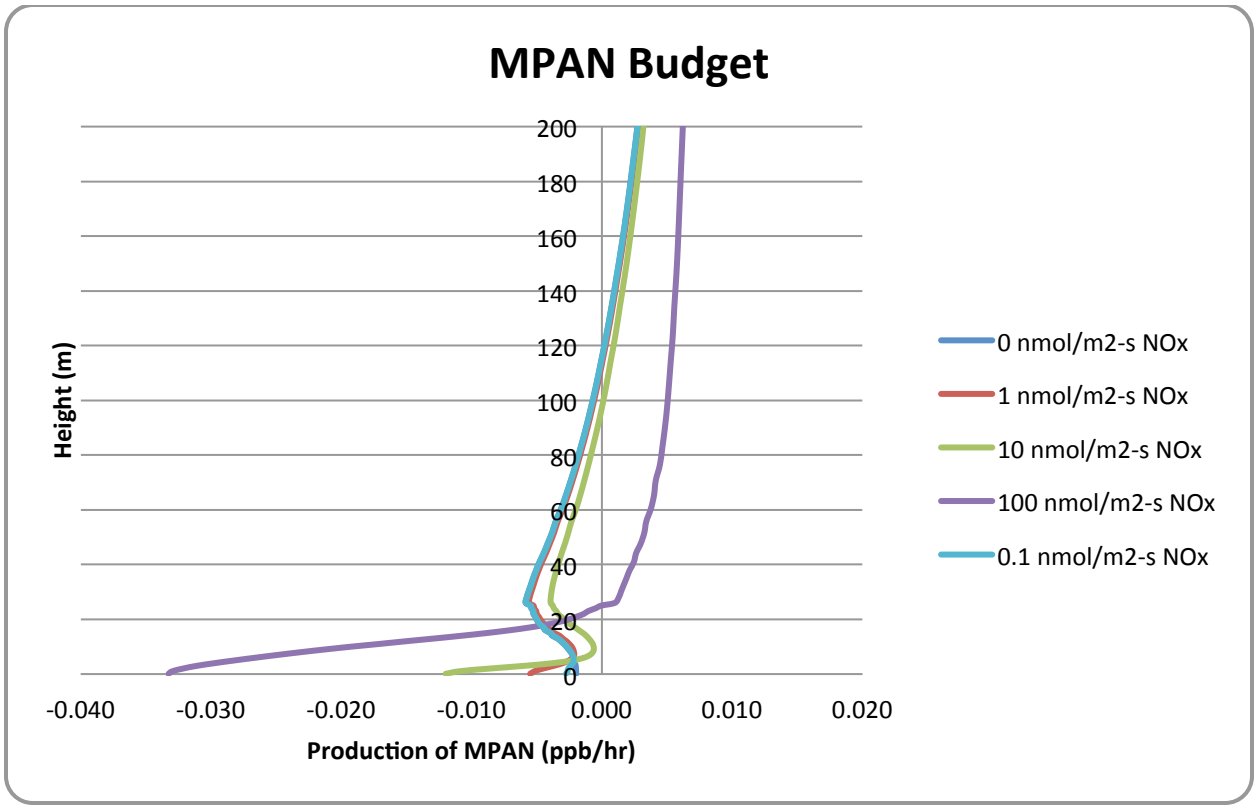




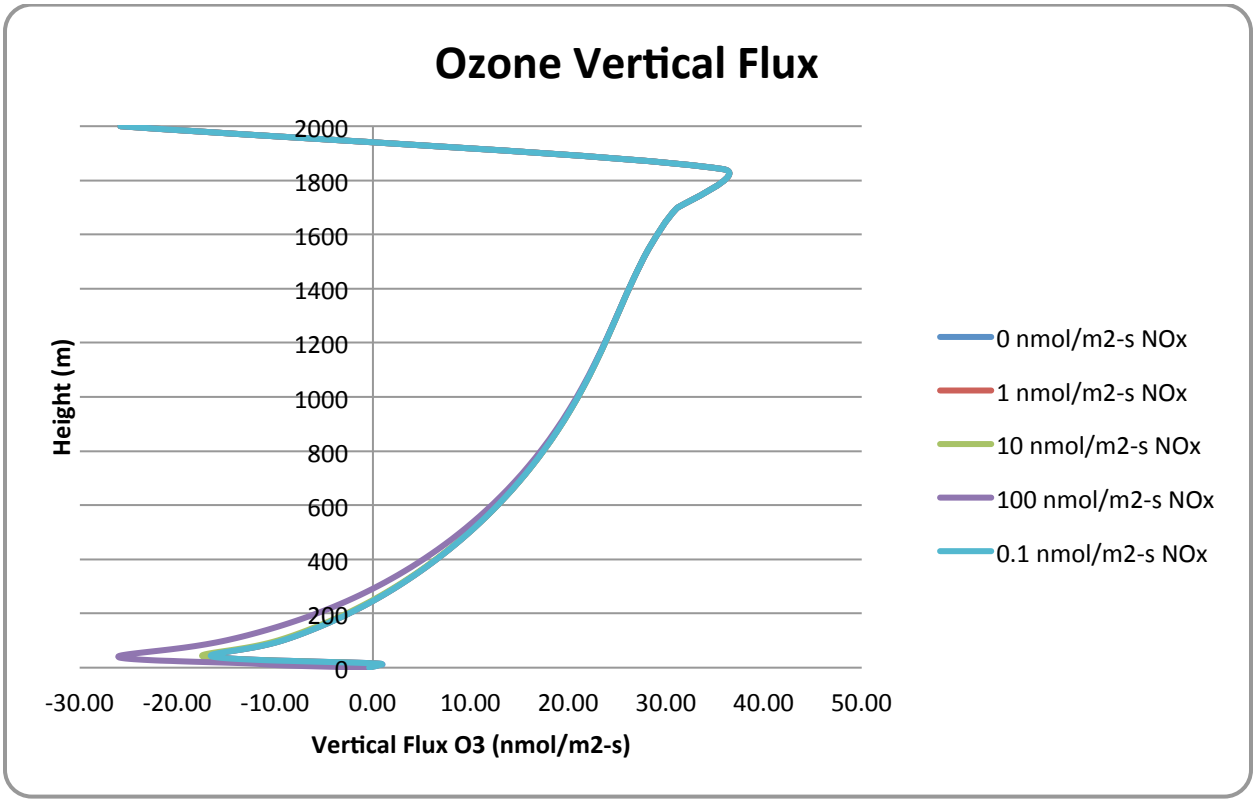
Chemical Production / Budget

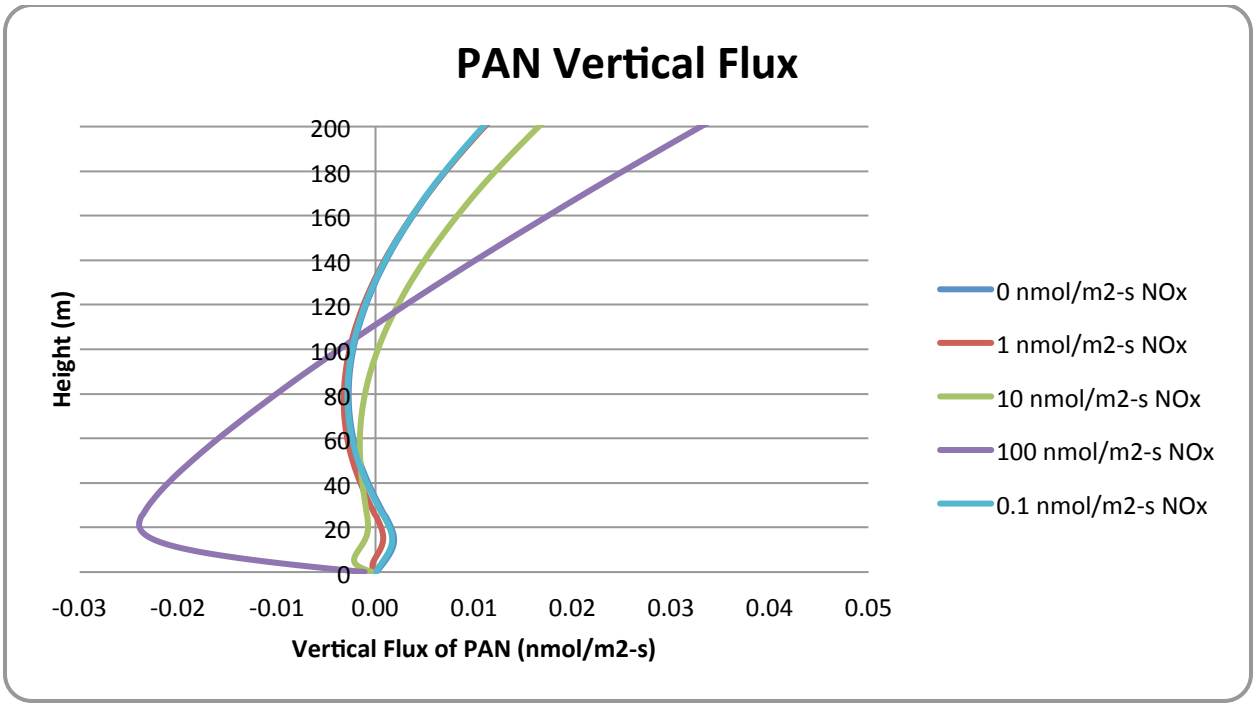


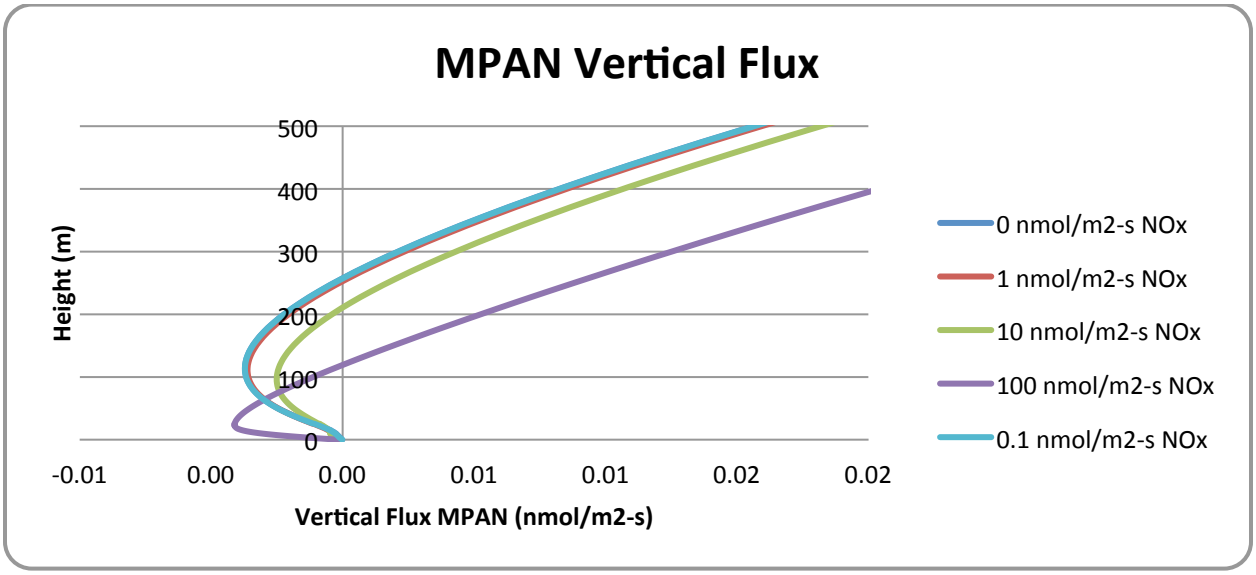


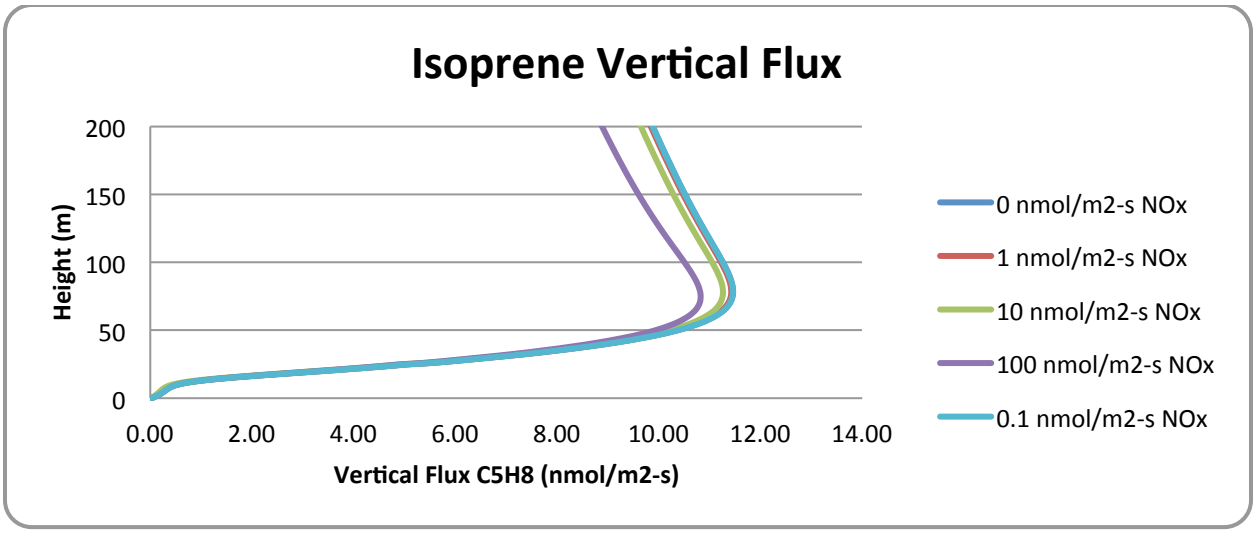

MPAN Budget
Height (m)
200
180
160
140
120
100
80
60
40
20
0
