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Project Summary

Evaluation of Chemical Reaction Mechanisms for Photochemical Smog: Part III. Sensitivity of EKMA to Chemical Mechanism and Input Parameters

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Six chemical reaction mechanisms for photochemical smog described in Parts I and II are used to study the effect of input parameters on volatile organic compound (VOC) control requirements needed to meet the National Ambient Air Quality Standard for ozone. The parameters studied are initial VOC composition, dilution rate, post-8-A.M. emissions, base-case (present-day) O_3 levels, entrainment from aloft of VOC and ozone, initial HONO and initial VOC/NO_x ratio. The Empirical Kinetic Modeling Approach (EKMA) was used to generate ozone isopleths for each chemical mechanism. The VOC control needed to reduce the maximum ozone concentration from some present-day value to 0.12 ppm, assuming no NO_x control and a specified initial VOC/NO_x ratio, was calculated using the six chemical reaction mechanisms. The initial VOC/NO_x ratio is found to have the largest effect of all the parameters studied on VOC control requirements. Choice of chemical mechanism, ozone entrainment from aloft and the composition of the initial VOC mixture also have a large effect on predicted control requirements. To reduce the degree of uncertainty in control predictions using EKMA it is necessary to establish as accurately as possible the composition of urban air in early morning. Also, because of the substantial effect the choice of chemical mechanism has on the predicted control requirements using EKMA, it is important that future work continue to be directed toward evaluating candidate chemical mechanisms with respect to their ability to simulate atmospheric smog chemistry.

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

Currently there are several chemical reaction mechanisms available for use in predicting hydrocarbon and NO_x reductions needed to meet the National Ambient Air Quality Standard (NAAQS) for ozone for a particular region. Because of the numerous organic species in the atmosphere, it is computationally infeasible to use a chemical reaction mechanism that contains every reaction of every species in carrying out a control calculation. Each chemical mechanism reduces the number of organic species in a somewhat different way. This reduction, or "lumping," would not be a concern if each of the chemical mechanisms gave similar predictions under typical atmospheric conditions. As discussed in Part II, however, several investigators have shown that different

Photochemical smog reaction mechanisms predict significantly different control requirements under the same conditions. In addition, these investigators have found that the sensitivity of the mechanism's predictions to changes in input parameters varies among mechanisms. Because of the importance of making intelligent hydrocarbon control decisions, it is necessary to understand in as fundamental way as possible how the choice of chemical mechanism, as well as the choice of input parameters, affects control predictions. The object of this work, therefore, was to present a comprehensive, systematic study of the sensitivity of predicted hydrocarbon control requirements for photochemical smog to the choice of chemical mechanism and choice of all input parameters in the control calculation.

To study the sensitivity of hydrocarbon control predictions to choice of chemical mechanism and input parameters, we used the U.S. Environmental Protection Agency's Empirical Kinetic Modeling Approach (EKMA) in which ozone isopleths are generated as a function of initial volatile organic compound (VOC) and NO_x concentrations using a chemical reaction mechanism. In the EKMA methodology, a chemical reaction mechanism for photochemical smog is used to predict the maximum ozone concentration achieved over a fixed time or irradiation, say 10 hours, as a function of initial precursor concentrations (VOC and NO_x). The maximum ozone concentrations corresponding to each set of initial concentrations are then represented as isopleths, from which control requirements are obtained graphically by assuming that the reductions in initial concentrations needed to lower the maximum ozone concentration from one isopleth (the base-case value) to another (usually the NAAQS of 0.12 ppm) are linearly related to the emissions of each precursor. The chemical reaction mechanism is integrated from early morning, e.g. 0800 hours, to calculate the evolution of species concentrations in a hypothetical air parcel that starts from center city and is advected by the wind. The air parcel may increase or decrease in size due to changes in the mixing height and acquire additional pollutants from both fresh source emissions and entrainment of aged pollutants from aloft. The simulations on which the isopleths are based can be performed at two different levels of detail: Level II, which requires a specific meteorological description of the air parcel trajectory and emissions along the trajectory, and Level III, which makes standard assumptions about the meteorology and which uses a region-wide average for emission rates. It has been shown that the sensitivity of ozone predictions to choice of chemical mechanism does not change appreciably when one imbeds the mechanisms in models that are more sophisticated than the simple Lagrangian box model on which EKMA is based. Therefore, we expect that the results of the current study, which we obtained by use of EKMA, are a valid indication of the effects of chemical mechanism and input parameters on predicted organic control requirements regardless of the level of sophistication of the air quality model in which the mechanism is imbedded.

