**Predicting Tropospheric Ozone at Quinnipiac’s Mount Carmel Campus with the Framework for 0-D Atmospheric Modeling (F0AM)**

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**Abstract.** In the troposphere, ozone is a pollutant, contributing to various adverse health effects and photochemical smog. The production of ozone in the troposphere results from a myriad of interactions between chemical species under changing meteorological conditions and fluctuating levels of emissions from various sources. Zero-dimensional (0-D) atmospheric models are a versatile tool that can be utilized to investigate these interactions and the contributions to ozone production by different sources of emissions. In this research, we describe the use of a 0-D atmospheric model to predict ozone production on Quinnipiac University’s Mt. Carmel Campus utilizing measurements made on campus. Inputs included NO₂ photolysis rates, which were estimated using three different methods, constrained concentrations of NO and NO2, temperature, relative humidity, and barometric pressure. These inputs were provided to the Framework for 0-D Atmospheric Modeling (F0AM), which simulated chemistry using the Regional Atmospheric Chemistry Mechanism v2 (RACM2). Ozone concentrations predicted by the model were then compared against measured ozone concentrations to assess model accuracy. The ability of the model to accurately predict ozone concentrations was highly dependent on the method of NO₂ photolysis estimation.

1. **Introduction**

0-D models are widely employed in research involving atmospheric chemistry for a wide variety of applications. The many areas of atmospheric research that have employed this tool include investigations of ozone chemistry (Zhao et al, 2020) and emissions from the burning of biomass (Decker et al., 2019). Not limited to data gathered in “uncontrolled” settings, 0-D models have also been utilized in the analysis of data generated in controlled experiments to such as those performed in photochemical chambers (Shi et al., 2021).

As opposed to more robust and computationally intense models that account for transport processes, 0-D models offer an advantage through their simplicity which results in their ability to efficiently utilize more explicit chemical mechanisms and potentially explore the chemistry in more depth (Wolfe et al., 2016). This of course comes with limitations as the assumptions that lead to this simplicity are not valid under all circumstances and can lead to unsound model outputs. Though the limitations of a 0-D box model must be accounted for, they still offer great value in their ability to glean insight into complex and dynamic chemical environments like the atmosphere.

In this research, data gathered from the Quinnipiac Mount Carmel Campus in Hamden, CT is used to constrain a 0-D model and predict levels of tropospheric ozone for comparison against measured values as a benchmark of model reliability, with a focus on accurately estimating the rates of NO₂ photolysis.

1. **Materials**
   1. **NO/NO2/NOx Measurement**

Measurement of NO/NO2/NOx was performed with a 41iQTL NOx Analyzer (Thermo Scientific, Franklin, MA)

* 1. **O3 Measurement**

Measurement of O3 was performed with a Model 205 ozone analyzer (2B Technologies, Boulder, CO)

* 1. **Meteorological Measurements**

Measurement of temperature and humidity was performed with a BME280 Humidity Sensor (Bosch Sensortec)

Measurement of light intensity was performed with a CdS photoresistor

* 1. **0-D Modeling**

The 0-D model reported on in this paper was created with the Framework for 0-D Atmospheric Modeling (F0AM) v4.2.2 (Available on GitHub: <https://github.com/AirChem/F0AM>) See (Wolfe et al., 2016) for further information. All setups utilized the RACM2 chemical mechanism. See (Goliff et al., 2013) for further information.

1. **Experimental**
   1. **Data Collection/Model Constraints (Measured Inputs)**

NO, NO2, O3, temperature, and humidity were measured at the collection site, which consisted of a tube running from the indoor instrumentation cited previously out a second story window on the Hamden, CT Quinnipiac University Mt. Carmel Campus on September 27th 2022. The sensor for temperature and humidity was placed on the windowsill. Data was taken in one minute increments over the course of approximately 10 hours.

The recorded values of NO, NO2, temperature, and humidity were used to constrain the model at each step. O3 was left unconstrained for prediction by the model.

* 1. **Model Constraints (Non-Measured)**
     1. **Setup 1: Model Estimated J-Values (NO2)**

In the first setup, J-values for NO2 were estimated by F0AM after input of longitude, latitude, and altitude of the collection site which the model uses to determine the solar zenith angle (SZA). The method used to estimate J-values involved applying this angle to a radiative transfer model that utilized literature values for cross-sections and quantum yields.

**3.2.2 Setup 2: Photo Stationary State Estimated J-Values (NO2)**

In the second setup, J-values were estimated by solving for JNO2 in the photo stationary state (PSS) utilizing measured values for gaseous concentrations. The calculated value for each step was imported to the model for direct input into the simulation.

**3.2.3 Setup 3: Photoresistor Output Estimated J-Values (NO2)**

In the third setup, J-values were predicted by scaling the output of a photoresistor. The reciprocal of the output was taken, so that higher values would correspond with more sunlight, then the minimum of the output range was subtracted from each point. The values were then multiplied by a factor determined by how closely the resulting values resembled the range of values predicted the photostationary state, with the maximum and minimum photoresistor-predicted values being close to those seen in the photostationary state predictions.

1. **Results/Discussion**
   1. **Describing the Emissions/Light Pattern/Measured Ozone Concentrations on Day of Measurement**

In this research we report model results produced from input measurements taken on September 27th 2022. Figure 1, below, illustrates the emissions profile at the measurement site indicated by the pattern of NO concentrations observed.



