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Final Report:
EPA Center for Airborne Organics

September 2002

MIT LFEE 2002-003 RP

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http://lfee.mit.edu/publications/
Publication No. LFEE 2002-003 RP

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EPA Agreement Number: R-824970-01
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Presented to the US Environmental Protection Agency
September 30, 2002

Caltech *MIT* *NJIT*

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Executive Summary

Overview of the Center

The Center on Airborne Organics was established at the California Institute of Technology (Caltech), Massachusetts Institute of Technology (MIT), the New Jersey Institute of Technology (NJIT) with support from the United States Environmental Protection Agency (USEPA) to address air pollution problems. The nation was struggling to implement and maintain compliance with the provisions of the Clean Air Act Amendments (CAAA) of 1990, and particularly those targeted at controlling tropospheric ozone and air toxics. Increased concern was being expressed about the health effects of ultrafine particles. Costly emission control measures that had been adopted had proved to be only partially successful in controlling ozone in urban area. Ozone concentrations still exceeded current standards in many areas despite the expenditures of many billions of dollars over the previous two decades. Dealing with air toxics presented many challenges in defining the magnitude of the problem posed by the many chemicals listed in the CAAA and establishing priorities for their control. Ultrafine cabonaceous particles continued to be implicated in human health effects. There was, however, large uncertainty as to the size, composition, and source of the particles of concern to human health. Airborne organics in general were known to be difficult to characterize and to control because they include an enormous variety of compounds with widely different impacts on health and the environment, they come from a wide range of sources, and once emitted, they may change chemically or physically in the atmosphere, complicating the task of matching airborne pollutants and their source(s). Given such complexities and uncertainties, it was difficult to forecast how a given regulatory strategy would influence ambient air quality.

To support the policy making process, the Center on Airborne Organics drew on the talents of recognized leaders at Caltech, MIT, and NJIT in the three following focus areas: sources and control, transportation and transformation, and monitoring and source attribution. The research program emphasized the following interrelated activities:

- Development and use of improved techniques to sample and analyze emissions from sources and material in the air;
- Determination of how emitted material is transported and changed in the environment;
- Refinement of existing methodologies for source attribution by identifying critical compounds and structures in airborne organics and their environmental stability; and

- Assessment of the potential effectiveness of specific control strategies.

The goals of the Center research were to provide:

- New tools for characterizing the generation, fate and transport, source attribution, and control of combustion generated organics pollutants;
- An entity greater than the sum of its parts, by fostering cross-fertilization between the different investigators; and
- Neutral forums for discussions on the scientific bases for some of the more contentious issues facing policy makers, by sponsoring summer symposia on tropospheric ozone, air toxics, low emission vehicles, advanced instrumentation for the air quality measurements, and fine particles in the atmosphere.

The Center successfully involved faculty members with major collateral research on different facets of airborne organics. As principal investigators of the Center's research projects, these faculty members brought to the Center their expertise and contacts and the Center provided the integration of the different studies to address complicated issues facing the nation.

The Center was fortunate in having a very able and active Scientific Advisory Committee (SAC) which worked very hard to make sure the Center achieved the goals for which it was established. The members of the SAC were subdivided into the three principal program focus areas and they prepared statements on the short- and long-term objectives of each focus area which were folded into the annual request for proposals for the Center. The SAC also wrote the specifications for format, length and information content of proposals, which was included in the request for proposals. At the recommendation of the SAC, the projects were funded for two-year periods, so that half the projects were terminated every year and replaced with new ones, or where justified, continued but usually with a new orientation. The SAC was particularly active in seeking opportunities for collaboration between the projects.

The Center was effective in bringing together expertise that was distributed at the three participating institutions. Frequent exchanges of information between the Center's directors, principal investigators, the EAP project officer, and members of the SAC took place via electronic mail which made possible a remarkable degree of coordination.

A strength of the Center which reflects the guidance provided by the SAC was the encouragement of redirections of activities within projects to take advantage of resources available elsewhere within the Center. Center projects lead to synergies that crossed institutional and disciplinary lines. Examples are MIT modeling studies which benefited from quantum calculations performed at NJIT, and the extension of rate coefficient calculations at NJIT to focus on the reactions of importance in smog studies at Caltech.

The students and the principal investigators (PIs) had an opportunity for direct contact one a year at the summer PI/SAC meeting held at MIT's Endicott House which is located in an informal setting near Boston. Oral presentations of the different projects were given and the SAC reviewed the progress made in each projected based on the oral presentation and the written annual report of the project which was provided to the SAC in advance of the meeting. A written summary of the SAC's evaluation was provided to the principal investigator. This arrangement gave the Center's investigators not only critical feedback from the SAC but also opportunities to learn about each other's activities and to obtain useful suggestions on their research from other participants within the Center and other meeting attendees. At the suggestion of the SAC the meetings were organized so as to separate the functions of outreach, addressed by a summer symposium directed to the specialized community, and the principal investigators meeting bring together the students and faculty in the Center.

The Center held annual summer symposia on topics of large current interest to the airborne organics community in general and especially to the policy makers of this community. The goal of the symposia was to bring together many of the key researchers and policy makers to focus on key topics of current interest at the interface of technology and policy in the field of airborne organics. The symposia provided opportunities for informal and sometimes spirited discussions between the participants in informal surroundings. The symposia, held at Endicott House, were well attended by federal, state, and local regulators, representatives from industrial and other non-governmental organizations, and members of the academic research community. The symposia were very successful in providing neutral forums for discussions of the scientific bases for some of the more contentious issues being faced by policy makers. As the Center approached its scheduled termination the strong interest and support enjoyed by the Summer Symposia indicated that the Symposia should be continued beyond the lifetime of the Center. Accordingly, the organization and management of the Symposium were transferred to the MIT Laboratory for Energy and the Environment (LFEE) which is continuing the Symposia. Summaries of the presentations and discussions for all but the earliest Symposia may be found on the Center's website <http://web.mit.edu/airquality/www>, or for the 2001 and later Symposia managed by the MIT LFEE, on <http://lfee.mit.edu/programs/airquality-endicott/>.

Research Accomplishments

Sources and Control

Center Research in the focus area of Source and Control concentrated on combustion sources, kinetics and mechanisms of formation, and methods for controlling emissions. The goal of combustion sources research was to develop models and experimental data sets for the formation of particulate matter in combustion engines. Combustion sources have been found to be major precursors to ozone, air toxics, and visibility degradation. The combustion sources research had both experimental and modeling components. Experimental research subjected combustion engines to typical loads, and analyzed the resulting hydrocarbon emissions and formation of particulate matter. Modeling research combined chemical kinetic and fluid mechanic models to predict combustion products. The goal of research in kinetics and mechanisms of formation was to provide quantitative predictions of airborne organics behavior. Understanding the kinetics and mechanisms of formation of airborne organics can lead to methods for manipulating the chemistry to minimize production, as well as provide a better assessment of chemical signature for use in source apportionment. Again, research in this area had experimental and modeling components. Experiments were concerned with the formation of hydrocarbons and soot. Models used elementary reactions to describe the chemistry. The research on methods for controlling emissions was concerned with both stationary and mobile sources. It included research on the simultaneous removal of soot and NO_x from diesel engines, and experimental and modeling efforts concentrated on catalyst research and the mechanism and competitive kinetics of soot reactions with oxidants.

Transport and Transformation

Research in the focus area of Transport and Transformation was concentrated on the formation of particulate matter, improving the predictive capability of air quality models, reactions of primary and secondary oxidation products and their impact on ozone, and reactions of peroxides. The goal of particulate matter formation research was to characterize the photo-oxidation mechanisms of volatile organic compounds forming atmospheric aerosols. Such research would allow for the development of predictive models for ozone and smog formation. Models were developed to predict the kinetics of aerosol particle growth. Experiments observing the kinetic profiles were then conducted to validate the models. In addition, photochemical smog chambers were used to determine the yields and chemical composition of the aerosol particles formed. Models and comprehensive data sets were developed for the gas-to-particle conversion of volatile organic compounds in the atmosphere. In addition, a new method for characterizing the very initial stages of aerosol particle formation was developed.

The goal of the research on improving the predictive capability of air qualify models was to construct new mathematical and computational frameworks describing the transport and transformation of airborne organics, building on past approaches and experimental data sets. By improving the predictive capability of air quality models, one can better describe the complex reaction schemes characterizing the photochemistry of airborne organics. Novel data analysis and modeling techniques were developed. It was found that the predictive capability of airshed models can be diminished by uncertainties in critical input parameters. A new air quality model predicting the evolution of single particles in the atmosphere was developed.

The goal of research into reactions of primary and secondary oxidation products was to quantitatively characterize the intermediates of such reactions and develop kinetic models. The atmospheric oxidation of aromatic compounds plays a crucial role in the generation of pollutants in the atmosphere. Characterizing the oxidation products is necessary for the development of predictive models of ozone and smog formation. Modeling proceeded by developing reaction mechanisms from elementary kinetic parameters and determining thermodynamic properties via literature evaluation or calculation. Experimental approaches either applied sensitive ultra-violet spectroscopy, or chemical ionization mass spectroscopy via a steady state turbulent flow reactor.

The goal of peroxide research was to characterize the photochemistry of organic peroxides. Hydrogen peroxide and other organic peroxides are important trace constituents in the atmosphere. They are the dominant oxidants of SO_2 found in clouds, fog, or rain in the atmosphere, and may contribute to forest damage due to their phytotoxic properties. Research evaluated the importance of photochemical destruction of organic peroxides with photolysis and assessing ultra-violet absorption cross sections. The absorption cross section and photodissociation quantum yield (action spectra) of hydrogen peroxide and other organic peroxides were measured.

Monitoring and Source Attribution

Research in the focus area of Monitoring and Source Attribution was concentrated on application of methodologies, development and application of new measurement methods and analytical techniques, and identifying and measuring new classes of compounds that serve as tracers for specific source types. The goal of the research was to provide quantifiable data on the transformation of atmospheric particles for testing future air quality models. Such research can further the understanding of source/receptor relationships for atmospheric organic compounds. The work proceeded by collecting source and ambient fine particulate matter and making comparisons on the basis of chemical composition and mutagenicity by experimental techniques, including high performance liquid chromatography and gas chromatography/mass spectroscopy. Field experiments were conducted to measure changes in the chemical composition of atmospheric aerosols in Southern California.

The goal of the development of new measurement methods was to develop new types of equipment to measure airborne contaminants. This research can assist scientists in extending monitoring and source attribution to new classes of organic compounds, identifying potential public health hazards, and assisting policy makers with a firmer analytical ground for their decisions. The research included fabrication of new sensors and sampling systems, performance evaluation, and sensitivity analysis. Several new measurement methods and techniques were developed including a mass spectrometer to measure airborne contaminants, a sensor to measure organic vapors, novel sampling and analytical techniques for polar atmospheric volatile organic compounds, and a micro-concentrator interface for real-time volatile organic compound sensors.

The goal of the research on identifying and measuring classes of compounds that serve as tracers for specific source types was to develop quantitative methods for the source attribution of organic compounds. The results are intended to provide a reliable means of identifying and measuring the true sources of airborne contaminants, and to assist policy makers in designing effective strategies against the principal sources. The research included experimental determination of soot microstructure with respect to varying conditions, and the development of methods for measuring soot microstructure and composition.

Future Research in Airborne Organics

The following area of need for future research in the field of airborne organics were identified.

- Identification and characterization of non-combustion sources of airborne organics, particularly in the context of source attribution which should take into account all sources.

- Development of methods for manipulating the chemistry of airborne organics to minimize production as well as provide a better assessment of chemical signature for use in source apportionment.

- Identification and characterization of atmospheric transformation of primary organic emissions that can result in the production or destruction of airborne compounds of concern for atmospheric health.

- Development of markers to delineate compounds of concern from the numerous compounds existing in the atmosphere.

- Development and application of new measurement methods that can extend existing techniques to new classes of organic compounds that impact human health.

- Identification and measurement of the classes of compounds that can serve as tracers for specific source types.

Introduction

Figure 1: The United States Capital Building

In 1990, the Clean Air Act Amendments (CAAA) were established to control tropospheric ozone and air toxics emissions. Particulate matter is a cause of decreased visibility in urban areas, and has been implicated in human health problems. The CAAA cited over 180 chemicals for control. Regulators were given the task of creating a strategy to improve ambient air quality.

Costly emission control measures were established, but they were only partially successful in controlling ozone in urban areas. Despite the billions of dollars spent, ozone concentrations continued to exceed the established standards. Much of the problem was attributed to insufficient knowledge of the sources, characteristics, and impacts of atmospheric organic compounds.

The Center on Airborne Organics was established to address air pollution problems and support the policy making process.

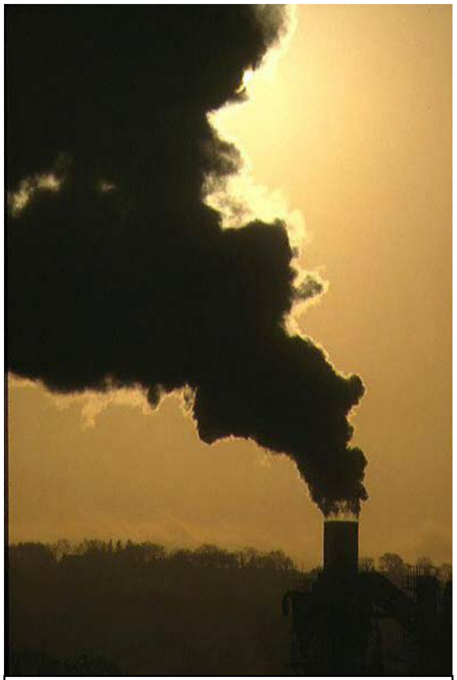


Figure 2: Factory Emissions from a Smoke Stack in Northumberland, U.K. – Photo by Ian Brittan

Overview of the Center

Description of the Center

The Center was founded and operated at California Institute of Technology (Caltech), Massachusetts Institute of Technology (MIT), and New Jersey Institute of Technology (NJIT) with support from the United States Environmental Protection Agency (USEPA). A Scientific Advisory Committee (SAC) was appointed to guide the Center through its activities.

The SAC established three principal focus areas for the Center:

- **Sources and Control**
- **Transport and Transformation**
- **Monitoring and Source Attribution**

The SAC maintained a close relationship with the Center. SAC members prepared short-term and long-term objectives for each focus area. The SAC was also active in seeking opportunities for collaboration between the projects within the Center and outreach programs sponsored by the Center. Thus the Center, in coordination with the SAC, was able to maintain strong ties with the greater airborne organics community.

