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Project Summary

Ozone Formation in Pollutant Plumes: A Reactive Plume Model with Arbitrary Crosswind Resolution

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A new two-layer reactive plume model was developed in which arbitrary crosswind resolution of the emission field of each precursor is preserved and dynamic plume-plume and plume-background interactions are explicitly accommodated. The model has a hybrid formulation, having Lagrangian downwind transport and Eulerian crosswind spread. It is applied in a diagnostic mode to simulate the observed behavior of plumes of the metropolitan St. Louis area and the Labadie power plant. The RAPS emissions inventory gave detailed spatial resolution of the emission field, numerous stationary and mobile upper air wind soundings provided the basis for transport simulation, and aircraft data provided detailed crosswind profiles of pollutant concentrations across the plumes at downwind sections.

Background ozone and sulfate production were found to be NO_x limited and poorly correlated with background NMHC/NO_x. Power plant plume ozone and sulfate production were both positively correlated with background NMHC/NO_x. Excessive ozone can form in a power plant plume without any interaction with a neighboring urban plume. Power plant emissions of NO_x, including those in rural locations, are a major contributor to the regional ozone burden in the eastern U.S. Their potency, however, is realized because of the biased precursor loading of the regional background (NMHC/NO_x around 30 ppbv/ppbv). This bias is a result of the strong disparity in the rates of consumption of NMHC and NO_x in urban plumes. Model simulations of ozone were generally good, even in crosswind detail, given an appropriate background characterization. Simulated values of the rate of SO_2 oxidation were quantitatively not as satisfying.

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

Introduction

Damaging effects of ozone on human health, forests and crops, and materials occur frequently during summer in relatively polluted regions such as the eastern United States. While natural emissions of organic vapors may play a significant role in the photochemistry leading to ozone production in the atmosphere, the predominant sources of the precursors NO_x and NMHC are anthropogenic in origin. Specifically, urban-industrial complexes and power plants (many of which are located in rural areas) are the principal sources of ozone precursors. The chemistry of ozone photosynthesis in the pollutant plumes of these sources is linked also to the production of other irritants (e.g., PAN), acidic matter (e.g., H_2SO_4, HNO_3) which is responsible for acidic deposition, and fine aerosols which contribute to visibility reduction and regional haze.

Ozone, both local and regional, originates mostly from specific urban and rural sources. Under typical summer midday conditions in the eastern U.S., ozone photosynthesis attains a peak rather promptly within a mesoscale range of urban sources as well as rural power plants. The regional impact follows as this

peak spreads by atmospheric dilution and is affected by subsequent nighttime chemistry followed by further daytime chemical reactions in a multi-day regional buildup process. To properly assess the problem, plume models must quantify the phenomena of mesoscale ozone peaking and subsequent dissipation within the time scale of a day. The results of such models should be adequate for assessing the local problem and must also provide the basis for sub-grid scale parameterizations to be used in regional models. Regional models can reciprocate by providing the basis for estimating the composition of the ambient environment into which the plumes are emitted.

Ozone formation in pollutant plumes, both the typical urban variety and the rural power plant plumes, is considered here. The investigative tools include both field observations and a new reactive plume model. There was a need to examine and interpret available *in-situ* mesoscale data collected in metropolitan plumes in the eastern U.S. An effort was initiated to develop a plume model with spatial resolution consistent with the available field data of St. Louis RAPS and MISTT (as well as PEPE/NEROS and NEROS I) and with the capability to examine in particular the role of plume-plume and plume-background interactions. This report describes the current state of the new model and its preliminary application to a field observation scenario. The model awaits some further development which would make it fully operational and applicable to arbitrary metropolitan and rural plume emissions and their reactive transport.

Features of the New Model

The principal features of the new model are outlined below:

- arbitrary crosswind resolution of the precursor emission field, as well as of the downwind concentration field;
- full dynamic interaction between typical urban plumes which are rich in NO_x and NMHC, and power plant plumes which are initially devoid of NMHC, but are very rich in NO_x;
- full dynamic interaction between a plume and its ambient environment;
- dynamic simulation of the ambient environment, both within the boundary layer and aloft, including the effect of regional emissions; and
- a chemistry module that is a modified form of the Demerjian-Schere chemical scheme and simulates the kinetics of 26 species.

In its present state, the model is not operational in a generalized mode of application. In particular, the primary emissions module needs revising and upgrading, and the chemistry module needs to be generalized to accept any scheme. Once these revisions are implemented, an operational version of the computer code can be prepared for more general application by a wider user community.

Goals of Model Application

Model application involved the following specific goals:

- characterization of the chemical composition of the ambient environment in terms of precursors, secondary products, as well as important intermediate species (e.g., OH, HO_2, H_2O_2);
- investigation of the sensitivity of ozone photosynthesis in the background to regional emissions of the precursors;
- investigation of the sensitivity of ozone formation in a power plant plume to the composition of the ambient environment;
- simulation of the transport and chemistry of the 1200 release of the Labadie power plant plume on July 9, 1976, and comparison of the observed ozone crosswind profile 190 km downwind at 2000;
- simulation of the transport and chemistry of the metropolitan St. Louis plume, emitted over the period of 1200 to 1500 on 9 July 1976, and comparison of the observed downwind ozone crosswind profile at 2000; and
- simulation of the chemistry of sulfur and nitrogen oxides in the St. Louis plumes and in the ambient environment.

Results of Model Application

The following conclusions based on field observations and model calculations are highlighted. They are believed to be of fairly general qualitative validity for the eastern U.S.

