

Ozone Assessment in North-Central Alberta

Prof. Oliver W. Wingenter

Department of Chemistry, New Mexico Tech., Socorro, NM, USA, 87801

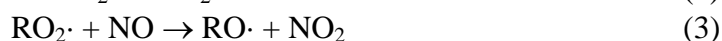
March 26, 2005

1. Background

Ozone (O₃) is a gaseous air pollutant that is formed in the atmosphere by reactions of gases that are emitted directly into the air by a variety of sources. The focus of this study is to determine the extent of ozone pollution in what will be referred to as the Northeast Strathcona County Residents (NESCRC) Grid Area, near Fort Saskatchewan, Alberta (53.8°N; 113.2°W). Model simulations were performed to determine the potential effect of additional increases of these O₃ precursors on air quality in the NESCRC Grid Area. Therefore this study aims to determine the effect of present and possible future local industry on ambient air quality.

2. Ozone Chemistry

Ozone is formed in regions with significant NO_x and NMHCs via Reactions (1-5):



Furthermore, the photodissociation of one ozone molecule in the presence of NMHCs and NO leads to the production of two ozone molecules, as follows: first ozone is photolyzed by ultraviolet light, producing an excited oxygen atom (O(¹D)):



The excited oxygen atom can then react with a water molecule and produce two OH radicals, which can then react with two nonmethane hydrocarbons (RH) in the presence of oxygen to produce two organic peroxy radicals (RO₂):



In the presence of nitrogen oxide (NO), an oxygen atom from each of the RO₂ radicals is taken to form two nitrogen dioxide radicals (NO₂).



The two NO_2 molecules quickly photolyze under visible light to regenerate two NO radicals and to form two ground state atomic oxygen atoms (O). (The two RO radicals go on to produce oxygenated hydrocarbons such as acetaldehyde and ketones, thus further contributing to poor air quality.)



The two O atoms quickly combine with molecular oxygen (O_2) producing two ozone molecules:



Thus, the photodissociation of one O_3 molecule can lead to the production of two O_3 molecules. In these ozone-forming reactions, NO acts as a catalyst while NMHCs serve as the fuel.

Nonmethane hydrocarbon reactivities can vary by several orders of magnitude. Compounds such as alkenes (i.e., ethene, propene) have atmospheric lifetimes of a few hours, whereas, ethane has a lifetime of a few months. This means a long lived molecule like ethane will have most of its local emissions transported out of the area before it can react with OH and contribute to O_3 formation. In contrast, nearly all of the short lived alkenes emitted into an area will react to form O_3 near their source.

3. Ozone Measurements

The hourly Alberta ozone air quality standard of 82 ppbv was exceeded several times in 2003 (Figure 1) and 2004 (Figure 2). That is, these figures illustrate that ozone air quality standards have already been exceeded as a result of current local/regional emissions. They also show that the measurements were made very close to NO_x sources, as explained below.

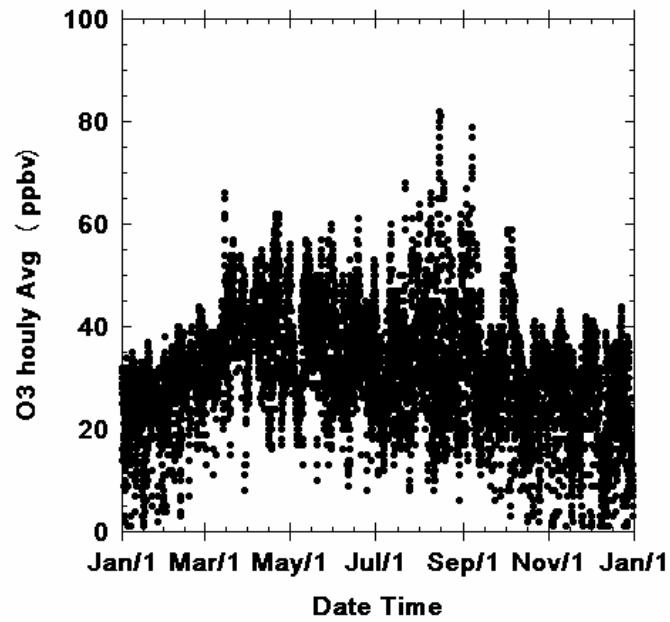


Figure 1. Measurements of average hourly ozone in parts per billion by volume (ppbv) at the Lamont Fort Air Partnerships air quality monitoring site during 2003.