Mission of the Center

To support the policy making process, the Center on Airborne Organics drew on the talents of recognized leaders at Caltech, MIT, and NJIT in the areas of sources and control, transport and transformation, and monitoring and source attribution to address the interrelated activities of:

- Developing and using improved techniques to sample and analyze emissions from sources and material in the air.
- Determining how emitted material is transported and changed in the environment.
- Refining existing methodologies for source attribution by identifying critical compounds and structures in airborne organics and their environmental stability.
- Assessing the potential effectiveness of specific control strategies.

Vision of the Center

To guide its activities, the Center had the following vision:

- To provide new tools for characterizing the generation, fate and transport, source attribution, and control of combustion generated organic pollutants.
- To become an entity greater than the sum of its parts, by fostering cross-fertilization between the various investigators.
- To provide neutral forums for discussions on the scientific bases for some of the more contentious issues facing policy makers.

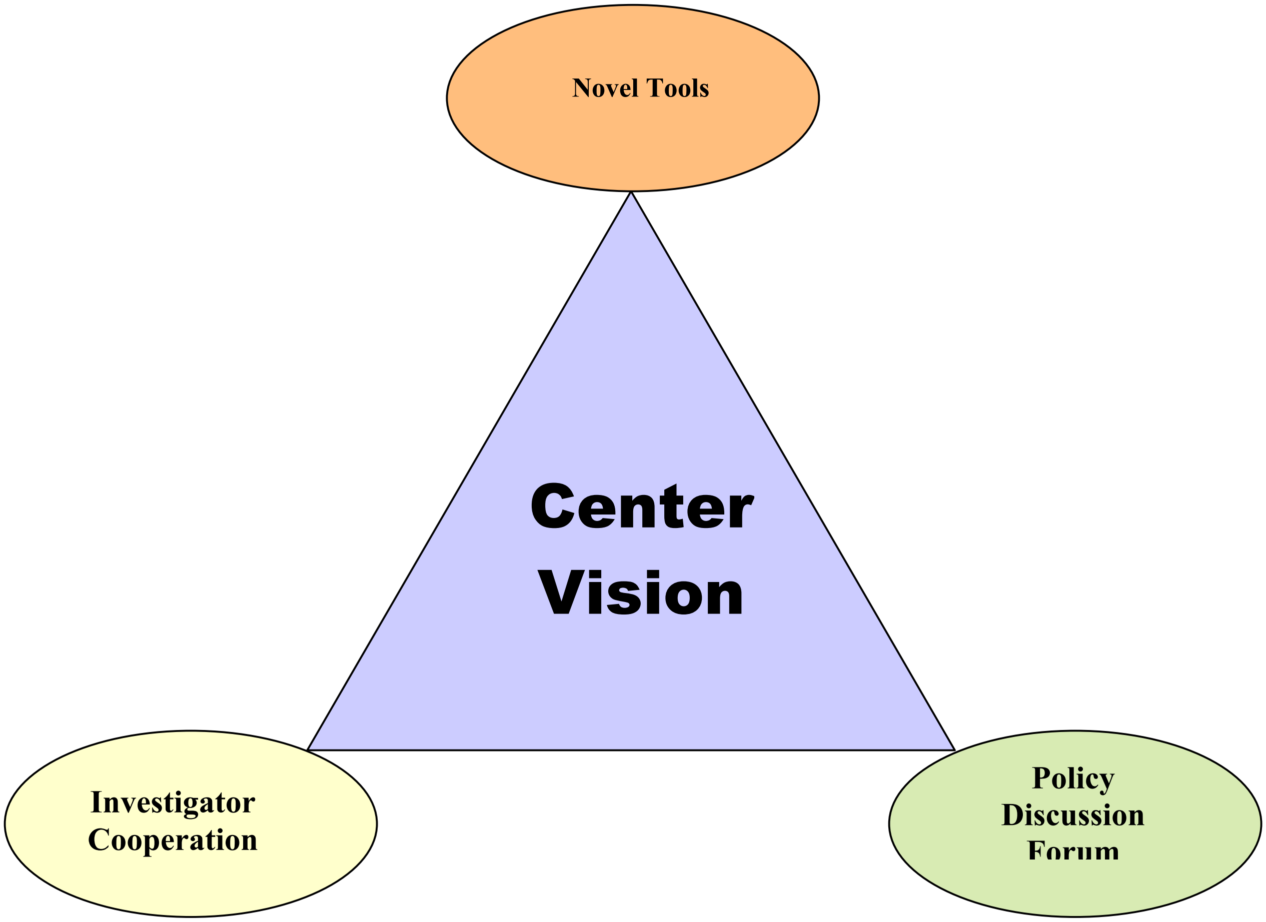


Figure 3: Construct of the Center's Vision. The Center on Airborne Organics served as conduit for fostering research alliances, policy making, and novel tools for study, analysis and development in both research and policy advancement.

Accomplishments of the Center

Institutional Accomplishments

The Center was founded carry out applied basic research in support of the policy making process. Trying to regulate atmospheric pollutants can be extremely complicated. There are a wide variety of sources, the nature of pollutants can change in the atmosphere, and attributing a pollutant to its source can sometimes seem near impossible. By characterizing the sources, transformation and matching pollutants to the source, the Center gave regulators a sound scientific basis on which to base policy. In this way, the Center was successful in providing the policy world with the tools necessary to evaluate different policies for atmospheric pollutants and examine the trade-offs.

By having a center as opposed to individual projects, a "go-to" knowledge base was created. One of the difficulties of having just a collection of research projects is that policy makers do not have a consistent contact when trying to get answers for broader scope questions. The Center provided a resource base to both the public and private sectors in addressing airborne organics issues.

From a learning standpoint, the Center format was particularly useful to both research investigators and to students interested in airborne organics. For investigators, it provided a mechanism for obtaining useful suggestions and critiques of their research, thus enhancing the quality of projects. For students, it allowed them to interact with researchers and other students. The Center funded over $1.9 million of research by undergraduate, graduate and post-doctoral students.

The Center maintained the SAC throughout its existence. The SAC consisted of members from academia, industry, government, and non-governmental organizations. The SAC served as a means for some of the best individuals in the field of airborne organics to become involved with the Center, and fostered a relationship between industry, government and academia.

At the recommendation of the SAC, the Center's projects were funded in two-year periods, so that half of the projects were terminated every year and replaced with new ones or, where justified, continued but usually with a new orientation. Many times, projects funded by the Center served as a means of gaining additional funding from other institutions. For example, a study by Profs. Shaw and Pfeffer at NJIT was co-sponsored by the National Science Foundation, and a study by Prof. Cass at Caltech was additionally supported by the California Air Resources Board and Caltech Center for Air Quality Analysis.

Members of the SAC played an active role not only in selecting projects, but also in guiding them to success. Some specific examples of direction of research projects as a result of Center collaboration include:

- Redirection at MIT of modeling studies of polycyclic aromatic hydrocarbon (PAH) formation to include rate coefficients computed at NJIT for reactions involving aromatic species.
- Extension of rate coefficient calculations at NJIT to focus on reactions of importance in smog formation studies at Caltech.
- Application in soot particle studies at MIT of electrical mobility analyzer techniques developed at Caltech.

The Center can be seen as a model of how research collaborations can work given the communications technology of the new century. Through the use of such technologies as electronic mail and the Internet, investigators were able to maintain a dialogue about projects, despite geographical distance. Collaborations ranged from as close as another department of the same university, to as far as a different continent.

The Center sponsored annual summer symposia on subjects of relevance to the airborne organics community. They included the participation of federal/state/local regulators, industry, non-governmental organizations, and the academic/research community. In addition to outreach meetings, the Center organized workshops bringing together its students and faculty. This allowed investigators to learn about each other’s activities and obtain useful suggestions about their research from other investigators in the Center.

Research at the Center, in some cases, directly translated into tangible results on the regulatory policy level. For example, work by Prof. Cass at Caltech led to the development of a nationwide atmospheric sampling program, and work by Prof. McRae at MIT initiated a focus on the coupling of atmospheric pollutants.

Research Accomplishments

Sources and Control

Research in the focus area of Source and Control concentrated in three subsets: combustion sources, kinetics and mechanisms of formation, and methods for controlling emissions.

Combustion Sources

The goal of combustion sources research was to develop models and experimental data sets for the formation of particulate matter in combustion engines. Combustion sources have been found to be major precursors to ozone, air toxics, and visibility degradation. The combustion sources research had both experimental and modeling components. Experimental research subjected combustion engines to typical loads, and analyzed the resulting hydrocarbon emissions and formation of particulate matter. Modeling research combined chemical kinetic and fluid mechanic models to predict combustion products. Profs. Heywood and Hochgreb (MIT) developed a model for combustion chamber deposit effects on hydrocarbon emissions. Prof. Hochgreb (MIT) also developed a model that explains the products of incomplete combustion in spark-ignited engines. Further, Profs. Hochgreb and Lafleur (MIT) developed a database and model to characterize particulate matter formation in spark-ignited engines.

Kinetics and Mechanisms of Formation of Airborne Organics

The goal of research in kinetics and mechanisms of formation was to provide quantitative predictions of airborne organics behavior. Understanding the kinetics and mechanisms of formation of airborne organics can lead to methods for manipulating the chemistry to minimize production, as well as provide a better assessment of chemical signature for use in source apportionment. Again, research in this area had experimental and modeling components. Experiments were concerned with the formation of hydrocarbons and soot. Models used elementary reactions to describe the chemistry. In the area of polycyclic aromatic hydrocarbon (PAH) mechanisms, Prof. Green (MIT) developed a method for the computer generation of detailed kinetic models which he is applying to PAH formation. Prof. Howard (MIT) developed a model that predicts PAH concentrations and the contribution of PAH to soot formation in flames. In the area of computational kinetic modeling, Profs. Barton and Green (MIT) developed new methods for the numerical analysis of large-scale kinetic models. In the area of soot formation, Prof. Béer (MIT) determined pathways leading to soot mass growth in stationary combustion systems and Prof. Howard (MIT) developed a model to characterize fine soot particles in combustion. Profs. Barton and Howard (MIT) extended this research in PAH and soot formation to premixed flames with axial diffusion. In the area of particulate matter formation, Prof. Cheng (MIT) developed a set of kinetics data for future use in kinetics modeling.

Methods for Controlling Emissions

A goal of the Center was to develop methods for controlling emissions. This would allow for the control of problematic pollutants from stationary and mobile engines. Research at the Center in this area concerned the simultaneous removal of soot and NO_x from diesel engines. Experimental and modeling efforts concentrated on catalyst research and the mechanism and competitive kinetics of soot reactions with oxidants. Profs. Shaw and Pfeffer (NJIT) showed that it may be possible to lower NO_x emissions from diesel vehicles by promoting chemical reactions between the NO_x and carbon monoxide emitted by the engine.

Transport and Transformation

Research in the focus area of Transport and Transformation concentrated in four subsets: formation of particulate matter, improving the predictive capability of air quality models, reactions of primary and secondary oxidation products and their impact on ozone, and reactions of peroxides.

Formation of Particulate Matter

The goal of particulate matter formation research was to characterize the photo-oxidation mechanisms of volatile organic compounds forming atmospheric aerosols. Such research would allow for the development of predictive models for ozone and smog formation. Models were developed to predict the kinetics of aerosol particle growth. Experiments observing the kinetic profiles were then conducted to validate the models. In addition, photochemical smog chambers were used to determine the yields and chemical composition of the aerosol particles formed. Profs. Seinfeld and Flagan (Caltech) developed models and comprehensive data sets on the gas-to-particle conversion of volatile organic compounds in the atmosphere. In addition, Prof. Krasnoperov (NJIT) developed a new method for characterizing the very initial stages of aerosol particle formation.

Improving the Predictive Capability of Air Quality Models

The goal of this research area was to construct new mathematical and computational frameworks describing the transport and transformation of airborne organics, building on past approaches and experimental data sets. By improving the predictive capability of air quality models, one can better describe the complex reaction schemes characterizing the photochemistry of airborne organics. Novel data analysis and modeling techniques were developed. Prof. McRae (MIT) showed that the predictive capability of airshed models can be diminished by uncertainties in critical input parameters. Prof. Cass (Caltech) developed a new air quality model predicting the evolution of single particles in the atmosphere.

Reactions of Primary and Secondary Oxidation Products and their Impact on Ozone

The goal of research into oxidation products was to quantitatively characterize the intermediates of such reactions and develop kinetic models. The atmospheric oxidation of aromatic compounds plays a crucial role in the generation of pollutants in the atmosphere. Characterizing the oxidation products is necessary for the development of predictive models of ozone and smog formation. Modeling proceeded by developing reaction mechanisms from elementary kinetic parameters and determining thermodynamic properties via literature evaluation or calculation. Experimental approaches either applied sensitive ultra-violet spectroscopy, or chemical ionization mass spectroscopy via a steady state turbulent flow reactor. Profs. Bozzelli and Lay (NJIT) developed reaction mechanisms and kinetic understanding of the atmospheric photochemical oxidation of certain aromatic and oxygenated aromatic compounds. Prof. Krasnoperov (NJIT) developed kinetic and thermochemistry methods to characterize the oxidation of airborne organic compounds. Prof. Molina (MIT) identified intermediates in the atmospheric oxidation of aromatic hydrocarbons.

Reactions of Peroxides

The goal of peroxide research was to characterize the photochemistry of organic peroxides. Hydrogen peroxide and other organic peroxides are important trace constituents in the atmosphere. They are the dominant oxidants of SO_2 found in clouds, fog, or rain in the atmosphere, and may contribute to forest damage due to their phytotoxic properties. Research evaluated the importance of photochemical destruction of organic peroxides with photolysis and assessing ultra-violet absorption cross sections. Prof. Wennberg (Caltech) measured the absorption cross section and photodissociation quantum yield (action spectra) of hydrogen peroxide and other organic peroxides.

Monitoring and Source Attribution

Research in the focus area of Monitoring and Source Attribution concentrated in three subsets: application of methodologies, development and application of new measurement methods and analytical techniques, and identifying and measuring new classes of compounds that serve as tracers for specific source types.

Application of Methodologies

The goal of this area of research was to provide quantifiable data on the transformation of atmospheric particles for testing future air quality models. Such research can further the understanding of source/receptor relationships for atmospheric organic compounds. The work proceeded by collecting source and ambient fine particulate matter and making comparisons on the basis of chemical composition and mutagenicity by experimental techniques, including high performance liquid chromatography and gas chromatography/mass spectroscopy. Prof. Cass (Caltech) conducted field experiments that measured changes in the chemical composition of atmospheric aerosols in Southern California.