Ambient Environment

- The ambient environment is dynamic and chemically quite active both in the mixing layer and aloft. It is not appropriate to assume the air aloft to be chemically inactive during the morning period.
- The boundary layer is even more reactive, being continuously fed by regional emissions of precursors and by entrainment of aged air from aloft. Both processes can have strong effects in shaping boundary layer composition and chemistry.
- Afternoon values of the concentration ratio NMHC/NO_x (ppbv/ppbv) of boundary layer air are around 30. In terms of ozone formation potential, such an environment is strongly NO_x limited. Regional emission flux of 2 -3x10^{11} molecules $cm^{-2}s^{-1}$ of NO_x appears to be appropriate for developing about 70 ppb of ozone typically observed in the eastern U.S. summer background. This flux is consistent with the total eastern U.S. anthropogenic emissions of NO_x. The depletion of NO_x is quite rapid in the summer daytime atmosphere.
- The high loading of NMHC in the boundary layer appears to be a result of the vast difference in the rates of NMHC and NO_x depletion in urban plumes. NO_x is consumed more rapidly, leaving behind the less reactive hydrocarbons to flow dilute into the regional background. Regional background values of NMHC in the Midwest and the Ohio River Valley region are probably around 100 ppbC (about 25 ppbv) on summer days.
- The formation of ozone in the background is relatively insensitive to increases in the regional emissions of NMHC. However, observed ozone formation in the Labadie plume is sensitive to background NMHC and requires the ratio of NMHC/NO_x in the regional emission flux to be about eight by volume. This is considerably higher than the average eastern U.S. anthropogenic flux ratio which is less than two but much less than the corresponding ambient concentration ratio on summer days which is about 30. The significance of natural emissions of NMHC may be greater than previously thought.
- Production of OH and hence the rate of gas-phase oxidation of SO_2 and NO_2 in the background are strongly sensitive to ambient NO_x. Gas-phase formation of acidic products in the ambient air appears to be inversely related to the concentration of ratio NMHC/NO_x.

Power Plant Plumes

- Power plant plumes are a major source of ozone in the eastern U.S. The NO_x-starved and NMHC-loaded background air is very responsive to NO_x loading from the power plant emissions. Following an initial depletion of ozone within the plume due

to reaction with primary NO in the fresh plume, there is rapid ozone recovery and ultimately a substantial ozone bulge in the plume, as NMHC and free radical species are entrained from the background.

- The ozone-forming potential of power plant emissions is, however, strongly dependent on ambient NMHC which are not emitted by the power plants. Presumably, while the polluted atmosphere under convective conditions is conducive to rapid ozone generation in power plant plumes, the clean atmosphere is not. An increase in ambient NO_x raises ambient ozone and reduces the potential for excess ozone formation in the plume. Ozone formation in the power plant plume is thus positively correlated with ambient NMHC/NO_x.
- There is also more direct evidence of the influence of background entrainment on the evolution of plume ozone dynamics. The developing crosswind profiles clearly show that plume ozone recovery is most rapid in plume edges where the NMHC/NO_x ratio is highest.
- It appears that the ozone recovery in the plume is complete when the cross-sectional average value of NMHC/NO_x in the plume exceeds about 1 ppbv/ppbv.
- The rates of oxidation of SO_2 and NO_2 in the plume appear to be positively correlated with ambient NMHC/NO_x. The correlation for SO_2 appears to be much better than the correlation of the SO_2 oxidation rate with ambient ozone. Hence, use of ambient ozone as a surrogate for ambient NMHC/NO_x in parameterizations of the SO_2 oxidation rate is not well founded. However, given the dearth of reliable ambient data for NMHC and NO_x and the approximate level of accuracy of estimates of the SO_2 oxidation rate based on field measurements, the continued temporary use of ozone may be justifiable in empirical parameterizations.

Metropolitan Plumes

- Urban emissions are rich in both precursors of ozone, and hence, urban plumes are less reliant on background entrainment for ozone photosynthesis than are power plant plumes.
- Metropolitan emissions are typically characterized by a diverse spatial distribution of the precursor mix and of source configurations. There is a corresponding wide range of spatial-temporal variability of ozone distribution. There is good evidence for the "source intensification" effect where plumes intersect. Improper treatment of the primary emissions distribution does lead to distortion of the ozone distribution. Urban emissions are capable of generating substantial amounts of ozone rapidly. The production of ozone then slows down as the NO_x becomes depleted long before the NMHC, thus passing on an excessive amount of NMHC to the regional background. This relative overloading of the background remains potent in terms of potential ozone production. This potential is realized when NO_x emissions, as from a power plant, are released into the background.

Research needs

- Proper chemical characterization of the primary emission field and of the ambient environment remain high priority needs for reliable prediction of ozone formation in the polluted atmosphere.
- Sub-grid scale effects are very important near precursor sources in the context of regional models. Mesoscale field observations and model applications must be directed at the study and quantification of such effects.

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***John F. Clarke, Francis Pooler, Jr.,** and **William E. Wilson** are the EPA Project Officers (see below).*

The complete report, entitled "Ozone Formation in Pollutant Plumes: A Reactive Plume Model with Arbitary Crosswind Resolution," (Order No. PB 86-236 973/AS; Cost: $11.95, subject to change) will be available only from:

National Technical Information Service
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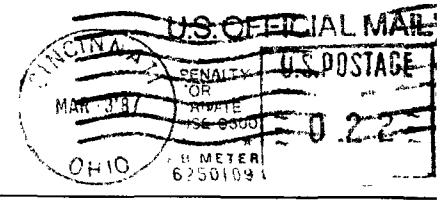

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