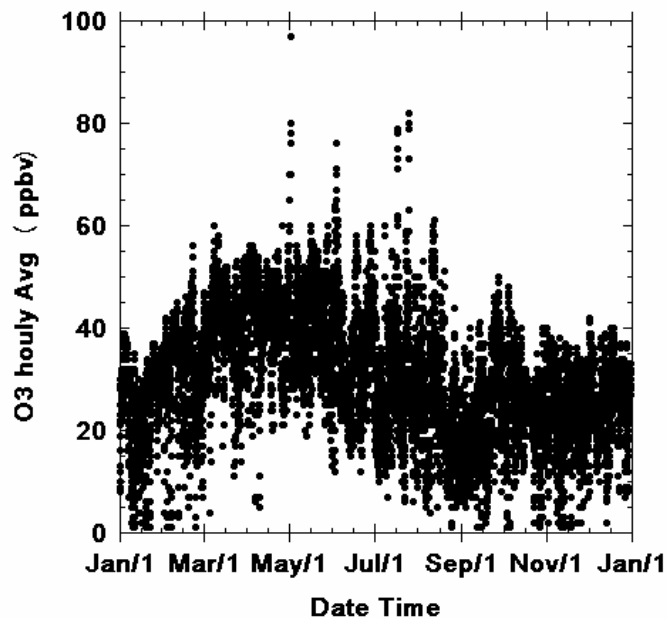
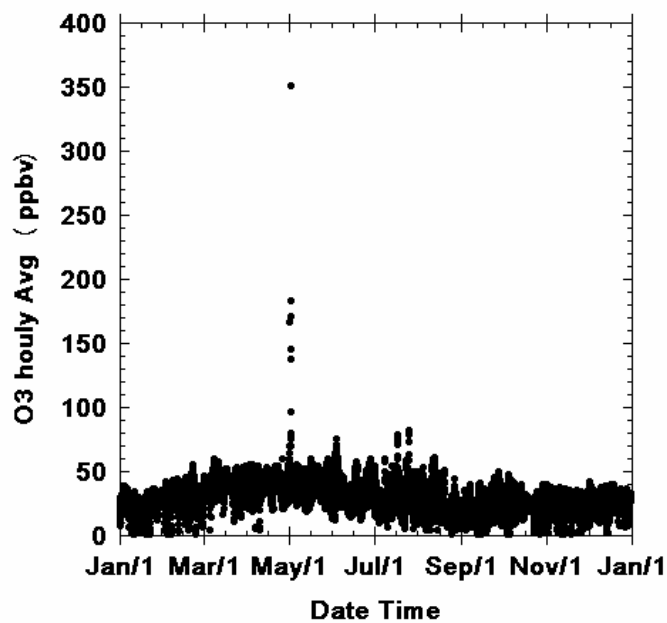
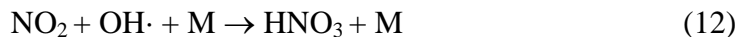


Figure 2. Measurements of average hourly ozone in parts per billion by volume (ppbv) at the Lamont Fort Air Partnerships air quality monitoring site during 2004. Upper panel: all measurements; lower panel: only measurements below 100 ppbv.

When NO is present in high concentrations it leads to ozone destruction:



The high levels of NO₂ can then react with OH in the presence of other molecules (M) to produce nitric acid (HNO₃):



This reaction effectively reduces the concentration of OH, thus inhibiting the formation of ozone by shutting down Reaction 1. Many of the air masses measured at Lamont show clear signs of this type of ozone loss, especially when compared to background ozone measurements made over the Edmonton area at an altitude of 2 km (Figure 3; from Fusco and Logan, 2003).