Development and Application of New Measurement Methods and Analytical Techniques

The goal of measurement methods research was to develop new types of equipment to measure airborne contaminants. This research can assist scientists in extending monitoring and source attribution to new classes of organic compounds, identifying potential public health hazards, and assisting policy makers with a firmer analytical ground for their decisions. The research included fabrication of new sensors and sampling systems, performance evaluation, and sensitivity analysis. Several new measurement methods and techniques were developed at the Center. Profs. Carr and Farmer (Caltech) developed a mass spectrometer to measure airborne contaminants, Profs. Kebbekus and Zaitsev (NJIT, Moscow State) developed a sensor to measure organic vapors, Profs. Mitra and Kebbekus (NJIT) designed novel sampling and analytical techniques for polar atmospheric volatile organic compounds, and Profs. Mitra and Misra (NJIT) developed a micro-concentrator interface for real-time volatile organic compound sensors.

Identifying and Measuring Classes of Compounds that Serve as Tracers for Specific Source Types

The goal of this research area was to develop quantitative methods for the source attribution of organic compounds. This would allow for a reliable means of identifying and measuring the true sources of airborne contaminants, and assist policy makers in designing effective strategies against the principal sources. The research included experimental determination of soot microstructure with respect to varying conditions, and the development of methods for measuring soot micro-structure and composition. Profs. Sarofim and Vander Sande (MIT) introduced a potentially quantitative method to fingerprint sources of airborne soot and began the development of a library of soot structures for use in future emissions source attribution studies.

Outreach and Policy-Making Impact of Center Research

Outreach Through Summer Symposia

The Center held annual summer symposia on topics of large current interest to the airborne organics community in general and especially to the policy makers of this community. The goal of the symposia was to bring together many of the key researchers and policy makers to focus on key topics of current interest at the interface of technology and policy in the field of airborne organics. The symposia provided opportunities for informal and sometimes spirited discussions between the participants in informal surroundings. The symposia, held at Endicott House, were well attended by federal, state, and local regulators, representatives from industrial and other non-governmental organizations, and members of the academic research community. The symposia were very successful in providing neutral forums for discussions of the scientific bases for some of the more contentious issues being faced by policy makers.

Policy Making Regarding EPA Research and Monitoring of Particulate Emissions

The work of Glen Cass (deceased) at Caltech has made a significant impact on policy-making regarding EPA research and monitoring of particulate emissions. The Center-sponsored work in which Glen Cass and students at Caltech measured and then modeled fine particle formation (fate and transport) in the Los Angeles area has been the basis for control strategy planning and design for fine particles of different types (sulfates and nitrates, primary and secondary organics, etc.). The importance of this work and its increasing significance are reflected in current national and international trends in PM policy decision-making. His measurement work on ambient PM2.5 (by speciation, elemental carbon, organic carbon, nitrates, sulfates, crustal material, trace elements, etc.) was the major reason that EPA chosen to pursue work beyond the measurement of only mass for PM. For this work, EPA has established a speciation network specializing in the complete chemistry of fine particles. This can be considered a major example of the use of sound science into policy formulation.

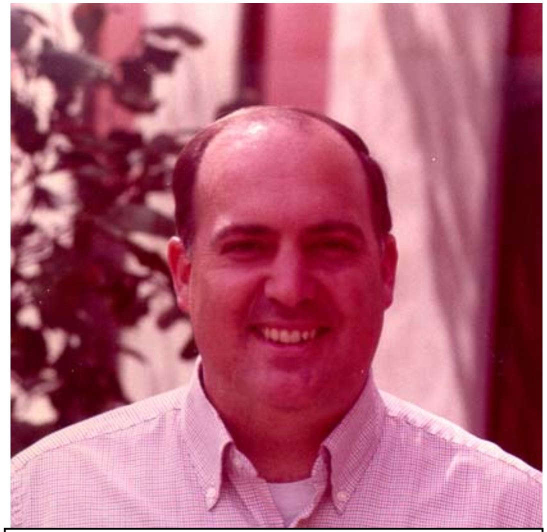


Figure 4: The work of Glen Cass (1947-2002) made tremendous contributions to air quality policymaking.

Policy Focus on the Coupling of Atmospheric Pollutants

The work of Gregory McRae at MIT initiated a policy focus on the coupling of atmospheric pollutants. Gregory McRae's Center-funded project entitled “Direct Treatment of Uncertainties in Mathematical Models of the Transport and Fate of Airborne Organics” was strongly technical but highly significant to policy. One of the consequences of using models to describe the formation and transport of the photochemical air pollution is that approximations are involved. The goal of this research was to identify the inputs that contribute most to the uncertainty in predictions. A new approach was developed, termed the Deterministically Equivalent Modeling Method (DEMM). Uncertain parameters were treated as random variables that, in turn, were approximated using orthogonal basis function expansions in the probability space. The project had two major accomplishments:

> (1) The predictions from three different mechanisms were found to be indistinguishable given current levels of parametric uncertainties.
>
> (2) Because all the chemical mechanisms investigated as well as the three-dimensional Caltech airshed model are sensitive to the same set of parameters, reducing parametric uncertainties should be a key research priority for model improvement purposes.

This work provided the centerpiece for discussions of “Advanced Instrumentation for Air Quality Measurements” at the 1996 Summer Symposium and “Cost and Benefits Estimation in Air Quality Regulations” at the 1998 Summer Symposium. At these Symposia, which were organized by the Center to provide a neutral setting for discussion of policy issues and pertinent research results, McRae demonstrated that improved estimations of emissions are necessary for an accurate cost-benefit analysis. In 1999, the topic was EPA’s Urban Air Toxics Strategy, where McRae’s research showed that a quantitative approach to uncertainty and variability is needed when conducting risk assessment. One of the key points in EPA’s Urban Air Toxics Strategy is the risk management of air toxics.

Research Project Descriptions

Source and Control

Numerical Tools for Large-Scale Kinetic Models
Paul Barton and William Green (Massachusetts Institute of Technology)
1999-2002

Goals
- To develop a software package for the numerical analysis of large-scale chemical kinetic models.
- To develop physically sensible and robust numerical methods for automatic model reduction appropriate to any specified range of reaction conditions with desired precision in specified variables.

Figure 5: Binita Bhattacharjee, a graduate student from MIT's Department of Chemical Engineering, who worked on the Barton/Green joint CAO project.

Background
The modeling of complex multi-component kinetics is important in the research of airborne organics formation and transformation. Users have found most numerical tools on the market inadequate for determining the kinetics of larger systems, demonstrating a need for a new generation of numerical tools for simulation, sensitivity analysis, and model reduction.

Method of Approach
The project was separated into two tasks:

Developing a software package for the numerical analysis of large-scale chemical kinetic models
CHEMKIN is a widely used reaction scheme generator and property database in airborne organics. There are issues of compatibility with CHEMKIN and the eventual need for a standard to replace it. The software package developed by the project, known as "DAEPACK," uses automatic differentiation technology that can automatically analyze the CHEMKIN library. The program increases the flexibility of problem formulation by allowing user interaction for specifying variables.

Developing physically sensible and robust numerical methods for automatic model reduction appropriate to any specified range of reaction conditions with desired precision in specified variables
Removing negligible reactions and species can speed the computation, reduce CPU time and memory requirements, and make interpretation of model predictions easier. Emphasis was placed on reactions and species that are negligible under specified reaction conditions. In general, model reduction was formulated as a mixed-integer dynamic optimization problem.

Accomplishments

- Completion of "DAEPACK," a software package for the numerical analysis of large-scale kinetic models.
- Novel reformulation of the fixed-point kinetic model reduction problem as a convex, algebraic optimization problem.
- Completion of a very detailed study of the benefits that arise from applying DAEPACK to CHEMKIN-II chemical kinetics models. Two codes that are distributed with the CHEMKIN-II package were studied, CONP and SENKIN, for constant pressure batch reactor simulations.
- Demonstration that symbolic information (code evaluating sparsity patterns and sparse analytic Jacobian matrices), extracted automatically from the CHEMKIN-II source code by applying DAEPACK, can facilitate the application of modern sparse ODE/DAE solvers that are potentially much faster.
- Development of an interface between the equation-based process simulator ABACUSS II and the chemical kinetics package CHEMKIN-II. This interface uses the high level equation-based input language of ABACUSS II to formulate the mass, energy and momentum balance equations for complex reacting flow systems, but to use calls to the relevant subroutines in the CHEMKIN-II library to furnish physical properties and net species production rates from reaction.

PAH and Soot Formation Modeling using Detailed Kinetics and Experimental Data

Paul Barton and Jack Howard (Massachusetts Institute of Technology)

2000-2002

Goals

- To extend the method of modeling with detailed kinetics and experimental data to premixed flames with axial diffusion.
- To demonstrate the new modeling capability for premixed flames with axial diffusion by applying the method to two flames for which experimentally measured profiles of several molecular species concentrations and soot particle concentration and size distribution are available.

- To present and publish the new method in a form suitable for use in providing general guidance for the control of emissions of polycyclic aromatic hydrocarbons (PAH) and fine soot particles.

Background

Soot formation in flames is a major source of the fine airborne particles of current health concern. A quantitative kinetics model of the formation and oxidation of soot in combustors is of strong practical interest because of the expected need for more effective controls. Such modeling capability is difficult to achieve because of the physical and chemical complexities of the process.

CAO researchers developed models describing the formation of PAH and soot particles in flames. The PAH formation model was applied in studies of benzene/oxygen flames and soot formation in an atmospheric pressure plug flow combustor.

Past efforts to apply modeling techniques to premixed flames with axial diffusion had not been successful because of inherent computational instabilities, but an approach for dealing with these difficulties was identified and employed in this research project.

Method of Approach

The new modeling method involved the incorporation of experimental data consisting of certain species concentrations expressed as polynomial functions of residence time, transforming the usual ordinary differential equation system of rate equations into a differential algebraic equation system constrained by the data functions. This was solved using dynamic simulation software along with an interpreter that calculates rate constants. The models developed in previous CAO projects were extended and a numerical simulation tool was developed to create a new generation of numerical tools for the simulation of premixed flames with axial diffusion.

Accomplishments

- PREMIX, the widely used computer program for premixed flame calculations, was adapted for use in this project. Due to the fact that the researcher does not have access to the source code for the commercial version of PREMIX, the source codes of older versions of PREMIX, versions 2.5d and 2.55, were worked with instead. These versions exhibited many bugs and produced erroneous results in the calculation of species concentration profiles for premixed flames with axial diffusion when compared with the commercial package. Version 2.55 was modified and made to work.
- For the large-scale problems, transport data and thermodynamic data files were built to enable testing of the new numerical techniques on flame systems that are fundamentally and practically useful for the investigation of PAH and soot formation. For instance, the compilation was completed for data required for an ethylene flame example that includes 256 reactants species and about 1200 reactions.

Such transport, thermodynamic and input data files enable the successful simulation of large-scale premixed flames systems such as, for example, a n-heptane flame system involving 546 species and about 2500 chemical reactions.

Soot Mass Growth in Stationary Combustion Systems

János Béer (Massachusetts Institute of Technology)

1994-1996

Goal

- To gain an improved understanding of the pathways leading to post-nucleation soot mass growth.

Background

Soot surface growth occurs under acetylene addition and polycyclic aromatic hydrocarbon (PAH) coagulation, however the relative contributions of these mechanisms under various temperatures and equivalence ratios had not been determined. It was believed that the role of PAH coalescence diminished with time and PAH concentrations tended to decrease due to soot scavenging. Acetylene concentrations were believed to play a dominant role in the later stages of surface growth. The objective of this study was to qualitatively determine the contributions from the two mechanisms.

Method of Approach

The study involved the comparison of soot formation rates and gas species concentrations obtained from an acetylene-lean environment against those from an acetylene-rich environment. The acetylene-lean environment was achieved through benzene injection. The study also involved the calculation of collision rates between soot particles and PAH molecules, and between soot particles and C_2H_2 molecules. These results were compared with observed soot formation rates.

Accomplishments

- In the acetylene-lean environment, the dominant soot growth agent was found to be PAH.
- In the acetylene-rich environment, both acetylene and PAH were found to be important contributors to soot growth.
- In the benzene injection experiments, the soot number density was not a strong function of the soot loading.

Fundamental Study on High Temperature Chemistry of Oxygenated Hydrocarbons as Alternate Motor Fuels and Additives

Joseph Bozzelli and Lev Krasnoperov, Tsan Lay (New Jersey Institute of Technology)

1996-2000

Goals

- To understand fundamental reaction processes of oxygenated hydrocarbons important to gasoline octane blending.
- To develop detailed mechanisms to allow for optimization of trend prediction in engine performance and emission reduction.

Background

Oxygenated hydrocarbons, such as methanol and ethanol, have been considered for use nationally as octane additives or alternative motor fuels. MTBE has been used as an anti-knock component and oxygenate additive in gasoline. An elementary reaction model can be used to develop optimal fuel blends that reduce undesirable emissions, while maintaining or improving engine performance.

Method of Approach

Experimental

Gas mixtures were reacted in a uniform, high temperature tubular flow reactor, and effluent is analyzed as functions of temperature, residence time and fuel equivalent ratio.

Modeling

Reaction mechanisms were built from elementary reactions with rate constants based upon fundamental principles of thermochemical kinetics, transition state theory, chemical activation, and quantum Rice-Ramsperger-Kassel theory for k(E) modified strong collision treatment for fall-off. Thermodynamic properties were used to in chemical activation and unimolecular reactions for rate constants.

Accomplishments

- A thermodynamic database and a pressure-dependent elementary reaction mechanism were assembled for MTBE oxidation. They were evaluated against experimental data. Sub-models were created for the oxidation of neopentane, isobutane, and isobutene.
- A pressure-dependent reaction mechanism was developed and tested for the oxidation of dimethyl ether. It was shown to be chain propagating through reactions with barriers below initial energies of reactants.
- Studies were performed at CBS-Q, CBS-q and G2 levels for hydrocarbon radical oxidation of methyl-tertbutyl, dimethyl ether, tertbutyl, isobutenyl, and isobutyl-radical. The calculated reaction paths explain the explosive nature of ethers relative to hydrocarbons.

- A website was created for graphical description and quantitative thermodynamic pathway analysis of MTBE oxidation and combustion.

Study of Fuel Rich Combustion Particulate Matter Formation
Wai Cheng (Massachusetts Institute of Technology)
2000-2001

Goal

- To establish a set of particulate matter formation data (the evolution of the particles through the production, growth and agglomeration processes) that can serve as a reference data set for particulate formation kinetics modeling.

Background

Carefully measured engine-like kinetics data of particulate formation as a function of fuel type can be important to future environmental regulations. Work in this area can lead to the development of quantitative kinetics mechanisms and can be used for devising engine and fuel strategies leading to lower particulate matter (PM) emission.