Results

We have examined the sensitivity of predicted VOC control requirements to the choice of chemical mechanism and to the variation of parameters associated with the chemical and meteorological nature of the atmosphere. Each chemical reaction mechanism was found to respond to a variation of the parameters in a somewhat different way; in many cases the relative sensitivity of the mechanism can be explained from an analysis of the intrinsic chemical features of the mechanism. The sensitivity calculations can be summarized concisely as follows:

Initial VOC Composition

The choice of chemical mechanism has a large effect on VOC control predictions and on the sensitivity of the predictions to a change in VOC composition. The ERT mechanism is most sensitive to a change in composition; the CBM least sensitive.

Aldehyde Content

Predicted VOC control is quite sensitive to the aldehyde content of the initial VOC mixture. Generally, the ERT mechanism exhibits the greatest sensitivity to changes in aldehyde content.

VOC/NO_x Ratio

The VOC/NO_x ratio was generally the parameter having the greatest influence on VOC control predictions. Generally, the ERT mechanism showed the greatest sensitivity to a change in the VOC/NO_x ratio, and the CBM exhibited the least sensitivity. In addition, the sensitivity of predictions to a change in the VOC composition is greatest at low VOC/NO_x ratios.

Base Case Ozone

Effects of changes in VOC composition are more pronounced the lower the base case ozone. The DEM mechanism is most sensitive to the choice of base case ozone.

Dilution

Differences among the predictions of the mechanisms are somewhat smaller at higher dilution rates than they are at low dilution rates.

Emissions

When emissions are assumed to be present, a given percent VOC reduction represents a larger reduction in total VOC in the atmosphere than in the absence of emissions.

VOC Entrainment from Aloft

Predicted VOC control requirements change by between 4 and 21% when VOC entrainment from aloft is included, regardless of the reactivity of the mixture assuming a base case ozone concentration of 0.24 ppm, and between 6 and 40% when a base case ozone concentration of 0.18 is assumed.

Ozone Entrainment from Aloft

All mechanisms exhibit a strong sensitivity to ozone entrainment from aloft. Ozone aloft is therefore a key variable in control studies. The sensitivity of VOC control to the VOC/NO_x ratio is influenced more by the entrainment of VOC than by the entrainment of ozone.

Initial HONO

Predictions obtained with the ERT mechanism are most sensitive to initial HONO; predictions from the PW mechanism are least sensitive.

Summary and Recommendations

The results obtained in the series of reports, of which this is the third, paint a consistent picture of the behavior of chemical reaction mechanisms for photochemical smog. Several key issues emerged that are suggestive of future work:

(1) In much of the existing laboratory smog chamber data base, chamber wall effects are important enough to make accurate discrimination among rival chemical reaction mechanisms difficult. Continuing extensive analysis of data from outdoor chamber facilities is recom-

mended as these systems seem to be characterized by smaller wall effects than indoor facilities.

(2) We have found that predicted VOC control requirements are highly sensitive to the assumed VOC/NO_x ratio and the VOC composition of the initial mixture and emissions. Therefore, it is important that these variables be as accurately characterized as possible for areas for which control strategies are to be designed.

(3) Because predicted VOC control can be quite sensitive to entrainment from aloft, the organic and especially the ozone concentration of entrained air aloft must be better characterized in areas where control strategies are to be designed.

(4) Continued effort should be placed on the evaluation of the performance of chemical reaction mechanisms in simulating both laboratory and outdoor smog chamber experiments. These experiments should include a wide range of conditions in order to gain a better understanding of the effects of input parameters (for example, initial VOC/NO_x, emissions and initial VOC composition) on control predictions.

(5) When determining control strategies, regulatory agencies should use several chemical mechanisms because at this time it is impossible to determine which chemical mechanism best simulates atmospheric chemistry.

(6) It is most important to know the input parameters as accurately as possible since the sensitivity of one input parameter may depend on the values assumed for other parameters.

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The complete report, entitled "Evaluation of Chemical Reaction Mechanisms for Photochemical Smog: Part III. Sensitivity of EKMA to Chemical Mechanism and Input Parameters," (Order No. PB 85-210 888; Cost: $11.50, subject to change) will be available only from:

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