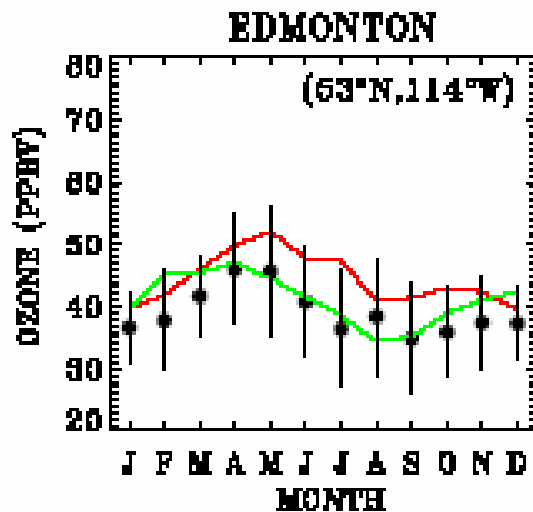


Figure 3. Model predictions of ozone over Edmonton at 2 km above sea level (red and green lines). The black symbols with the vertical error bars are actual measurements of ozone concentrations made over Edmonton during 1994 (from Fusco and Logan, 2003).

From the balloon borne ozone measurements (Fusco and Logan, 2003), it is apparent that background concentrations of ozone are 25 ppbv or higher over Edmonton at an altitude of 2 km. Thus, any ozone measurements made at the Lamont FAP station that are below 25 ppbv (Figures 1 and 2) are indicative of removal of ozone by high levels of NO. This can be further illustrated by plotting the measurements of ozone versus NO₂ made at the Lamont station during 2004 (Figure 4). When NO₂ is at its highest concentrations (0.03 ppmv and higher), ozone is at its lowest concentrations (11 ppbv or lower). Conversely, when NO₂ is at its lowest concentrations the highest ozone levels occur. This means that downwind of Lamont, it is expected that even higher ozone concentrations would be found, after the extremely high NO_x concentrations from the source region have dissipated and the ozone formation chemistry outlined earlier has had time to "cook".

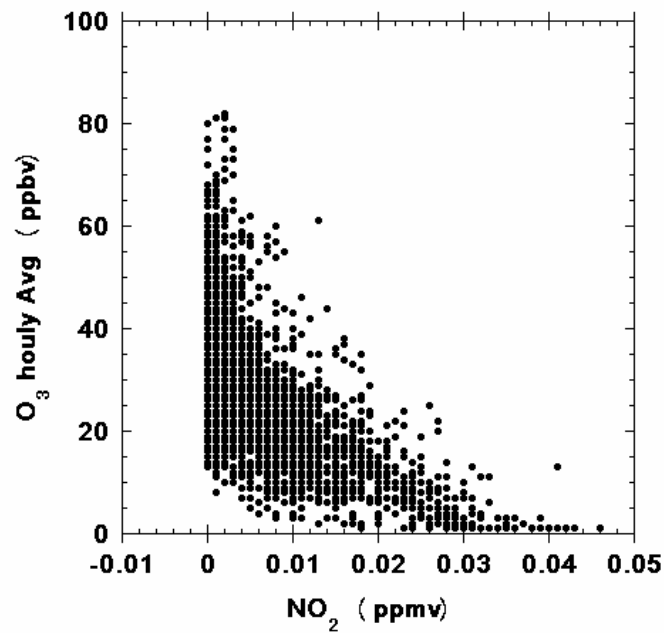
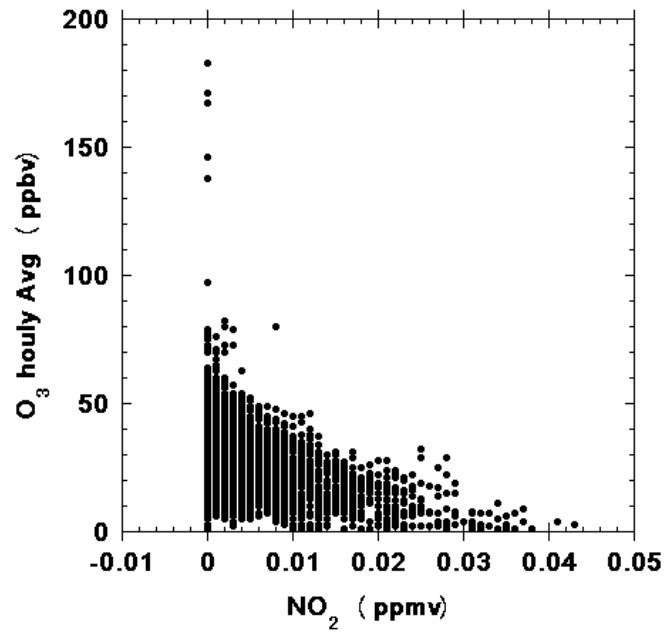