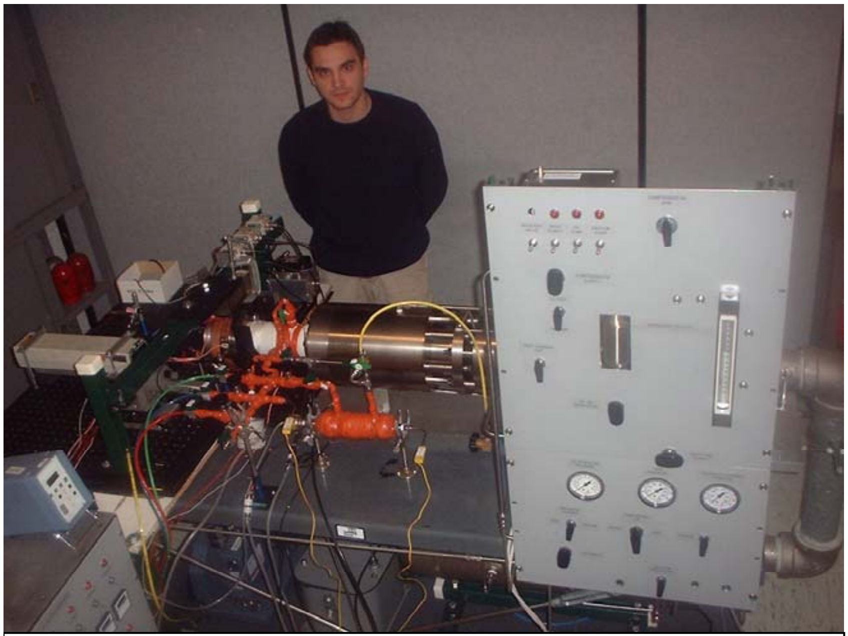


Figure 6: The Rapid Compression Machine (RCM) has been extremely useful for studying chemical reactions and particulate matter in engine-like environment for Ioannis Kitsopanidis from the Cheng group at MIT.

There has been a significant lack of data on particulate formation kinetics because of difficulty in reproducing and interpreting the results. Rapid Compression Machines (RCMs) provide a useful means for studying chemical reactions in an engine-like environment. They consist of a single stroke piston/cylinder apparatus in which a uniform fuel/air mixture is rapidly compressed to a thermal environment similar to that in an internal combustion engine. RCMs allow for unambiguous interpretation of data because the mixture and environment are well defined.

Method of Approach

A RCM was used to study PM formation in a thermal environment similar to an internal combustion engine. Iso-octane was used as a base fuel in the study, and single component oxygenates were added to the base fuel to assess their effects. A line-of-sight absorption technique was used to continuously monitor the PM during the combustion process.

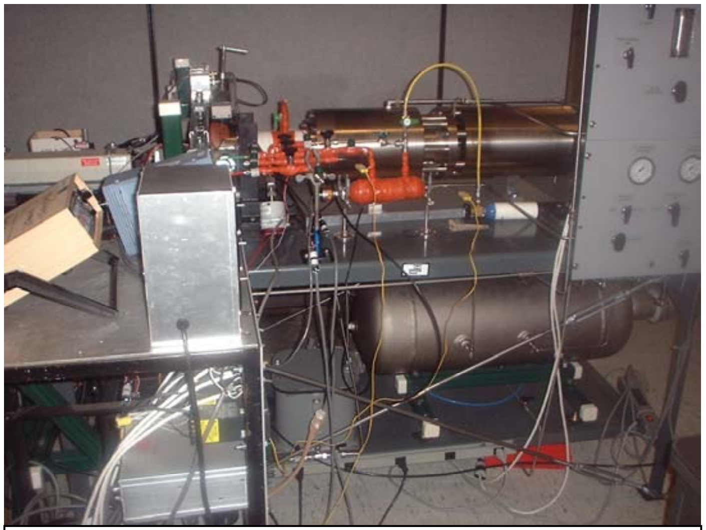


Figure 7: The Rapid Compression Machine (RCM) is a single stroke piston/ cylinder apparatus in which a uniform fuel/ air mixture is rapidly compressed to a thermal environment similar to that in an internal combustion engine.

Accomplishments

- A new rapid compression machine (RCM) was designed, built and used to study the combustion of simple single-component fuels under diesel conditions at pressures up to 120 bar
- The measurements include pressure and transmission signals from the experiment with air and respectively n-octane, n-butane, iso-octane, toluene and ethylbenzene mixtures at the same compression conditions. Because of the variation of the auto-ignition resistance of these fuels, there were substantial differences in the ignition delays –almost negligible for n-octane; 8 ms for n-butane and 19 ms for iso-octane. The transmission signals show that for all the fuels, the soot formation was rapid, commencing within a fraction of a millisecond at the point where rapid pressure rise/heat release began.
- The combustion is homogeneous in space and the rate is sensitive to temperature, which varied as a function of time. Furthermore, the temperature history and hence, the reaction rates also varies with the mixture compositions and other initial conditions. Both the pressure rise rate and the soot formation rate increase with increase in compression temperature.

Computer Generated Kinetic Models for PAH Formation
William Green (Massachusetts Institute of Technology)
1997-2001

Goal

- To develop a detailed kinetic model of polycyclic aromatic hydrocarbon (PAH) formation in fuel rich flames.

Figure 8: Researcher William Green is highly active in kinetic modeling at the MIT Department of Chemical Engineering.

Background

Models are needed to allow quantitative predictions about how changing fuel compositions or combustion conditions would affect the production of specific emissions. Past successful kinetic models in literature were mostly constructed by hand using rate constants derived by analogy. These models needed improvement in their rate estimates. This can be achieved by using systematic computer methods to avoid leaving out important reactions and identify the critical rate parameters.

Method of Approach

The approach included quantum chemistry/transition state theory calculations on individual reactions, validation against experiment where possible, and generation into rules valid for whole reaction families. This led to the construction of a model. Validation included sensitivity analysis and subjecting the model to varying experimental conditions.

Accomplishments

- Methods for computing individual PAH reaction rates were developed and validated. These calculations were generalized into reaction family rate estimation rules. The project developed an excellent methodology for generalizing from high-level small-molecule reactions into reaction family rate estimates, using group-additivity techniques for Transition State properties.
- Calculations reveal that one must consider the pressure-dependence of PAH reactions even in high-pressure flames despite the large size of the molecules involved. This observation is very important since most of the detailed data are measured at low pressure, but the chief technological applications (e.g., in diesel engines) occur at high pressure where the rates and products will be very different

from those at lower pressures. Methods were developed for identifying when the pressure dependence calculations are necessary and for automating the pressure dependence calculations to make it feasible to deal with this complexity for a large number of systems each with multiple possible products and isomers.

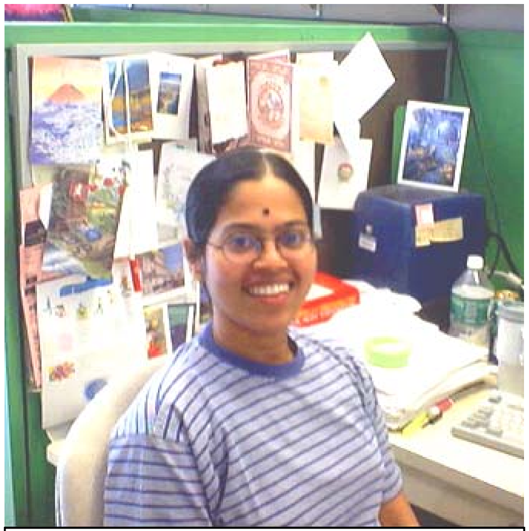


Figure 9: Sumathy Raman, a postdoctoral student in the Green research group at MIT, pausing from her research.

- The results include a compilation of large number of reaction family rate estimates for various types of H abstractions. Group additivity was used to preserve available information on the transition state properties from quantum calculations. Both the quantum calculations and the treatment of the hindered rotors and conformers are considerably improved, giving better rate estimates. A large number of reaction rate estimates were performed for free radical PAH reactions. An improved general transition-state theory method for computing rates for reactions involving resonance-stabilized radicals with internal rotors has been developed, which explicitly treats the relative orientation of the stabilizing p orbitals. The results include a detailed study of the reaction of napthyl radical with acetylene that revealed that even large systems can be significantly pressure dependent even at high pressures. Criteria were derived for establishing when detailed pressure-dependence calculations are required for large molecule reactions.

Combustion Chamber Deposit Effects on Engine Hydrocarbon Emissions
John Heywood, Simone Hochgreb (Massachusetts Institute of Technology)
1992-1997

Goals

- To design a carefully controlled experiment for deposit accumulation and hydrocarbon emission measurement.
- To assess the effects of combustion chamber deposits on the hydrocarbon emissions from a modern production spark-ignition engine.
- To measure the effect of combustion chamber deposits on the hydrocarbon emissions from single-component fuels.
- To develop and validate a model for the mechanism(s) by which combustion chamber deposits lead to additional hydrocarbon emissions.
- To study the effects of combustion chamber deposits on NO_x emissions.

Background

Engine deposits increase hydrocarbon (HC) emissions. Past data has suggested that they may also increase NO_x emissions. To meet future emissions standards, the emissions due to deposits will have to be reduced. These emissions need to be quantified, and the mechanisms involved in their formation need to be understood.

Method of Approach

A four-cylinder, dual-overhead-cam Saturn engine was subjected to a standardized deposit build-up cycle. An additized fuel (which keeps the intake valves and ports clean) was used to isolate the effects of the combustion chamber deposits on emissions. HC and NO_x emissions were measured continuously during the deposit accumulation process. A model was developed to explain the effect of deposits on HC emissions.

Accomplishments

- The deposit accumulation process developed showed that deposits can be built up systematically and reproducibly in engine dynamometer tests. Deposit build-up may cause an increase in HC emissions of about 15%, depending on fuel, engine and operating condition details.
- HC emissions increased rapidly for about the first 24 hours of operation, and then stabilized, even though deposits continued to build up. Cylinder head deposits dominated HC emissions.
- A model was developed to explain the observed increase in HC emissions as deposits build up and the lack of sensitivity of this increase to fuel compound.

Chemical Kinetic Modeling of Products of Incomplete Combustion in Spark Ignited Engines

Simone Hochgreb (Massachusetts Institute of Technology)

1996-1998

Goals

- To determine under what engine conditions the production of products of incomplete combustion are most likely.
- To determine the relative roles of mixing and reaction on oxidation during the different phases of post flame oxidation.
- To determine how well predictions of unburned hydrocarbon product hold against experimental data.

Background

Hydrocarbon emissions from spark-ignited engines have been responsible for a large fraction of ozone precursors in the atmosphere. The process of oxidation of unburned hydrocarbons in spark ignited engines involves the emergence of hydrocarbons from cold engine walls and subsequent diffusion through the thermal boundary layer into the hot burned gases. The understanding of the physical and chemical phenomena leading to the products of incomplete combustion in spark ignition, however, had remained largely correlative and semi-empirical. The hydrocarbon oxidation process can be understood by combining chemical kinetic and fluid mechanical mixing models.

Method of Approach

The project used a one-dimensional mixing layer model that included convective and diffusive transport, as well as chemical production, destruction and energy release. Boundary conditions were set to match those expected around the engine walls. The evolution of the species released at different times during the expansion process was investigated, and the contributions of different factors (reaction, diffusion and convection) to the overall process was determined.

Accomplishments

- Development of a one-dimensional gridding code for calculations of the post-flame oxidation of fuel in spark ignited engines.
- Understanding the role of chemistry and diffusion on the process of post-flame oxidation in spark ignited engines.
- Quantification of the factors limiting oxidation.

Investigation of the Formation of Particulate Matter in Spark-Ignition Engines

Simone Hochgreb and Arthur Lafleur (Massachusetts Institute of Technology)

1996-1999

Goals

- To develop an experimental database of particulate matter emissions from spark ignited engines operating at steady and transient conditions as a function of fuel type, operating conditions, and fuel delivery technique.
- To develop and apply a time-resolved diagnostic for the measurement of instantaneous particulate matter concentrations during transients as a function of engine operating conditions, fuel type, and fuel injection characteristics.
- To use the developed database to characterize and quantify the important processes that control particulate matter formation and oxidation in the engine.
- To develop a physical model for the particulate matter formation and oxidation processes.

Background

Atmospheric particulate matter (PM) has been an important factor correlating with mortality rate increases in urban areas. Internal combustion engines, and in particular spark-ignited (SI) engines, have been shown to contribute a substantial fraction of PM to the atmosphere. Research identifying the mechanisms of PM formation in SI engines has been fairly limited. The goal of this project was to produce a systematic study of the mechanisms leading to the formation of PM in gasoline engines.

Method of Approach

The project was divided into three tasks.

Baseline PM mapping at selected steady state and cold start conditions

Total PM mass, size distribution, and chemical composition were determined for selected steady state and cold start conditions in a modern four-stroke, four-cylinder engine. Identification of the origin of PM matter was determined using chemical and elemental analysis.

Development and implementation of a time-resolved total PM measurement technique for transient and cold-start emission testing

Laser induced incandescence (LII) was employed to measure time-resolved PM concentrations. The technique has been used for sizes less than 100nm, as well as for the measurement of soot in diesel engines. The LII signal is linearly proportional to soot volume fraction, allowing for easily interpretable data.

Identification of possible important PM formation mechanisms

The baseline and transient PM measurements were used in conjunction with variations in engine parameters to identify the effects of fuel, injection strategy, and operating conditions. Certain variables, such as fuel type and injection type, were isolated in order to separate potential mechanisms during start-up or transient tests.

Accomplishments

- Determination of the effect of air-fuel ratio and liquid fuel presence on PM matter measurements.
- Fuel sensitivity studies show that aromatic fuels produce substantially more PM than paraffinic fuels for similar volatility.
- Addition of oxygenated fuels (MTBE) to indolene does not significantly affect PM emissions. Lubricant oil was found to contribute negligible amounts to PM formation.
- Development of a physically based model to explain the observed PM measurements.
- Transient PM measurements showed that the characteristic time for PM change is much longer than that for the change in engine conditions, and that particle growth dynamics continues for a long time.

Combustion Chemistry of Polycyclic Aromatic Compounds
Jack Howard (Massachusetts Institute of Technology)
1992-1998

Goal

- To enhance predictive capabilities of the model previously developed for polycyclic aromatic hydrocarbon formation for use in source attribution studies and in the development of emission control strategies.

Background

Polycyclic aromatic hydrocarbons (PAH) have been major contributors to air pollution from combustion sources. Basic understanding of the factors that govern the detailed composition of the effluents from combustion systems is necessary for source attribution and development of control strategies. The mechanistic and kinetic model developed in this project provide basic understanding and predictive capabilities of PAH generation in combustion.

