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Project Summary

A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models

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During the second year of a two-year program, a surrogate species chemical mechanism was refined, evaluated, and adapted for use in air quality simulation (AQS) models. The purpose of the program was to develop an improved chemical mechanism for use in the AQS models that are used to develop ozone control strategies.

The updated chemical reaction mechanism was evaluated against data from 491 environmental chamber experiments conducted in indoor and outdoor facilities. The results of the evaluation indicate the mechanism's predictions are qualitatively and quantitatively consistent with the data from a large number of single organic-NO_x and multi-organic NO_x experiments.

The mechanism was adapted for use in the single-cell and multi-cell AQS models. Guidelines were developed for using the mechanism. These include procedures for assignment or individual organic species to the chemical classes in the mechanism and default organic speciation profiles. Sensitivity analysis was performed to identify the AQS model inputs that strongly influence predicted volatile organic compound (VOC) control requirements.

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 two separate volumes of the same title (see Project Report ordering information at back).

Introduction

Atmospheric simulation models are essential planning tools for the development of emission control strategies for regions that presently exceed the ambient air quality standard for ozone. The models are used to estimate the emission control requirements needed to prevent exceedances of the air quality standards in the future. One of the most important components in air quality simulation (AQS) models is the chemical mechanism that describes the formation of ozone from volatile organic compounds (VOC) and nitrogen oxides (NO_x). As part of a coordinated research program to develop reliable ozone control strategies, the U.S. Environmental Protection Agency sponsored this research study to develop and test an improved chemical mechanism.

Many chemical mechanisms have been developed in the last 10 years for simulating ozone formation from VOC and NO_x. All of the mechanisms intended for atmospheric applications incorporate approximations and condensations of species and reactions because it is currently impossible to explicitly include reactions for the hundreds of organic compounds present in ambient air. Several approaches are available for lumping the organic species into a manageable number of chemical classes in the mechanisms. The approach adopted in this study was to use the surrogate species approximation where the explicit chemistry of selected compounds is used to represent

the chemistry of all similar compounds. For example, reactions for propene and trans-2-butene are used as surrogates for the reactions of terminally double-bonded and internally double-bonded alkenes. Provided the mechanism is formulated with a sufficient number of surrogate species (~10), the surrogate species approach is quite capable of representing the majority of organic species present in urban air.

The surrogate species approach has several advantages over other schemes such as the carbon bond lumping approach. Surrogate species mechanisms can easily be updated and expanded since the reactions for each surrogate species are independent of other parts of the mechanism. Also, since whole molecules rather than lumped bond groups are used in the surrogate mechanism, they are not reliant on the assumption that different parts of the molecules react independently.

Prior to this study, surrogate species chemical mechanisms had been subjected to only limited testing against environmental chamber data. A key purpose of this study was to extensively test the predictive abilities of the surrogate species mechanism against chamber data for a broad range of conditions.

Testing of the New Mechanism

The new mechanism was tested against data from 491 experiments. The experiments were carried out in four different environmental chambers: the University of North Carolina's (UNC) 150,000-liter dual outdoor chamber, the Statewide Air Pollution Research Center's (SAPRC) 50,000-liter outdoor Teflon chamber (OTC), SAPRC's 6,400-liter indoor Teflon chamber (ITC), and SAPRC's 5,800-liter evacuable indoor chamber (EC). Procedures were developed to represent the light intensities and spectral distributions in the different chambers. Appropriate methods were also developed to characterize the major chamber effects, such as NO_x offgassing, ozone deposition, and the chamber free radical sources in a consistent manner for all four chambers.

The types and number of environmental chamber experiments used in the testing program are listed in Table 1. The NO_x-air, NO_x-CO-air, and n-butane NO_x runs were used to test the inorganic chemistry and refine the chamber characterization procedures. Single organic compound-NO_x experiments were employed to test the reactions for each of the organic precursor species included in the mechanism. Experiments with organic mixtures were used to test the predictive ability of the mechanism for conditions representative of the real atmosphere. These ranged from simple mixtures like propene/n-butane to complex mixtures including more than 15 compounds and automobile exhaust.

Table 1. Summary of Environmental Chamber Runs Used for Mechanism Evaluation

Type of Environmental Chamber Run		Number of Runs*				
		EC	ITC	OTC	UNC	Total
Characterization	NO_x-air and NO_x-Co-air	10	14	10	37	71
Single Organic-NO_x	Oxygenates	7	1	2	15	25
	Ethene	6	2		6	14
	Propene	15	7	5	22	49
	Butenes	6	5		5	16
	Toluene	13	2		5	20
	Other Aromatics	7	13		4	24
	n-Butane	14	5	1	7	27
	C5+	6	8		6	20
Known Mixtures	Simple Mixtures	22			18	40
	Surrogate Mixtures	11	45	62	33	151
Auto Exhaust	Catalyst and Noncatalyst				25	25
Dynamic Injection	Simple Mixtures				9	9
Totals		117	102	80	192	491

*UNC = UNC outdoor chamber, EC = SAPRC evacuable indoor chamber, ITC = SAPRC indoor Teflon chamber, OTC = SAPRC outdoor Teflon chamber.

The average bias and error in the mechanism's predictions for maximum ozone concentrations are listed in Table 2. The evaluation data indicate the mechanism underpredicts ozone yields in carbonyl-NO_x experiments by 5% on the average. The average error in the maximum ozone predictions is ±25% for carbonyl-NO_x systems. Mechanism performance for formaldehyde is better than for higher aldehydes and ketones.

The performance data show that the mechanism overpredicts ozone yields in alkene-NO_x experiments by 3% on the average. The average error in the maximum ozone predictions is ±21% for these systems. Mechanism performance for ethene and propene is significantly better than that for butenes.

