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Project Summary

Relationships Between Ozone Precursor Levels and Response to Emissions Reductions: Analysis of Regional Oxidant Model Results for the Northeastern United States

Jana B. Milford, Dongfen Gao, and Antigoni Zafirakou

A detailed analysis of results from the Regional Ozone Modeling for Northeast Transport (ROMNET) study has been conducted to examine the conditions under which alternative control strategies were predicted to be effective in improving air quality. The ROMNET study had predicted that for most of the northeastern United States, reducing nitrogen oxides (NO_x) emissions by about 60% would be more effective in reducing ozone (O_3) than reducing anthropogenic reactive organic gas (ROG) emissions by approximately the same proportion. However, for the New York City and Baltimore-Washington areas, ROG controls were predicted to be highly effective and NO_x controls to be counterproductive. ROMNET results for cases in which the reactivity of ROG emissions was reduced were similar to those for cases in which the mass of ROG emissions was reduced. Plots of O_3 versus the concurrent NO_y concentration in each model grid cell indicated that O_3 increased with NO_y concentrations up to 10 - 15 ppb; and either increased or decreased with higher NO_y depending on the associated ROG levels. The analysis also showed that reducing NO_x emissions by about 60% was uniformly beneficial for grid cells with NO_y concentrations less than about 25 ppb, but counterproductive for some grid cells with NO_y above 25 ppb. Ozone was relatively insensitive to reductions in ROG emissions in grid cells with NO_y concentrations below 5 - 10 ppb. We recommend further investigation of the idea that NO_y concentrations could serve as an indicator of the likely sensitivity of O_3 to ROG or NO_x controls, if NO_y was monitored along with peak ozone during photochemical air pollution episodes.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research report that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The success of efforts to reduce summertime concentrations of ozone throughout the northeastern United States depends on our understanding of the chemistry involved in ozone formation in this region. Three questions that are currently the subject of controversy illustrate the importance of our ability to describe the chemistry that is occurring:

(1) What is the relative contribution to ozone formation of biogenic versus

anthropogenic emissions of reactive organic gases (ROG)?

(2) Where would reductions in emissions of nitrogen oxides (NO_x) help reduce ozone, and where would they be counterproductive?

(3) What benefits could be gained through control strategies such as substituting methanol-based fuel for gasoline, which lower the reactivity of ROG emissions, rather than cutting the overall mass of emissions?

For the Northeast, the questions listed above have been addressed in the Regional Oxidant Modeling for Northeast Transport (ROMNET) study conducted by the U.S. Environmental Protection Agency and state and local agencies within the region. The study used EPA's three-dimensional, regional scale photochemical grid model, the Regional Oxidant Model (ROM), to simulate the air quality impacts of a variety of control strategies for ROG and/or NO_x emissions. This study extends the analysis of the ROMNET results, focussing on understanding the chemical interactions (as predicted by ROM) that underlie the impact of alternative control measures on air quality.

Used in predicting how air quality will respond to emissions reductions, the role of a photochemical air quality model is to integrate descriptions of the fundamental physical and chemical processes that govern ozone formation, destruction, and transport. The physicochemical system that produces ozone on regional and urban scales is extremely complex, and many features of the system are difficult, if not impossible, to elucidate empirically. Despite well recognized limitations (notably, inadequate evaluation by comparison with observations, but also including the expense and time required to apply them), photochemical air quality models represent the best means currently available to predict how air quality might respond to altered emissions.

Because of the limitations of the models, however, considerable interest exists in finding observable "indicators" of how real air masses are likely to respond to emissions controls (e.g., of NO_x versus ROG-based strategies). Examining model predictions of the associations between chemical species, and the chemical conditions under which controls are predicted to be more or less effective, can help to identify possible indicators. Once key associations have been ferreted out from model results, the next step is to look for them in field observations.

The study reported here has examined the predicted distributions and interactions of chemical species in the ROM simulations, which underlie predictions of how concentrations of ozone and other secondary species might respond to controls. The analysis has explored relationships between chemical species, and how predicted concentrations of ROG classes, radicals, NO_x, NO_y, etc., differ from one location to another, and change from simulations with base case emissions to simulations of controlled emissions levels. The associations between chemical species seen in the model outputs result from the modeled interactions of chemical reactions, transport processes, emissions distributions, etc., and therefore are not necessarily apparent in the input data or in theoretical descriptions of individual processes. Some of the associations predicted by the model should be observable, and some suggest new strategies for predicting the effect of controls, evaluating models, and monitoring the progress of control efforts.