Method of Approach

A predictive model of PAH formation in flames was developed using elementary reactions to describe the basic flame chemistry and PAH growth up to a mass of 400 amu, and aerosol dynamics to describe all species with mass above 400 amu. Particular pathways were isolated using a data incorporation technique (DIT). The model was then validated with experiments involving a jet-stirred reactor/plug-flow reactor apparatus.

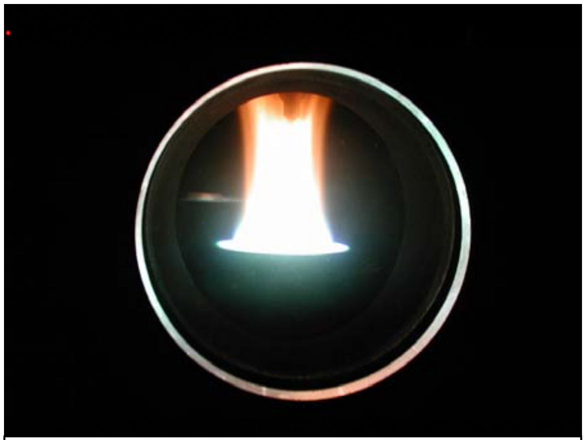


Figure 10: A sooting flame (right) generated in the Howard laboratory at MIT to study soot formation in flames. The yellow tinge denotes radiation and the presence of carbon particles.

Accomplishments

- DIT was used to develop a soot nucleation model that includes PAH-PAH coagulation reactions.
- An automated optimization algorithm has been developed and implemented that works in conjunction with the DIT to explore parameter subspaces for optimal solutions. This improves the ability to describe PAH-soot interactions because of improvements to the soot model.
- Broadening of the description of PAH to include the whole spectrum of molecular weights from 100 amu to 1600 amu.

Origin and Characteristics of Fine Soot Particles in Combustion
Jack Howard (Massachusetts Institute of Technology)
1998-2002

Goals

- To extend previous jet-stirred/plug-flow reactor data to include measurements of particle size and structure at different residence times corresponding to different particle formation and burnout stages including any oxidative fragmentation.
- To extend the present polycyclic aromatic hydrocarbon-soot model to include oxidative enlargement of pores and fragmentation of soot particles.
- To critically test the model against data so as to evaluate and improve the mechanistic understanding and accuracy of model predictions of soot particle and polycyclic aromatic hydrocarbon emissions from combustion.

Background

Soot formation in flames is a major source of fine airborne particles of current health concern. There is reason to believe that the fine soot particles of health concern may originate in combustors in different ways. The complexities of environmental soot sources have been poorly understood and thus the model developed in this project can provide basic guidance for the development and optimization of control strategies.

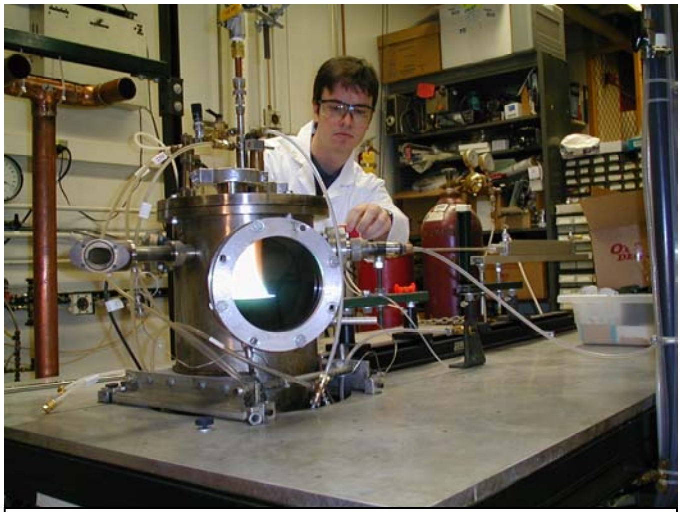


Figure 11: Murray Height, a graduate student of the Howard group at MIT adjusts the gas feed on a 1-dimensional burner used to study soot formation in flames.

Method of Approach

The project performed time-resolved measurements of soot particle size and concentration for different flame configurations and conditions. The results were then used to study the mechanisms of soot particle generation and growth in flames. Results from a scanning mobility particle size analyzer were compared with those from transmission electron microscopy for complete characterization of the soot.

Accomplishments

- A scanning mobility sizing method applied to the measurement of soot particle size distributions in flames was found to be suitable for measuring relative changes and to be faster than the collection of samples followed by electron microscopy.
- The limited injection of oxygen into sooting flames can either increase or decrease the amount of soot formed depending on whether the temperature is relatively low

or high, respectively. Further increasing the amount of oxygen injection reduced soot number concentration and eventually decreases the particle mean diameter.

- Observed rates of soot formation under various conditions in a plug flow reactor and in premixed flames exhibit similar oscillations to those observed in the concentration of polycyclic aromatic hydrocarbons while the concentration of acetylene varies monotonically, consistent with the hypothesis that polycyclic aromatic hydrocarbons are the main reactants for soot growth.
- Soot from atmospheric-pressure combustion was found to contain curved layers of carbon as well as the well-known planar layers. The curved layers contained pentagons within the otherwise hexagonal carbon network, which may be centers of increased reactivity. The fraction of the carbon residing in curved layers may be an important parameter in the characterization of soot reactivity.

Simultaneous Removal of Soot and NO_x from the Exhaust of Diesel-Powered Vehicles

Henry Shaw, Robert Pfeffer (New Jersey Institute of Technology)

1994-1997

Goal

- To gain a scientific understanding associated with the catalytic oxidation of soot with the concomitant reduction of NO_x to molecular nitrogen.

Background

Past catalyst technology has involved the passage of zeiolite to oxidize diesel soot, or Pt-based oxidation of NO to NO_2 which is then used to oxidize soot collected on a filter. There are shortcomings in both catalysts. In the first case, zeiolite can act as a filter for soot capture and plug when the catalytic surface becomes ineffective due to low temperature operating conditions. In the second case, much of the NO_2 is reduced to NO rather than N_2, thus emitting excessive quantities of NO_x. A mechanistic understanding is required to develop a catalyst to reduce NO_x while oxidizing soot. In addition, a rotating fluidized bed reactor may promote the soot-NO_x reaction.

Method of Approach

The project consisted of experimental and computer modeling of commercial and experimental catalysts.

Experimental

Packed and fluidized quartz reactors were used to generate effluent, which was subsequently analyzed by an on-line gas chromotograph using thermal conductivity detection (TCD) and flame ionization detection (FID).

Computer Modeling

The study combined catalytic oxidation and poisoning on a particle with a moving external surface area. The model was of a single spherical particle on which carbon soot builds up at low temperature and reacts at elevated temperatures. The carbon oxidizes and reacts with NO_x on the catalyst surface. The particle represents a fluidized bed and is considered independent of neighboring particles. A set of kinetic rate constants were obtained.

Accomplishments

- CO is a possible intermediate reducing gas needed to react with NO at 400-600^{o}C.
- Sufficient CO is formed at 300^{o}C from soot or other solid carbon sources to effectively reduce 1000 ppm NO to N_2. The CO is oxidized to CO_2.
- CO is as effective as light hydrocarbon gases in reducing NO.
- An experimental and modeling program was designed to quantitatively describe the process for control of diesel soot and NO_x and to develop catalysts that are resistant to water and sulfur poisoning.

Transport and Transformation

Kinetics, Reaction Path Analysis and Elementary Reaction Mechanisms Development for Atmospheric Photochemical Oxidation of Aromatics and Oxygenated Aromatics

Joseph Bozzelli and Tsan Lay (New Jersey Institute of Technology)

1996-2001

Goal

- To develop a model based on elementary kinetics, pathways, and thermodynamic properties incorporating the photochemical oxidation of aromatic hydrocarbons under atmospheric conditions.

Background

The development of a mechanism for modeling atmospheric reactions of aromatic compounds in photochemical oxidation is important for understanding atmospheric reactions and product formation rates on aromatics. It can also facilitate the development of models of photochemical smog, air-shed transport and oxidation processes to incorporate aromatic species.

Method of Approach

The project developed reaction mechanisms utilizing elementary kinetic parameters, coupled with microscopic reversibility and calculation of steady state levels of active intermediates. Pressure dependent and chemical activation reaction analysis was conducted. Thermodynamic properties and transition state parameters were determined via literature evaluation, high level ab initio or density functional molecular orbital methods and group additivity.

Accomplishments

- A detailed reaction mechanism was established with microscopic reversibility and a thermodynamic database has been established for toluene and benzene atmospheric oxidation.
- An initial mechanism for styrene was developed.
- Extension of thermodynamic property database of aromatics through biphenyls, styrene dimers, dioxins, and dibenzodioxins.
- Bond energies for C-H bonds on styrene, fulvene and other aromatic-like systems, and on hydrocarbon esters, were found to be slightly higher than literature estimates.
- Rate constants for HO_2 addition to olefins were found to increase with increased hydrocarbon substitution on the olefinic carbon.

- Two computer codes were developed for thermodynamic property interpretation of output from ab initio and density functional calculations and for calculation of rate constants from ab initio data.

Modeling and Analysis of the Evolution of the Size and Composition Distribution of Atmospheric Organic and Inorganic Aerosols
Glen Cass (California Institute of Technology)
1996-2000

Goal

- To construct and test data analysis techniques and mathematical models that relate the emissions of gases and primary particles to atmospheric particulate matter concentrations.

Background

Older aerosol air quality models have assumed that atmospheric particles were of the same chemical composition. Newer research has shown that atmospheric particles are derived from different major source types and may evolve separately from each other. Field experiments studying the evolution of size distribution and chemical composition of the urban aerosol complex were conducted in the Los Angeles area from 1996 to 1997. This provides an air quality model verification data set. The purpose of this study was to apply atmospheric models and data analysis methods to the field experiments.

Method of Approach

Data analysis and model testing were conducted in trajectory model format, to mimic the experimental design used in the field experiments. Air quality models were applied to explain the relationship between emissions and air quality for both organic and inorganic particulate matter at nearly the single particle level. These models incorporated models in literature as well as new chemical mass balance receptor models that relate source contributions to ambient PM concentrations.

Accomplishments

- A model was developed that follows the evolution of single particles in the atmosphere. Model predictions are in good agreement with detailed measurements of the particle size and bulk chemical composition, and reveal the major emissions source types that contribute to the Los Angeles fine particle problem.
- Methods were developed for correcting and displaying the massive amount of data taken on single particle size and chemical composition during the field experiments modeled.

Kinetics and Thermochemistry of Primary Steps in Oxidation of Airborne Organic Compounds

Lev Krasnoperov (New Jersey Institute of Technology)

1996-2002

Goal

- To characterize the UV absorption spectra, reaction rate parameters and thermochemistry of the transient intermediates in the oxidation of airborne aromatic compounds. The main objective was the quantitative characterization of the UV absorption spectra of hydroxycyclohexadienyl (HCHD) radicals, measurements of rate constants of these radicals with molecular oxygen and determination of thermochemical parameters the reaction $C_6H_6OH + O_2 \iff C_6H_6(OH)OO$, which is the major route of the transformation of benzene in the atmosphere.

Background

Understanding the fundamental chemistry, kinetics and thermodynamics is critical for developing predictive models of ozone and smog formation. Intermediate radicals in the oxidation of aromatic hydrocarbons are important for understanding the whole oxidation process, however the transformations have not been characterized well in literature due to the lack of a simple way to generate the intermediates. Laser induced fluorescence (LIF) has been shown to monitor radicals after laser photolysis. Direct methods of detection could also be possible with transient UV absorption or chemical ionization mass spectrometry.

Method of Approach

A novel multi-pass cell approach to high-sensitive absorption detection was developed and used. In contrast to the other known techniques (such as the White cell, Cavity Ring Down Spectroscopy, etc.) the cell is simple and can operate with traditional, non-laser, non-pulse, CW sources. A multi-pass sell designed to operate at 315 nm for hydroxycyclohexadienyl radical transient monitoring was designed, built and tested. The cell consists of a spherical and planar dielectric mirrors with the reflectivity at the monitoring wavelength, 315 nm, of ca. 99%. Conventional high pressure Hg arc lamp (100 W) is used as a light source. The light modulation “gain” of the cell is 52 times. With the signal accumulation, this allows to record transient absorptions at 315 nm of ca. $2x10^{-5}$ to be recorded with a time resolution of 3 μsec and a signal/noise ratio sufficient to resolve double-exponential decays arising due to the partial equilibration of the reaction of hydroxycyclohexadienyl radical with molecular oxygen. The performance of the cell is excellent, it allowed to increase the sensitivity of the radical detection almost two orders of magnitude. Experiments on the kinetics of hydroxycyclohexadienyl radical were performed using this multi-pass cell.

Interfering reactions have complicated quantitative studies of cyclohexadienyl radicals. The production of relatively high concentration hydroxyl radicals is necessary for absorption spectra characterization, but can be difficult due to the strong UV absorption of aromatic compounds. An evaluation of mechanisms showed that the photogeneration of an excited metastable oxygen O(1D) was the best indirect source of cyclohexadienyl radicals. Photodissociation of nitrous oxide at 193 forms O(1D) atoms with 100% quantum yield. These atoms are quantitatively converted to two hydroxyl radicals when reacted with water. An attempt was made to develop a direct photolytic source of hydroxycyclohexadienyl radicals based on the photolysis of proper halogen substituted cyclohexadienes

Quantitative UV absorption cross-sections of hydroxycyclohexadienyl radical were obtained, as well as measurements of the UV absorption spectrum of cyclohexadienyl radical. Rate constants were measured for the reaction of hydroxycyclohexadienyl radicals with NO_2 and for the reaction of hydroxycyclohexadienyl radicals with O_2.

Accomplishments

- Several methods of indirect photolytic production of substituted cyclohexadienyl radicals for quantitative kinetics studies were modeled and evaluated. A required precursor molecule was designed and initiated.
- UV absorption spectra of hydroxycyclohexadienyl radical (quantitative cross sections) and cyclohexadienyl radical (relative spectrum) were measured.
- Rate constants of the reactions of hydroxycyclohexadienyl radical with NO_2 and O_2 were measured directly by monitoring the temporal absorption profiles of the radical.
- Equilibration type kinetic profiles were obtained in the reaction of hydroxycyclohexadienyl radical with molecular oxygen. A preliminary for the bond energy between the hydroxycyclohexadienyl radical and oxygen in the adduct was obtained.
- The $C_6H_6(OH)$-OO bond energy in the adduct of HCHD radical with molecular oxygen was accurately determined. The standard entropy of the reaction was obtained based on theoretical calculations of the structure and the of vibrational frequencies of the adduct. The rate constant of reaction of HCHD radical with molecular oxygen was also refined based on more accurate kinetic profiles.
- Experimental investigation of the cavity matching with the light source, and the use of shorter wavelengths.