The evaluation data indicate the mechanism overpredicts ozone yields in aromatic-NO_x experiments by 1% on the average. The average error in the maximum ozone predictions is ±21% for aromatic-NO_x systems. The mechanism tends to overpredict ozone yields in benzene and toluene-NO_x systems and underpredict ozone yields in m-xylene, o-xylene, and mesitylene-NO_x systems on the average. This level of performance on aromatic runs is surprisingly good considering that the aromatic mechanism is highly parameterized and that the identity and subsequent chemistry of half or more of the aromatic photooxidation products are unknown.

The evaluation results for alkane-NO_x simulations are not satisfactory. The mechanism's maximum ozone predictions show large errors (±69% on the average) and a bias toward overprediction. The poor mechanism performance for alkane-NO_x runs is due to uncertainty in the alkane chemistry, especially for the C6+ alkanes, and uncertainty in the chamber radical source strength. Alkanes are less reactive than the other compounds employed in the testing program, and simulations of alkane-NO_x experiments are extremely sensitive to the assumed chamber radical source strength. Because of the uncertainty and variability of the chamber radical source, the alkane mechanism cannot be evaluated without ambiguity using chamber data.

The mechanism's performance simulating mixtures of organic compounds is good. Overall, the mechanism predicted the maximum ozone in 225 mixture experiments with an average bias

of +4% and an average error of ±24%. The predicted rates of NO_x oxidation and timing of the ozone maximum also have little bias and less than 30% error. The mechanism's performance for simple mixtures was not quite as good as its performance for the surrogate mixtures and auto exhaust. However, overall these results show the mechanism is qualitatively and quantitatively consistent with the chamber data. Good performance in testing against organic mixture experiments is important because the mechanism will primarily be used to simulate mixtures in atmospheric modeling.

Adaptation of the Mechanism

Condensed versions of the mechanism employed in the testing program were developed for use in AQS models. Mechanisms were developed for use in single-cell models that can accommodate large chemical mechanisms and for use in multi-cell models that require fairly small chemical mechanisms. Very little mechanism condensation was required for the mechanism designed for use in single-cell models such as the OZIPM AQS model. Significant mechanism condensation assumptions were implemented in the mechanism designed for use in the multi-cell models such as the Urban Airshed Model.

Predictions from the condensed versions of the mechanism were compared to predictions of the detailed mechanism for a range of mixtures and $NMOC/NO_x$ ratios. The results showed the single-cell model mechanism's predictions are almost identical (i.e., within ±2%) to the detailed mechanism's predictions for all of the key species. Predictions from the multi-cell model mechanism agree with those from the detailed mechanism within ±10% for all key species.

Information on speciation of organics for the classes in the mechanism was developed. First, a master list showing the assignment if individual organic compounds to organic classes in the mechanism was compiled. The uncertainty of each assignment was ranked, based on whether or not the surrogate species employed for the assigned class could represent the reactivity of the individual species well. Second, ambient speciated NMOC data collected at the ground and above the mixed layer in the mornings in urban areas were analyzed. A default NMOC composition profile for emissions and ambient concentrations near the surface were developed from ambient data collected in 25 cities using a consistent measurement and speciation protocol. A default composition profile for NMOC aloft was compiled from aircraft data collected upwind of four cities. These default profiles can be used in atmospheric modeling applications where site-specific data are not available.

Table 2. *Average Model Performance for Maximum Ozone*

Run Type	Bias (%)	Error (%)
Formaldehyde	−1	19
Acetaldehyde	−26	26
Other Carbonyls	+4	44
All Carbonyls	−5	25
Ethene	+2	18
Propene	+3	18
Butenes	+4	34
All Alkenes	+3	21
Butane	+31	67
Branched Alkanes	+34	49
Long-chain Alkanes	+83	84
All Alkanes	+46	69
Benzene	+3	5
Toluene	+11	24
Xylenes	−9	16
Mesitylene	−11	21
All Aromatics	+1	19
All Single HC Runs	+12	33
Simple Mixtures	+10	35
Mini Surrogates	+10	22
Full Surrogates	+3	23
Auto Exhaust	−11	15
All HC Mixtures	+4	24
All Run Average	+7	28

**Positive bias indicates model overprediction.*

Sensitivity analysis was carried out using the updated chemical mechanism in the OZIPM AQS model. The sensitivity analysis was designed to identify the input parameter that most strongly influences the NMOC control requirements in EKMA analyses. Almost all of the sensitivity runs were performed at several $NMOC/NO_x$ ratios and dilution rates since the sensitivity of the model to parameter variations is known to depend on these parameters. The results of the analysis confirmed the importance of the following input parameters:

- $NMOC/NO_x$ ratio
- NMOC composition
- Post-8 a.m. emission rates along the trajectory
- Future changes in NO_x emission rates
- Ozone and NMOC concentrations aloft

Other relatively important parameters include the mixing height, radiation, and initial PAN concentrations. The results of the sensitivity analysis are intended to help air quality planners prioritize efforts for obtaining input data for the photochemical models used to develop control strategies.

A set of sample problems and instructions for implementing both versions of the mechanism in AQS models were developed. These will allow users of the mechanism to ensure the mechanism is properly implemented.

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***William P. L. Carter** is the EPA Project Officer (see below).*
The complete report, consists of two volumes, entitled "A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models:"
"Volume I. Adaptation of the Mechanism," (Order No. PB 87-180 592/AS; Cost: $24.95)
"Volume II. Guidelines for Using the Mechanism," (Order No. PB 87-180 600/AS; Cost: $18.95)
The above reports will be available only from: (costs subject to change)
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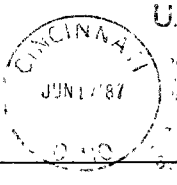

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