Figure 4. Hourly average O_3 concentrations versus NO_2 at Lamont measured in 2004 (upper panel) and in 2003 (lower panel). The highest O_3 concentrations occur when NO_2 levels are at their lowest. Conversely, the lowest O_3 concentrations are found when NO_2 levels are at their highest.

4. Model Simulations Depicting Additional Ozone Formation

Model simulations were performed in order to estimate the concentration of ozone after an air mass moves further downwind from the Lamont station. These simulations assess the potential of the air mass for further ozone production downwind.

The Georgia Institute of Technology/NASA Langley photochemical box model was used. Since the 1980s, this model and its predecessors have been used extensively to describe ozone chemistry during numerous NASA field studies [e.g., *Chameides et al.*, 1987, *Davis et al.*, 2003]. Seventy-one reactions describe the $H_xO-N_xO_y-CH_4$ chemistry and 184 VOC reactions, based on a highly modified Carter, Atkinson and Lurmann (CAL) scheme [*Lurmann et al.*, 1986] describing the organic photochemistry. Heterogeneous removal of soluble species follows descriptions by *Logan et al.* [1981]. Photolytic coefficients are estimated using the U.S. National Center for Atmospheric Research DISORT radiative transfer model. The numerical method utilizes the Gear solver. The estimated model uncertainty due to rate coefficients has been previously estimated to be about 25% based on comparisons with actual measurements [e.g. *Davis et al.*, 2003].

The measurements made at the Lamont FAP station were used as model input. These measurements include O_3 , NO_2 , relative humidity and temperature. Because only total NMHCs are reported at Lamont, the ratios of the median speciated NMHCs observed by Prof. Blake's research group were used to convert the measured total NMHCs to speciated hydrocarbons needed for the model. Thus, the total NMHCs measured at Lamont remain the same, but the speciation ratio was that measured by the University of California, Irvine. The median CO and methane measurements made by UC-Irvine were also used as model input. Clear sky conditions were chosen because solar radiation measurements were not available. We are currently performing on-going additional model runs using the UC-Irvine NMHC data (rather than the Lamont total NMHC data) along with the Lamont O_3 , NO_2 , relative humidity and temperature. Because the UC-Irvine measurements show much higher VOC levels in the NESCR Grid Area than the FAP VOC measurements at Lamont (see sister report by D. R. Blake), there is an even greater potential for additional impact by ozone pollution within the study area.

The input data described above together with the GIT/NASA model were used to calculate the formation, destruction, and net ozone production for all air samples collected at Lamont during 2004 that had measured ozone concentrations of 50 ppbv or higher. Specifically, the model was used to determine how much added ozone would be formed after two additional hours of photochemistry, once the air masses measured at Lamont traveled further downwind.

Because of the proximity of the Lamont site to the NO_x sources, the measured O_3 concentrations are lower than they would be if the site were further downwind from the O_3 precursors. It is evident from Figure 5 that the most polluted samples would have only small increases in O_3 concentration with additional time. By contrast, the samples less enhanced in O_3 show an average ozone increase of 10 ppbv after just 2 additional hours. This is a result of their NO_x and VOC levels still being high enough for substantial O_3 production. With the additional two hours of photochemistry, the number of violations of Alberta ozone air quality in 2004 would increase from the 5 measured at Lamont to 27.