Kinetics of Photochemical Aerosol Formation from Airborne Organic Compounds
Lev Krasnoperov (New Jersey Institute of Technology)
2000-2002

Goal

- To develop and characterize a new experimental technique for direct time-resolved studies of the photochemical aerosol formation.

Background

During recent years, there has been significant progress in atmospheric aerosol research. The majority of the experimental studies, however, were performed using photochemical smog chambers and focused mainly on the final or late stages of the process of aerosol formation and on the chemical composition of the aerosol particles formed. This project focused on the kinetics of the very initial stages of aerosol particle formation.

New experimental technique for direct time-resolved studies of the earlier stages of photochemical aerosol formation was developed and characterized. The developed technique is based on a combination of a double excimer laser pulsed photolysis and spatially and time resolved monitoring of scattered light by a gated intensified CCD (ICCD) camera. Improvement in the sensitivity, and, hence, in the limiting detectable particle size, was achieved due to the use of short wavelength UV monitoring light and a pulsed laser as a monitoring light source. The ability to resolve individual particles and the time resolution of the technique greatly increased the information gained in the experiments.

Method of Approach

The experimental approach was based on the combination of time/wavelength resolved light scattering/absorption spectroscopy with excimer laser pulsed photolysis. Gas mixtures containing a photochemical aerosol precursor and oxygen were irradiated with a powerful UV light pulse from an ArF excimer laser. Free radicals formed in the primary (hydrocarbon photolysis) and/or secondary (OH + hydrocarbon) reactions then reacted with molecular oxygen forming the photochemical aerosol precursors under well controlled conditions in a short time. Transforming the bimolecular reactions of aerosol particle growth into a system of ordinary differential equations and bringing the problem to a dimensionless form allowed for the development of a model for aerosol particle growth kinetics.

Accomplishments

- Experimental set-up for direct time resolved monitoring of photochemical aerosol formation after pulsed initiation by an excimer laser was designed and assembled.
- Kinetics of photochemically induced aerosol formation in several chemical systems, containing nitrogen oxides and air was studied. Aerosol particle formation was observed in mixtures of 1,4- cyclohehadiene/ NO/ air and cyclohexene/NO/air. The evolution of the particles number concentration and the size distribution function as well as the variation of the scattered light intensity with the delay time after the photolysis pulse were measured. In the two other investigated chemical systems – mixtures chlorobenzene/NO/air and toluene/NO/air the increase of the total scattered light intensity with the delay time was observed.

- Several numerical models of the aerosol particle growth that incorporate reversibility of reactions were formulated and several computer codes were written and executed to process the particle images as well as to calculate the modeled particle size distribution function evolution. The experimental data were compared with the numerical calculations and the experimentally observed evolution of the size distribution was rationalized based on critical nucleation phenomenon.

Direct Treatment of Uncertainties in Mathematical Models of the Transport and Fate of Airborne Organics

Gregory McRae (Massachusetts Institute of Technology)
1993-1997

Goal

- To develop a new mathematical and computational framework for the systematic sensitivity and uncertainty analysis of the complex transport and transformation processes that control the concentration dynamics of airborne organics.

Background

One of the consequences of using models to describe the formation and transport of the photochemical air pollution is that approximations are involved. There are also measurement errors in the data used to develop inputs and kinetic parameters for the reaction mechanisms. The goal of this research was to identify the inputs that contribute most to the uncertainty in predictions.

Method of Approach

A new approach was developed, termed the Deterministically Equivalent Modeling Method (DEMM). Uncertain parameters were treated as random variables. These variables were in turn approximated using orthogonal basis function expansions in the probability space.

Accomplishments

- The predictions from three different mechanisms were found to be indistinguishable given current levels of parametric uncertainties.
- Because all the chemical mechanisms investigated, as well as the three-dimensional CIT Airshed model, are sensitive to the same set of parameters, reducing parametric uncertainties should be a key research priority for model improvement purposes.

Laboratory Studies of the Atmospheric Oxidation of Aromatic Hydrocarbons

Mario Molina (Massachusetts Institute of Technology)

1997-2001

Goals

- To identify and monitor in the laboratory various intermediate species formed in the atmospheric oxidation of aromatic compounds, in order to improve the current understanding of the mechanism of their atmospheric degradation process.
- To measure directly rate constants for various elementary reaction steps of atmospheric importance involving such intermediate species.

Background

Atmospheric oxidation of aromatic compounds plays an important role in the generation of pollutants in urban atmospheres. Reaction rate constants have been well established only for the initial oxidation step. Most of the subsequent steps have not been directly characterized in the laboratory. Reliable measurements of such rate constants will increase current understanding of the mechanism of formation of ozone and other pollutants in urban atmospheres, and will enable improved model predictions of photochemical smog production.

ecipient Mario Molina has actively participated in research with the Center as a principal investigator.

Method of Approach

Reaction intermediates were formed in a steady state turbulent flow reactor, fitted with a chemical ionization mass spectrometer (CIMS) for the detection of reactants and products. The intermediates of interest were generated in the flow tube by mixing the parent aromatic compound, present at small concentrations in an inert carrier gas, with a radical such as OH generated with a microwave discharge.

Accomplishments

- Several intermediates in the atmospheric oxidation of toluene were successfully generated and detected.
- Ion-molecule rate constants were measured for the reactions of the toluene-OH adduct. OH decays and adduct growth curves for the toluene-OH system were also determined. Results corroborate the formation of a bicyclic peroxy radical whose existence had been postulated previously on the basis of theoretical calculations.
- Several elementary reactions involving intermediates in the atmospheric oxidation of propylene was investigated. This work represents the first direct detection of

both the hydroxypropyl peroxy radical and also the hydroxypropyl alkoxy radical, as well as the first set of direct measurements of elementary reaction rates involving these intermediate species.

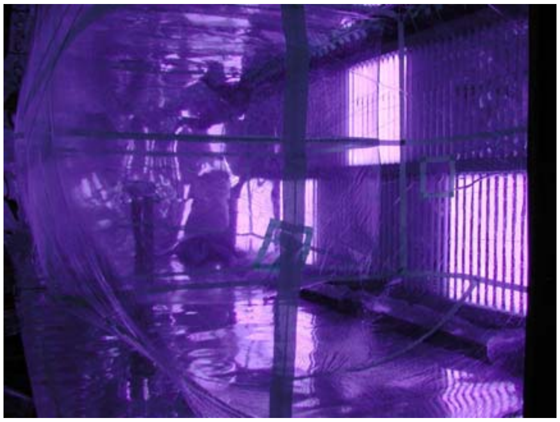
Secondary Organic Aerosol: Yields, Formation Mechanisms, and Molecular Speciation

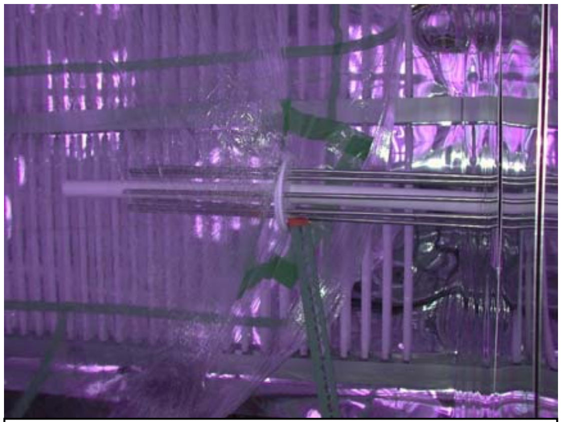
John Seinfeld, Richard Flagan (California Institute of Technology)

1992-2001

Goal

- To gain a better fundamental understanding of the atmospheric oxidation of volatile organic compounds important to urban and regional air quality.
- To elucidate the mechanisms of formation of organic aerosols from the atmospheric oxidation of VOCs.





Figures 13 and 14: The smog chamber used at Caltech by the Seinfeld group to study environmental chemical reactions in smog. Figure 14 (directly above) is the injection port used to introduce chemical variables into the chamber.

Background

Gas-to-particle conversion determines the size and composition of particles from the polluted urban atmosphere to the remote marine boundary layer. Understanding the detailed chemistry and physics allows us to predict the effects of primary gaseous and particulate emissions on the generation of cloud condensation nuclei in the remote atmosphere.

Method of Approach

Caltech outdoor reactor and ab initio molecular simulation was used to determine the mechanisms of photooxidation and secondary aerosol formation in the atmosphere for a number of important anthropogenic and biogenic hydrocarbons. A smog chamber was used to study integrated gas-phase and gas-to-particle conversion dynamics.

Accomplishments

- A comprehensive data set on the atmospheric aerosol-forcing potential of biogenic hydrocarbons was obtained.

- It was found that semi-volatile compounds are produced either by the initial oxidation of the parent organic or by oxidation of a first-generation oxidation product. The compounds partition themselves between the gas and organic aerosol phases depending on the amount of already-produced organic aerosol.
- A three-dimensional gas/aerosol model was created.
- Ab initio reaction mechanism studies revealed the behavior of alkoxy radicals.
- Initial experiments investigating the effect of relative humidity and temperature on SOA partitioning have been performed, as well as a complete analysis of the cyclohexene-ozone dark reaction. The work includes investigation of SOA of semi-volatile parent hydrocarbons and study of hygroscopic properties of chamber aerosol.
- An investigation into the hygroscopic nature of Pasadena fine particulate matter was carried out with a TDMA.
- A new, state of the art indoor air quality environmental chamber was designed and completed.
- Aerosol formation was studied in both wet and dry systems. Contrary to what has been observed with biogenic aerosol, relative humidity has little effect on aromatic aerosol yields.

Laboratory Studies of the Photochemistry of Organic Peroxides: Determination of the Photolysis Rate for Conditions Appropriate for Use in Urban and Regional Air Quality Models

Paul Wennberg (California Institute of Technology)

1999-2001

Goal

- To measure the action spectra of hydrogen peroxide and organic peroxides as a function of wavelength and temperature.

Background

Hydrogen peroxide and organic peroxides are important trace constituents of the urban and global atmosphere. They are the dominant oxidants of SO_2 found in clouds, fogs or rain in the atmosphere. Peroxides are removed from the atmosphere by photolysis. The photolysis rates are determined by the magnitude of the absorption features. Accurate UV absorption cross sections are required to assess the importance of photochemical destruction of atmospheric hydrogen peroxide and organic peroxides.

Method of Approach

Peroxide photolysis: A parametric oscillator was used to generate tunable laser light. Photolysis occured by directing the laser across a slow flow of ROOH in a cooled tube.

OH detection: A laser induced fluorescence (LIF) detection method was used to measure OH concentrations.

HO_2 detection: HO_2 was detected by chemical titration of the HO_2 to OH with nitrous oxide.

Determination of cross sections: The absorption cross sections was determined by appropriate parameters in the UV optical power and photolysis laser tuning.

Accomplishments

- Studies of the HNO_4 system revealed the unexpected, but atmospherically significant, dissociation from transition lying below the thermodynamic dissociation limit.
- Extended frequency measurements at wavelengths longer than about 300nm were achieved by changing the pump laser configuration to frequency mix the 1064nm fundamental of a newly constructed Nd:YAG laser with the signal output of an optical parametric oscillator system.

Monitoring and Source Attribution

Micro-Engineered Mass Spectrometer for In-Situ Measurement of Airborne Contaminants

William Carr and Kenneth Farmer (California Institute of Technology)

1996-1997

Goal

- To develop a prototype microengineered mass spectrometer for in-situ measurement of airborne contaminants.

Background

By developing a low-cost, portable mass spectrometer, on-site testing can be conducted at unprecedented levels.

Method of Approach

The device was fabricated using two silicon substrates. One substrate contained a novel microtip field emitter cathode electron source and ion extraction electrodes; the other provided ion collector, extraction and focusing electrodes. Mass was measured as a current through individual detector electrodes.

Accomplishments

- Successful fabrication of improved gated microtip arrays, and the subsequent achievement of relatively stable electron emission from these tips.
- An ion current has been observed from residual molecules in the UHV system.
- Mass separation in a magnetic field.

Experimental Investigation of the Evolution of the Size and Composition Distribution of Atmospheric Organic Aerosols

Glen Cass (California Institute of Technology)

1996-1998

Goals

- To conduct a field experimental program in which the evolution of the size distribution and chemical composition of the urban aerosol complex is observed using methods that focus on the evolution of the individual aerosol particles.
- To directly observe how gas-to-particle conversion processes in the atmosphere modify primary particles emitted from the many air pollution sources in a major city.

EPA ambient air quality standards require emissions controls to be devised. In order for these strategies to achieve specified improvements, it is necessary to understand the relative contributions that primary particle emissions sources make to ambient particle levels and how those particles are modified over time in the atmosphere by gas-to-particle conversion processes. Aerosol time-of-flight mass spectrometers have been designed that can determine both the size and the chemical composition of individual aerosol particles at the rate of hundreds of thousands of particles per day. Models have been developed that account for the particle-to-particle differences in chemical composition for particles of the same size. Experiments proposed in this project can be used to observe and describe the transformations of individual particles by chemical reaction in the atmosphere and could be used in the future to test air quality models against data on single particle composition in the atmosphere.

Method of Approach

Experiments were conducted in which the background marine aerosol was first characterized as it flows across the Pacific coastline in Southern California. Lagrangian air parcels were sampled as they were transported across Los Angeles to Riverside, California. Organic and inorganic aerosol species were sampled simultaneously by time-of-flight mass spectrometers, cascade impactors, filter-based samplers, and electronic instruments.

Accomplishments

- Field experiments were conducted. Gas-to-particle conversion processes were observed at the single-particle level, and read in terms of absolute particle number concentrations and chemical species concentration.

Development of Semiconductor-Based Adsorption-Modified Photosensitization (SAMP) Sensors for a Sensor-Array Device for the Monitoring of Organic Gases

Barbara Kebbekus (New Jersey Institute of Technology) and
Vladimir Zaitsev (Moscow State University)
1999-2001

Goal

- To carry out the initial studies which will lead to the development of a small, easily fieldable instrument to measure organic vapors in air from sources, in industrial atmospheres, or in the ambient air.

Background

Policy making and source identification for airborne organic vapors depend heavily on analytical techniques, however, such analyses are an exacting and expensive process. A solution of arrays of simpler sensor, as proposed in this project, shows promise for much greater selectivity than has been practical with other sensors. This project has developed semiconductor-based adsorption-modified photosensitization (SAMP) sensors.