Discussion and Conclusions

Summary

A key assumption underlying this study is that photochemical air quality models such as ROM, despite their limitations, are useful tools for integrating existing understanding of the complex array of physical and chemical processes that act together to form, transport and destroy secondary pollutants. In particular, models are a primary tool for investigating how secondary pollutants might respond to altered precursor emissions rates. We thus hoped that detailed examination of ROM results showing the chemical conditions under which alternative control strategies were predicted to be effective might suggest ways in which air quality monitoring programs could be improved, to better assist in evaluating models and ultimately in predicting the effects of control strategies.

Within the ROMNET simulation period of July 2 - 17, 1988, July 8 was singled out as the focus of this analysis, as representative of a high ozone day. With meteorological conditions for the July 1988 episode but with emissions projected to the year 2005, predicted ozone concentrations in the ROMNET domain on July 8 peaked at around 250 ppb, in New York City. To reduce ozone concentrations, the ROMNET study predicted that reducing NO_x emissions by about 60% would be more effective, for most of the model domain, than reducing anthropogenic ROG emissions by approximately the same proportion. Combining the ROG and NO_x reductions was predicted to yield similar reductions in ozone to those achieved with NO_x controls alone. However, countervailing results were predicted for portions of the New York City and Baltimore-Washington metropolitan areas, where peak ozone concentrations on July 8 were higher under the NO_x control strategy than in the base case.

The response of PAN concentrations to the ROG or NO_x control strategies was predicted to be similar to that for ozone. NO_x controls were predicted to be uniformly most effective in reducing HNO_3; ROG controls in reducing H_2O_2 and formaldehyde.

Two additional ROMNET scenarios that we examined were designed to predict the effect of measures that reduce the reactivity of volatile organic compound emissions without substantial reductions in the mass of emissions. Results for ozone in the CS20 scenario, in which the reactivity adjustment was the only change from the 2005 base case, were similar to those of CS12, with substantial reductions limited to the New York City area. Although unweighted ROG concentrations in urban areas were 30 to 40% higher in CS20 than in CS12, reactivity weighted ROG concentrations in CS20 generally fell within 10 to 20% of CS12 levels.

Because predicted responses in New York City were so different from those occurring elsewhere, time series of predicted concentrations were examined along an air mass trajectory ending in the core of the city at 4 p.m. on July 8. The New York City core was characterized by extremely high ROG and NO_y concentrations, relative to the rest of the model domain. Based on the time series of precursor and radical concentrations along the New York City trajectory, one factor in the sharp drop in ozone concentrations in the area that results from ROG controls appears to be an increase in the lifetime of NO_x. With reduced ROG emissions, OH concentrations are also reduced, and consequently the conversion of NO_x to inactive forms of NO_y is slowed. ROG controls thus appear to extend the period during which ozone levels are suppressed by high NO_x emissions.

Preliminary analysis of the ROMNET results looked at associations of ozone levels with concentrations of NO_x, NO_y, ROG and ROG/NO_x in the same grid cell. Consistent with the findings of Sillman et al. (1990), the association of ozone with NO_y showed the clearest trends with the least scatter, supporting its use as a reference variable. As discussed by Sillman et al., NO_y has a similar lifetime to that of ozone, and reflects time-integrated NO_x emissions received into an air mass.

Scatter plots of 4 p.m. ozone versus 4 p.m. NO_y concentrations in each grid cell for the ROMNET 2005 base case and for the ROG (CS12) and reduced reactivity (CS20) control cases are consistent in indicating that ozone increases with NO_y concentrations up to 10 - 15 ppb; then increases or decreases with NO_y depending on the associated ROG levels. Scatter plots of the change in ozone from the base case to the NO_x control case (CS11) and from CS12 to the combined control case (CS10) indicate that NO_x controls are uniformly beneficial for grid cells with 4 p.m. NO_y concentrations less than about 25 ppb. The NO_x control scenarios were predicted to be counterproductive for some grid cells with NO_y concentrations above that level. Ozone concentrations were relatively insensitive to reductions in ROG emissions in grid cells with NO_y concentrations below 5 to 10 ppb. The associations of PAN concentrations and of the response to NO_x controls with NO_y were qualitatively similar to those found for ozone.

Discussion

Results from the ROMNET study for the association of ozone with NO_y, and specifically the threshold NO_y concentrations below which NO_x controls are uniformly beneficial, appear to be consistent with results from several other modeling studies (*Sillman et al.*, 1990; *Sadeghi et al.*, 1992; *McKeen et al.*, 1991; *Milford et al.*, 1992). The fact that this association is so consistent across modeling studies suggests that NO_y measurements may be a useful empirical indicator for the sensitivity of ozone to emissions.