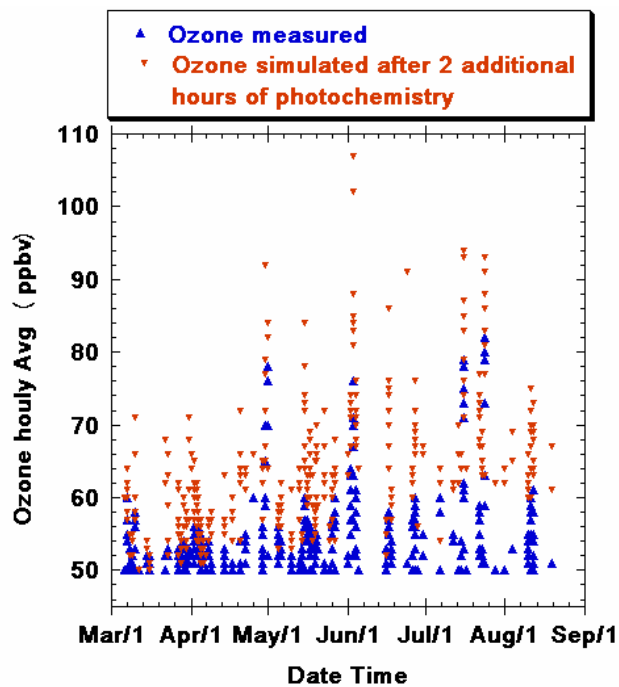
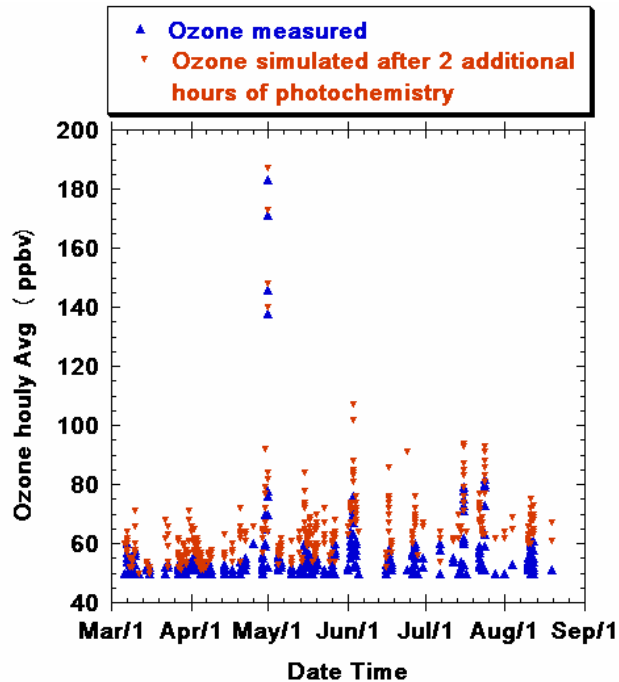


Figure 5. Ozone concentrations measured at the Lamont FAP site (blue triangles) and the simulated ozone concentration if the air masses were measured 2 hours downwind of Lamont (red triangles). On average, the extra 2 hours of photochemistry results in an additional O_3 increase of 10 ppbv. The y-axis scale in the lower panel is changed to show only O_3 concentrations below 110 ppbv.

5. Recommendations

BA Energy has stated that their bitumen upgrader would increase NO_x levels in the region by 7% and would increase VOC emissions by several tonnes per day. My model predictions suggest that, each year, regions only a couple hours downwind of Lamont already have many more instances of violations of Alberta ozone air quality standards than in Lamont. It is clear that any additional increases of O₃ precursors would result in even greater noncompliance with Alberta's 1 hour average ozone standard of 82 ppbv.

There are only two sites where ozone is presently being monitored in the region. The site at Fort Saskatchewan unfortunately does not measure NO_x, NO, or NO₂, limiting the use of this station in assessing ozone air quality. It is evident that additional fully-equipped air quality measurement sites are needed in the region in order to make informed decisions on future industrial emissions. Measurement sites 20 to 40 kilometers further away from the source region are badly needed. In addition, existing sites should be outfitted with a full complement of measurements including speciated hydrocarbons, CO, O₃, NO, NO₂, and solar radiation (i.e. at a minimum, Eppley radiometers should be installed). At the very least, the type of gridded sampling and speciated NMHC measurements performed Prof. Blake's group should be repeated in each of the remaining three seasons and under various meteorological conditions. At this time, emission reductions at existing facilities should be implemented immediately. Furthermore, no additional industrial facilities should be established in the area without further measurements and modeling studies to allow for a more complete assessment of ozone production in the area.

References

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