Method of Approach

SAMP sensors were developed at Moscow State University. At NJIT, responses were measured in toluene, saturated and unsaturated hydrocarbons, and aromatic hydrocarbon vapors.

Accomplishments

- Solid state CdS sensors coated with Rhodamine B dye have been made. The sensors operate on the principle that adsorbed molecules which have a spectral overlap with the dye molecules will cause a change in photoresistance.
- Initial testing of the sensors shows sensitivity to toluene at levels of 0-4 ppm and ability to operate at atmospheric pressure.

Micro-concentrator Interface for Real-time VOCs Sensors

Somenath Mitra and Durgamadhab Misra (New Jersey Institute of Technology)

2000-2001

Goals

- To develop a micro-concentrator interface for chemical sensors, with initial focus on the development of a highly sensitive VOCs sensor for air monitoring.

Background

The detection and quantitative measurement of volatile organic compounds (VOCs) at trace levels in air emissions is of considerable importance in view of the hazard they pose to public health and their contribution to the formation of ozone in the troposphere. Recently, techniques have been developed for the real-time monitoring of VOC's using traditional instruments by using a micro-concentrator. The successful development of a micro-machined microtap that can be coupled to any chemical sensor would allow easy minaturization, flexibility, and cost reduction.

Method of Approach

Channels of different dimensions were fabricated on silicon wafers by etching them in the field oxide, followed by deposition of nitride and metal layers patterned to form the conducting layer. The channels were lined with a conducting layer, a glass layer was spun on to the metal layer, and the device was coated with a polymeric sorbent layer. The size of the micro-concentrator is comparable with the size of a penny.

Accomplishments

- An in-situ heating system was fabricated inside a micro-channel. Heating of the micro-channel was accomplished and tested by use of repeated pulses.

- Wafer bonding techniques were tried and established.
- Experiments demonstrated the feasibility of a micro-concentrator interface for sensors.
- Reproducibility of retention time and peak high were each very good for the microconcentrator. This work demonstrated that the microconcentrator can be used as an effective injector for gas chromatographs.

Methodology for Sampling and Analysis of Polar Organics
Somenath Mitra and Barbara Kebbekus (New Jersey Institute of Technology)
1994-1996

Goal

- To develop sampling and analysis techniques for polar volatile organic compounds in air.

Background

Polar and oxygenated VOCs are an important class of pollutants but methods for their sampling and analysis have not been well established. Some of these problems have been addressed in this project, including the interference of certain gases in air analysis, and techniques for continuous monitoring of VOCs at trace levels.

Method of Approach

A Thermoionic Ionization Detector (TID) was used for selective detection of VOCs in a complex matrix containing different hydrocarbons as well as gases such as CO, CO_2, and H_2O. Continuous GC monitoring was achieved with a novel sampling device that passed air through a hollow fiber membrane and a micro sorbent trap designed to serve both as an injection system and a sample concentrator. VOCs selectively permeated through the membrane and were carried into a sorbent trap or canister via counter-current flow of N_2.

Accomplishments

- Evaluation of the parameters affecting enrichment factors during sampling using a canister.
- Study of the trapping and desorption characteristics of different adsorbents for VOCs.

Markers for Carbonaceous Emissions from Combustion Sources
John Vander Sande and Adel Sarofim (Massachusetts Institute of Technology)
1992-1999

Goal

- To develop methods for quantifying the soot structure and elemental composition in order to determine their potential use as signatures for the source of particulate carbon in ambient air.

Background

Combustors, a major source of airborne organics, contribute to health hazards and visibility degradation. It is important to have reliable means for identifying true sources of organic contaminants in ambient air so that effective corrective engineering and policy strategies can be formulated and implemented in a timely manner.

Method of Approach

Methods were studied for obtaining potentially quantitative measures of the soot structure and composition. A relationship of soot microstructure and composition to combustion conditions and fuel type was pursued through the use of well defined experiments. A library of soot structures was begun for use in emissions source attribution studies.

Accomplishments

- A "truth table" was introduced as a means of simple and decisive source assignment of unknown samples. The successful development of such a table would allow sample identification and source assignment to be accomplished without relying on subjective judgments.
- The use of scanning transmission electron microscopy coupled with energy dispersive x-ray analysis and electron energy loss spectroscopy was used to characterize the chemical composition of soots.
- Comparison of the analyses of diesel mining soot and jet engine soot showed significant chemical differences.
- Electron energy loss spectroscopy was used to characterize the extent of oxidation in these soots.

Summer Symposia

The goal of the Symposia was to bring together many of the key researchers and policy makers to focus on key topics of current interest at the interface of technology and policy in the field of airborne organics. The Symposia provide opportunities for informal and sometimes spirited discussions between the participants in informal surroundings. Summaries of the presentations and discussions for all but the earliest Symposia may be found in the Center website:

http://web.mit.edu/airquality/www/

1994: Prioritizing Hazardous Air Pollutants: Establishing a Scientific Basis

Organizers
Glenn Cass (California Institute of Technology)
Richard Magee (New Jersey Institute of Technology)
William Thilly (Massachusetts Institute of Technology)

Goals

- To assess the methodologies available and being developed for determining which hazardous air pollutants really affect human health.

Background

Title III of the Clean Air Act regulated 189 chemicals under hazardous pollutant and accident prevention provisions. Setting priorities for research and action regarding these compounds provides a challenge to regulators.

Approach

The symposium consisted of technical presentations on the following aspects of hazardous air pollutants:

- The formulation of and responses to present regulations
- Environmental transport and transformation
- Health effects of airborne toxics
- A critical assessment of current and emerging diagnostic techniques for assessing the hazards posed by air pollutants
- Methodologies for reducing emissions

Conclusions

- There are available methodologies for assessing the emissions, atmospheric transformation, pathways for exposure and health effects.
- A scientific basis should be established for deciding if an airborne compound is a human health hazard. Evidence of health effects from currently identified hazardous air pollutants should be examined.
- There are methodologies currently available for prioritizing the hazardous air pollutants for regulatory action.
- Scientific questions need to be addressed in order to further define human health impacts and improve the decision making process.

1995: Effective Technologies for Reducing Vehicle Emissions

Organizers

John Heywood (Massachusetts Institute of Technology)
Robert Sawyer (University of California, Berkeley)

Goal

- To analyze the progress that has been made in controlling vehicle generated air pollution, and provide recommendations for effective technologies needed to realize future emissions reductions.

Background

The symposium drew upon the expertise of professionals in regulatory agencies, the automotive industry, the fuels industry, and research community to examine how well new emission control technologies, changes in fuels, and implementation of surveillance, inspection and maintenance programs are contributing to solving our urban air pollution problems.

Approach

Speakers were invited to address the following critical issues:

- What is our current assessment of the relative importance of motor vehicle emissions in urban air pollution?
- What does air quality data say about our progress in resolving this problem?
- How effective are current emissions control technologies in controlling light-duty motor vehicle emissions?
- Is it correct that emissions from current light-duty vehicles come largely from malfunctioning vehicles?
- Can practical surveillance, inspection and maintenance programs be designed which deal effectively with these “high emitters”?
- What is the current and future role of heavy-duty vehicles emissions in urban air pollution?

- Are there radically different propulsion system technologies and fuel options that might be substantially better?
- What are the most effective strategies for moving forward in this complex, as yet not fully understood, important urban environmental problem?

Conclusions

- Motor vehicle emissions are a bigger problem than we thought; motor vehicles are the largest source of carbon monoxide and ozone precursor emissions.
- Evidence is steadily building that confirms emissions from current light-duty vehicles come largely from malfunctioning vehicles.
- Heavy duty vehicles play a big role both on road and off road emissions.
- There is a love/hate relationship with emissions models. There are many deficiencies in these models due to lack of data, but they are the only tools we have for the task.

1996: Advanced Instrumentation for Air Quality Measurements

Organizers

Richard Flagan (California Institute of Technology)
Charles Kolb (Aerodyne Research, Inc.)

Goal

- To summarize present advanced measurement technologies and provide a framework for future research.

Background

The symposium was organized by Prof. Richard Flagan and Dr. Charles Kolb. Much of our knowledge of atmospheric processes is based on measurement data. Future advanced measurement technologies have two critical needs. The first issue deals with improving the scientific understanding of sources, processes, and effects of air pollution. The second issue deals with the need to monitor regulatory compliance.

Approach

The symposium was divided into five sessions:

- What is being done now?
- What do we need to do?
- What is happening in related fields?
- How could new technology improve gaseous pollutant measurements?
- How could new technology improve particulate measurements?

Conclusions

- There is a need for performance based monitoring.
- Close interrelation exists between measurements and modeling.

- There is a need to test the validity/consistency of field measurements.
- Long range simultaneous measurement of O_3 and particles is available by LIDAR.
- The measurement of $PM_{2.5}$ will provide the biggest challenges in the near future.

1997: Fine Particles in the Atmosphere

Organizers
Praveen Amar (North East States for Coordinated Air Use Management)
Glenn Cass (California Institute of Technology)
Jane Warren, (Health Effects Institute)

Goal
- To summarize current work in particulate matter research, and provide guidance to the industrial, governmental, and research communities in addressing future challenges.

Background
Particulate matter has been connected with adverse health effects. National Ambient Air Quality Standards (NAAQS) set guidelines for characterizing PM. Challenges exist in airborne organics research with regard to atmospheric characterization, future epidemiological research, and examining emission sources.

Approach
The symposium was divided into four sessions:
- Overview of current regulations and research in particulate matter.
- Connecting emission sources to atmospheric concentrations; regulation and control of PM; and issues confronting states in meeting PM standards.
- Frontiers of health effects research: what new data are likely to become available to inform future decisions?
- Effectiveness of standards in addressing health issues.

Conclusions
- There are many unanswered questions related to the mechanisms of particulate matter on health. Future research will need to take a multi-disciplinary approach, coordinating toxicology, epidemiology, clinical studies, and aerometrics.
- There is a lack of necessary PM emissions data, and this will delay the implementation of controls.

1998: Cost and Benefits Estimation in Air Quality Regulations

Organizers

Robert Sawyer (University of California, Berkeley)
Robert Slott (Massachusetts Institute of Technology)

Goals

- To provide case studies of cost-benefit estimation in air quality regulations
- To outline some of the challenges faced in cost estimation and quantifying physical benefits.

Background

Air pollution control is an important regulatory function provided by the federal government. The United States spends approximately 2.3% of GDP on environmental compliance. Cost-benefit analysis has been used to provide regulators with a framework for the evaluation of environmental programs. It must be recognized, however, that many costs and benefits are particularly difficult to quantify. There are categories of cost that are often not considered in cost estimation. Benefits, such as the estimated benefit of reduced pollution on premature death, play a significant role in the calculation of benefits.

Approach

The symposium focused on 6 key areas:

- Federal legislator and regulator perspectives on cost-benefit estimation
- Air modeling and monitoring
- The challenge of measuring health benefits of air pollution regulation
- Stationary source case histories
- Transportation case histories
- Improving the accuracy of cost and benefit predictions

Conclusions

- We need more good data on health, emissions and economics.
- We must give more effort toward quality assurance and uncertainty.
- Quantifying uncertainties is extremely important. Monitoring and extracting data is a difficult but necessary task.
- Looking at case studies, there is a bias in estimating the cost of control, but the market creates competition and drives costs down.

1999: EPA's Urban Air Toxics Strategy

Organizers

Praveen Amar (North East States for Coordinated Air Use Management)
Larry Cuppitt (US Environmental Protection Agency)
Debra Kaden (Health Effects Institute)
Robert Slott (Massachusetts Institute of Technology)

Goal

- To discuss scientific aspects of EPA's Urban Air Toxics Strategy, including the influence of science on policy and the influence of policy on scientific research.

Background

The Urban Air Toxics Strategy focuses on protecting urban areas, where there are concentrations of people and sources, sensitive populations, and larger percentages of minority and low-income populations. The Strategy has three risk reduction goals:

- Ensure a 75% reduction in cancer incidence from hazardous air pollutants in urban areas nationwide
- Substantially decrease non-cancer health risk in urban areas nationwide
- Target and address disproportionate risk in urban areas.

EPA has identified over 30 hazardous air pollutants from area sources with the biggest health risk. Assessments are to be updated every three years. The models are incorporating multi-pathway risk assessments, and multi-pollutant assessments. Pilot projects will be conducted in different cities to establish protocols.

Approach

The symposium was divided into 7 key areas:

- HAP monitoring: history, current methods, future needs
- Sources: Sources of toxic air contaminants, mobile sources
- Risk assessment: Tools, quantitative analysis of variability/uncertainty, education/outreach
- Mercury: public interest, power plant control, state control
- Exposure assessment in air toxics
- Health effects: Biological effects, risk assessment, current programs
- Research needs

Conclusions

- We need a national system for obtaining ambient data. Data challenges include a lack of prescribed methods and a need to better understand variability.
- There is a need to understand indoor versus outdoor sources and exposures. Source apportionment tools need to be developed; this is critical to developing cost-effective control strategies.
- There is still debate on whether diesel emissions constitute an air toxic, and how large the risk is. Mercury is a very public issue because of fish advisories and TRI data. We know the primary anthropogenic sources, and control is possible, although at a cost.

- The current data set for the quantitative risk assessment of health effects is inadequate. Unanswered is whether we are aiming for an acceptable level of risk, or an acceptable level of control.

2000: The Future of Diesel: Scientific Issues

Organizers

Praveen Amar (North East States for Coordinated Air Use Management)
John Heywood (Massachusetts Institute of Technology)
Diane Mundt (Health Effects Institute)
Robert Sawyer (University of California, Berkeley)
Robert Slott (Massachusetts Institute of Technology)

Goal

- To discuss scientific aspects of diesel engines and fuel, including what is known about the science, uncertainties and their magnitude, and what research is needed.

Background

Diesel is used extensively in commerce in the US and Europe. Diesel is the most economical engine to own and operate due to its high power density. It is also very reliable and durable. Diesel contributes to PM and NO_x and attention must be paid to diesel air pollution issues.

Approach

The symposium was divided into 5 key areas:

- Where are we now?
- Regulations in the US, Europe, and Asia
- The road to clean diesel: the issues
- Health effects and risk assessment
- Views of the future: where will diesel fit in?

Conclusions

- Diesel engines are in widespread use due to their economics, high reliability, and functionality.
- Diesel emissions have been essentially uncontrolled for the past thirty use, while the use of diesel vehicles has been increasing.
- Diesels have become a large part of the NO_x pollution problem, and also contribute substantially to ambient concentrations of particulate matter. Regulations of diesel have been proposed by the US and Europe, but control of NO_x and PM continues to be a problem.
- Environmental health and new technology will be the keys to future regulation.