-0.040
-0.030
-0.020
-0.010
0.000
0.010
0.020
Production of MPAN (ppb/hr)
0 nmol/m2-s NOx
1 nmol/m2-s NOx
10 nmol/m2-s NOx
100 nmol/m2-s NOx
0.1 nmol/m2-s NOx

Vertical Flux Profiles






MPAN Vertical Flux
Height (m)
500
400
300
200
100
0
-0.01
0.00
0.00
0.01
0.01
0.02
0.02
Vertical Flux MPAN (nmol/m2-s)
0 nmol/m2-s NOx
1 nmol/m2-s NOx
10 nmol/m2-s NOx
100 nmol/m2-s NOx
0.1 nmol/m2-s NOx


Isoprene Vertical Flux
Height (m)
200
150
100
50
0
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Vertical Flux C5H8 (nmol/m2-s)
0 nmol/m2-s NOx
1 nmol/m2-s NOx
10 nmol/m2-s NOx
100 nmol/m2-s NOx
0.1 nmol/m2-s NOx

REFERENCES

1. Saylor, R. D. (2012). The Atmospheric Chemistry and Canopy Exchange Simulation System (ACCESS): model description and application to a temperate deciduous forest canopy. *Atmospheric Chemistry and Physics*, *12*(9). Retrieved from http://www.atmos-chem-phys.net/13/693/2013/acp-13-693-2013.pdf.