**Figure 1.** Concentrations of NO measured at Quinnipiac University’s Mt. Carmel Campus on September 27th 2022 between approximately 7 AM and 5 PM.

The pattern observed showed a spike in NO around 8 AM. The concentrations decreased to a baseline level and remained relatively steady from 10 AM onwards with the only notable exception being a small spike around 11:30 AM.

The pattern of light intensity for the day can be seen in Figure 2, below.



**Figure 2.** Light intensity indicated by the reciprocal output of a CdS photoresistor measured at Quinnipiac University’s Mt. Carmel Campus on September 27th 2022 between approximately 7 AM and 5 PM.

The light intensity at the site where measurements were made for input were observed to steadily increase throughout the measurement period.

The measured ozone profile, to which model predictions were compared, is seen in Figure 3, below.



**Figure 3.** Concentrations of ozone measured at Quinnipiac University’s Mt. Carmel Campus on September 27th 2022 between approximately 7 AM and 5 PM.

Ozone production began rapidly around 9 AM, and concentrations then increased steadily throughout the day.

* 1. **Model Predictions of Ozone Production**

**4.2.1 Model Prediction in Setup 1 (SZA Method)**

In the setup presented in Figure 4, below, ozone was left unconstrained, while data was input to constrain NO, NO2, temperature, humidity, and pressure. J-values for NO2 were estimated based on geographical information used to calculate the SZA.

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**Figure 4.** A comparison of ozone concentrations predicted by the model vs measured concentrations with a setup in which the rate of NO2 photolysis was determined using the solar zenith angle (SZA).

The resulting model output failed to accurately predict ozone concentrations throughout the entire collection period. The disparity between the model and the measurements was greatest where ozone production was the highest.

**4.2.2 Model prediction in Setup 2 (PSS Method)**

In the setup presented in Figure 5, below, ozone was left unconstrained, while data was input to constrain NO, NO2, temperature, humidity, and pressure. J-values for NO2 were estimated based on solving the photostationary state equation for JNO2.



**Figure 5.** A comparison of ozone concentrations predicted by the model vs measured concentrations with a setup in which the rate of NO2 photolysis was determined using the photostationary state (PSS).

The resulting model output captured some of the definition in fluctuations of ozone concentrations early on in the day when ozone production was low, then fell off later in the day, exhibiting increased disparity as ozone concentrations increased.

**4.2.3 Model prediction in Setup 3 (Photoresistor Method)**

In the setup presented in Figure 6, below, ozone was left unconstrained, while data was input to constrain NO, NO2, temperature, humidity, and pressure. J-values for NO2 were estimated based on the output of a photoresistor, with the highest photolysis values being input when the resistor indicated sunlight was the strongest and the lowest values being input when the resistor indicated sunlight was the weakest.



**Figure 6.** A comparison of ozone concentrations predicted by the model vs measured concentrations with a setup in which the rate of NO2 photolysis was estimated using data on light intensity at the collection site from the output of a CdS photoresistor.

The resulting model had the lowest disparity, and most closely matched the shape of fluctuations in the measured plot, in the morning and early evening. The model had the highest disparity with this method from about 10 AM to 1 PM.

* 1. **Discussion of Model Results**

The vehicular emissions profile, indicated by the measured concentrations of NO throughout the day in Figure 1, showed a large spike around 8 AM, correlating with the time at which vehicle traffic is heaviest near the collection site. Light intensity (Figure 2) was indicated to be steadily increasing throughout the day, as was expected at the collection site which is a west-facing window. The measured ozone (Figure 3) seems to indicate that ozone production started at around 9 AM on this day, when concentrations of emitted gases such as NOx are high and the intensity of the sun is beginning to increase.

Both the SZA method (Figure 4) and the PSS method (Figure 5) of estimating NO2 photolysis were most prominently inadequate in the later periods of the day when ozone concentrations were high and continuing to increase.

For the SZA method this discrepancy is probably a result of the method not accounting for the collection site being on the side of a building. The method assumes the sunlight will be strongest in the early afternoon, while the data gathered from the photoresistor indicates this is not the case at the collection site, which receives the most direct sunlight later in the day. This method also does not account for things such as passing clouds, which result in fluctuations in available sunlight that the oversimplified method has no way to account for.

The failure of the PSS method in the later afternoon as possibly the result of the assumptions associated with the equation not being valid. The PSS is known to deviate under certain conditions/circumstances in which the steady-state assumptions made do not hold true (Griffin et al., 2007).

The method in which input photolysis rates were scaled to the photoresistor output did show a relatively improved ability to predict ozone levels in the later afternoon when concentrations were high, although there was high discrepancy in the afternoon, with the model being “late” in predicting when the ozone concentrations would exhibit a rapid increase. This could be due to some of the flaws inherent in the method, which is only an estimate to the wavelengths of light that are actually driving the photolysis of NO2. The photoresistor is only detecting visible light, which is not perfectly correlated with the amount of UV radiation coming from the sun (Gray et al., 2010). Accurate measurement of the relevant range of radiation would require a spectroradiometer, which was not available for this study (Shetter & Miller, 1999).

The results of this study highlight the importance of inputting accurate rates of photolysis when modeling the production of ozone. The uncertainty often present in the rate constants of key reactions is a known difficulty in producing accurate 0-D models (Wolfe et al., 2016).

The next steps to improving this model of ozone production will be understanding the shortcomings present in the photolysis rate prediction of the photoresistor in the afternoon and developing a more reliable proxy to UV radiation.

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