It is well known that the balance between ROG and NO_x levels controls the sensitivity of ozone to precursor emissions reductions, with ROG/NO_x ratios used to characterize this balance. Problems with the use of ROG/NO_x ratios as empirical indicators of ozone sensitivity have been noted in Section 2.2 of the full report. Reflecting those problems, preliminary analysis of the ROMNET results showed that the response of ozone to ROG or NO_x controls was more consistently related to simultaneous NO_y concentrations than to ROG/NO_x ratios.

As a measure of cumulative NO_x emissions, NO_y may serve as an adequate indicator of whether an air mass is ROG or NO_x-limited in part because effective ROG levels are relatively uniform (*Chameides et al.*, 1992). Figure 34 in the full report was notable in supporting this argument, showing the association of propylene-equivalent ROG concentrations with unweighted ROG in the range that encompasses the concentrations in most of the urban grid cells in the ROMNET domain, except those in the New York City area. No correlation is apparent between these two measures of ROG levels. In most urban grid cells outside of New York City, even though unweighted ROG concentrations were relatively high, Propy-Equiv ROG concentrations were close to the domain average. Gradients of NO_y concentrations are generally much sharper than those of Propy-Equiv ROG.

Our analysis suggests the possibility that measured NO_y concentrations could be used as indicators of the photochemical sensitivity of air at times of high ozone and as a critical test of model performance. Establishing a network of NO_y monitors would permit evaluation of models such as ROM against a variable that is directly related to the simulated effectiveness of ROG versus NO_x control strategies, thus increasing confidence in the use of the models. However, before such a network could be created, several issues need to be addressed.

Although measurement techniques for total NO_y have performed well in research applications (*Fehsenfeld et al.*, 1987; *NRC*, 1991), consideration should be given to how readily these techniques could be adapted for more widespread use. Another critical issue is monitor siting and sample timing. Use of NO_y measurements as indicators of ozone sensitivity would require that monitoring locations be removed from direct emissions of NO_x, and that sampling coincide with peak ozone concentrations.

A final question is the correspondence between modeled and measured NO_y. The CBIV mechanism (*Gery et al.*, 1988; 1989) included in ROM uses a condensed treatment of organic nitrate species, and neglects gas to aerosol conversions, such as formation of ammonium nitrate from nitric acid. The fraction of aerosol nitrate recovered in NO_y measurements is unknown. Moreover, there is some "lost" nitrogen in the CBIV mechanism, in that nitrogen-containing products of some reactions are not tracked. According to *Trainer et al.* (1991), during the summer of 1986, NO, NO_2, HNO_3 and PAN accounted for 85% or more of the NO_y measured at their field site in rural Pennsylvania. Thus, for the rural to urban conditions found in the northeastern U.S., discrepancies between measured and modeled NO_y are probably not large. Nevertheless, the sources of potential discrepancies warrant further study.

Recommendations

Further investigation is warranted of the idea that NO_y concentrations could serve as an empirical indicator of the likely sensitivity of ozone to ROG or NO_x controls, if monitored along with peak ozone during photochemical air pollution episodes. Assessment of the adaptability of NO_y measurement techniques for routine use in urban areas is needed, along with detailed evaluation of errors introduced by the simplified treatment of reactive NO_y species in ROM and other photochemical air pollution models.

To recommend that the Regional Oxidant Model should be evaluated more extensively, especially with regard to its performance for ozone precursors, is approaching a cliche. However, the dependence of predicted ROG or NO_x control effectiveness on NO_y levels displayed by the ROM results underscores the importance of this recommendation. To emphasize the point, the ability of the model to predict responses to alternative control strategies is tied to its ability to simulate grid cell averaged NO_y levels. With respect to ROG levels, the lack of spatial correlation between ROG and Propy-Equiv ROG concentrations suggests the need for speciated ROG measurements, rather than measurements of total ROG. The model results also point to the importance of measuring concentrations of carbonyl species.

Finally, a targetted field experiment would be of interest to verify the ROMNET result that in the New York City area, in association with peak ozone concentrations, very high ratios of NO_x to NO_y persist throughout the day. If observed, unusually large NO_x fractions would support the prediction that ROG emissions reductions will be highly effective for the New York City area.

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Jana B. Milford, Dongfen Gao, and Antigoni Zafirakou are with the University of Connecticut, Storrs, CT 06269.
***Thomas E. Pierce** is the EPA Project Officer (see below).*
The complete report, entitled "Relationships Between Ozone Precursor Levels and Response to Emissions Reductions: Analysis of Regional Oxidant Model Results for the Northeastern United States," (Order No. PB93-186 294/AS; Cost: $27.00, subject to change) will be available only from:
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