2001: Exporting and Importing Air Pollution: Regional and Global Transport

Organization and management of Symposia transferred to MIT. Summary of presentations and discussion is posted on the web:

http://lfee.mit.edu/programs/airquality-endicott/

As the Center approached its scheduled termination the interest and support enjoyed by the Summer Symposia were strong enough to indicate that these Symposia should b be continued and supported beyond the lifetime of the Center. Dr. Robert Slott who had already been leading the organization, program planning and fund raising for the Summer Symposia agreed to continue in these roles as the hosting of the Symposia was shifted from the Center to the MIT Energy Laboratory. This research entity has recently been renamed the MIT Laboratory for Energy and the Environment (LFEE). Dr. Slott continued to obtain inputs from the Center's Scientific Advisory Board in the selection of topics for the Symposia up to and including the last meeting of the SAC.

2002: Greenhouse Gas Reduction Policies and Technologies

Organization and management of Symposia transferred to MIT. Summary of presentations and discussion is posted on the web:

http://lfee.mit.edu/programs/airquality-endicott/

Research Synergies

One of the Center's goals was to foster cross-fertilization between the different investigators and between different interest groups. The Center fulfilled this goal by providing the opportunity for research synergies within focus areas, between focus areas, between institutions, and between researcher and policy makers in annual symposia.

Within and Between Focus Areas

- Modeling tools developed in Profs. Barton and Green's project were used in Prof. Green's project on kinetic models for PAH formation.
- Prof. Barton applied numerical tools to Prof. Howard's projects of PAH and soot formation.
- Prof. Bozzelli's work on the chemistry of oxygenated hydrocarbons had relevance in Prof. Hochgreb's study examining the effect of oxygenated fuels on PM emissions in spark-ignited engines.
- Prof. Bozzelli's modeling study of benzene and toluene was incorporated in Prof. Krasnoperov's study on the oxidation of airborne organic compounds.
- Prof. Cheng's study of fuel effect on particulate matter formation in combustion models coincided with Profs. Hochgreb and Lafleur's analysis of fuel type effect on the particulate matter emissions from spark ignited engines, and integrated kinetics mechanisms developed by Profs. Green and Howard for PAH and soot formation in combustion.
- Prof. Green conducted Quantum RRK with modified Beta Collision and Master Equation analysis on reactions important in benzene oxidation for Prof. Bozzelli's study on high temperature chemistry of oxygenated hydrocarbons.
- Prof. Howard conducted experiments on the formation of acenaphthalene to validate Prof. Green's kinetic models for PAH formation.
- Prof. Molina's characterization of the kinetics of the oxidation intermediates using chemical ionization mass spectrometry is a method of detection that could be used to verify Prof. Krasnoperov's study on the kinetics and thermochemistry of primary steps in oxidation of airborne organic compounds.
- Profs. Seinfeld and Flagan's partitioning approach of secondary organic aerosol formation was incorporated in Prof. Cass's study of atmospheric organic and inorganic aerosols.
- Profs. Seinfeld and Flagan's focus on final photooxidation products and PM formation incorporated in Prof. Krasnoperov's study on the kinetics and thermochemistry of primary steps in oxidation of airborne organic compounds.

Between Institutions

- Prof. Green conducted group additivity calculations for thermodynamic properties and intramolecular rotor contributions to entropies for Prof. Bozzelli's study on high temperature chemistry of oxygenated hydrocarbons.
- Prof. Howard evaluated the software codes of Prof. Bozzelli on atmospheric photochemical oxidation of aromatics.
- Partnership with Moscow State University: Prof. Kebbekus of NJIT partnered with Prof. Zaitsev of Moscow State University on a Center project regarding SAMP sensors for monitoring organic gases.
- Partnership with University of California at Riverside: Prof. Prather of University of California at Riverside collaborated in the measurements of single particle size and chemical composition during field experiments with Prof. Cass of Caltech on his study regarding the evolution of size and composition distribution of atmospheric organic and inorganic aerosols.
- Profs. Seinfeld and Flagan developed and validated the accuracy of the density functional/Complete Basis Set Method for calculating transition state energies and geometry for Prof. Bozzelli's study on high temperature chemistry of oxygenated hydrocarbons.
- Profs. Seinfeld and Flagan's scanning mobility particle sizing of soot in flames were used in Prof. Howard's study on the origin and characteristics of fine soot particles in combustion.

Symposia

1994: Prioritizing Hazardous Air Pollutants: Establishing a Scientific Basis

- The symposium was co-sponsored by a number of institutions, including the EPA Atmospheric Research and Exposure Assessment Laboratory, National Institute for Environmental Health Sciences Superfund Basic Research Program, Caltech Center on Air Quality Analysis, MIT Center for Energy Policy Research, MIT Center for Environmental Health Sciences, MIT Energy Laboratory, MIT Program in Environmental Engineering Education and Research, and NJIT Emission Reduction Research Center.
- Prof. Cass gave a presentation on source contributions to toxic organics concentrations, and Peter Venturini (California Air Resources Board) gave a presentation on setting priorities for air toxics control in California. Their speeches coincided with Prof. Cass' Center experimental investigation of the evolution of the size and composition distribution of atmospheric organic aerosols in California.
- Debra Kaden (Health Effects Institute) gave a presentation on research priorities for mobile source air toxics. Her speech coincided with work at the Center being conducted by Profs. Bozzelli, Heywood, Hochgreb, Shaw, and Pfeffer.

1995: Effective Technologies for Reducing Vehicle Emissions

- The symposium was co-sponsored by a number of institutions, including Atlantic Richfield Company, Caltech Center for Air Quality Analysis, Ford Motor Company, General Motors Corporation, MIT Energy Laboratory, MIT Program in Environmental Engineering Education and Research, MIT Sloan Automotive Laboratory, Mobil Oil Company, Shell Oil Company, and the US Department of Transportation.
- The symposium was particularly relevant to the automotive emissions source work at the Center being conducted by Profs. Bozzelli, Heywood, Hochgreb, and Lafleur.
- Nick Gallopoulos (General Motors) and Tom Cackette (California Air Resources Board) gave presentations on reducing light-duty vehicle emissions through changes in fuels. His speech coincided with Prof. Bozzelli's Center work on the high temperature chemistry of alternative motor fuels and additives.

1996: Advanced Instrumentation for Air Quality Measurements

- Prof. McRae gave a presentation on uncertainty analysis methodologies in advanced instrumentation. His speech coincided with his own Center project on the direct treatment of uncertainties in mathematical models in airborne organics.
- Prof. Cass gave a presentation current methods being used to determine the nature of particulate matter and particulate matter processes in the atmosphere. His speech coincided with his Center experimental investigation of the evolution of the size and composition distribution of atmospheric organic aerosols.
- Prof. Prather (University of California at Riverside) gave a presentation on recent advances in the characterization of atmospherically relevant aerosols. Her discussion of single particle analysis coincided with her Center collaboration with Prof. Cass on the evolution of the size and composition distribution of atmospheric organic aerosols.
- Steven Cadle (General Motors) gave a presentation on remote sensing technology for mobile emissions measurements. His speech coincided with Prof. Carr's Center research on the development of a microengineered mass spectrometer for in-situ measurement of airborne contaminants.

1997: Fine Particles in the Atmosphere

- Profs. Hochgreb and Lafleur investigated the formation of particulate matter in spark-ignition engines. Their study to systematically identify the mechanisms of PM formation was very much in line with the conclusions of the symposium.
- Prof. Cass conducted an experimental study relating the emissions of gases and primary particles to atmospheric PM concentrations. This research provided a verification data set for PM models.

1998: Cost and Benefits Estimation in Air Quality Regulations

- Prof. McRae demonstrated that improved estimations of emissions are necessary for an accurate cost-benefit analysis. This was part of the background of his Center research.

1999: EPA's Urban Air Toxics Strategy

- Prof. Cass's research has shown that toxic air contaminants can be characterized by different sources. In the symposium, he provided examples of compounds that deserve attention.
- Profs. Mitra and Kebbekus developed a methodology for sampling and analysis of polar organics. Their work provided a mechanism for obtaining some of the critical data in the EPA Urban Air Toxics Strategy.
- Prof. McRae's research showed that a quantitative approach to uncertainty and variability is needed when conducting risk assessment.
- The symposium was very much in line with the previous year's symposium on cost-benefit instruments. One of the key points in EPA's Urban Air Toxics Strategy is the risk management of air toxics.
- The symposium was co-sponsored by a number of organizations, including: MIT Energy Lab, MIT Center for Environmental Initiatives, Center, EPA, NESCAUM, California Air Resources Board, Health Effects Institute, Mickey Leland National Urban Air Toxics Research Center, DOT-Volpe Center, American Petroleum Institute, Chevron, British Petroleum, Amoco, Sun Oil, Engine Manufacturers Association, Chemical Manufacturers Association, Electric Power Research Institute, Pennsylvania Power and Light Company.

2000: The Future of Diesel: Scientific Issues

- Alison Pollack (ENVIRON International Corp.) and Robert Sawyer (University of California, Berkeley) gave presentations on NO_x issues in diesel engines. Their speeches coincided with Profs. Shaw and Pfeffer's Center project on NO_x removal from the exhaust of diesel powered vehicles.
- The symposium was co-sponsored by a number of organizations, including: American Petroleum Institute, California Air Resources Board, Chevron Products, Cummins Engine, Engine Manufacturers Association, ExxonMobil, General Motors, Health Effects Institute, MIT Center for Environmental Initiatives, MIT Energy Laboratory, NESCAUM, Pennsylvania Power and Light Company, Sun Oil Company, Volkswagen America, DOT-Volpe Center, and EPA Office of Research and Development.

Future Research in Airborne Organics

While the Center on Airborne Organics has completed its mission, there is still a great deal of work to be done in the field of airborne organics, including:

- Identification and characterization of non-combustion sources of airborne organics, particularly in the context of source attribution which should take into account all sources.

- Development of methods for manipulating the chemistry of airborne organics to minimize production as well as provide a better assessment of chemical signature for use in source apportionment.

- Identification and characterization of atmospheric transformation of primary organic emissions that can result in the production or destruction of airborne compounds of concern for atmospheric health.

- Development of markers to delineate compounds of concern from the numerous compounds existing in the atmosphere.

- Development and application of new measurement methods that can extend existing techniques to new classes of organic compounds that impact human health.

- Identification and measurement of the classes of compounds that can serve as tracers for specific source types.

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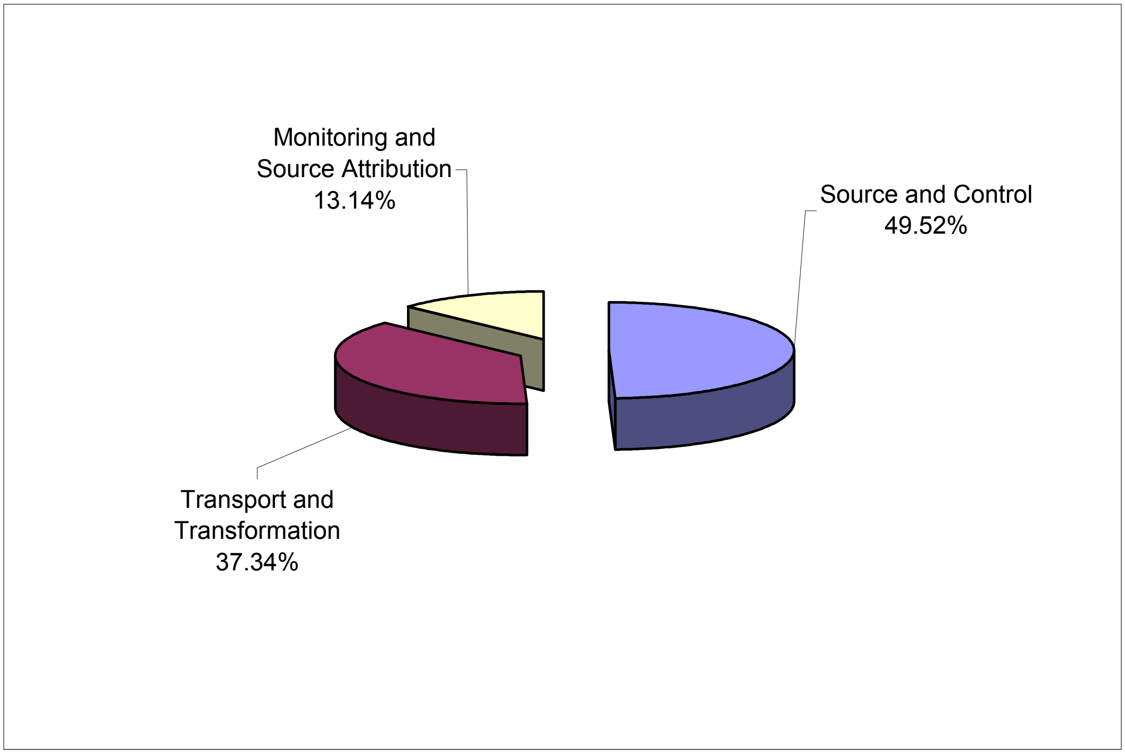
Appendix

Research Funding Allocation

Chart 1: Funding Allocation by Project Focus Area (in $millions)



EPA CENTER KEY STAFF AND PERSONNEL LISTING 1993-2002

Center Administration

Adel Sarofim
Director (1992-1997)

Jack Howard
Director (1998-2002)

John Seinfeld
Associate Director

Richard Magee
Associate Director (1992-1997)

Robert Pfeffer
Associate Director (1998-2002)

Key Personnel

Professor Paul Barton
Massachusetts Institute of Technology
Binita Bhattacharjee, Graduate Student
John Tolsma, Postdoctoral Student

Professors Paul Barton and Jack Howard
Massachusetts Institute of Technology
M. Bahy Noureldin, Postdoctoral Student

Professor János Beér
Massachusetts Institute of Technology
Arne Hoffman, Visiting Engineer
Scott Macadam, Graduate Student
Cord Manegold, Visiting Scholar

Professor Joseph Bozzelli
New Jersey Institute of Technology
Ashish Agrawal, Research ASsistant
Chiung-Ju Chen, Graduate Student
Dawoon Jung, Graduate Student
Tsan Lay, Graduate Student
Gem Patel, Undergraduate Student
Allen Petrin, Undergraduate Student
Chad Sheng, Graduate Student
Hongyan Sun, Graduate Student
Ruth Wei, Graduate Student
Takahiro Yamada, Graduate Student

Professors Joseph W. Bozzelli and Lev N. Krasnoperov
New Jersey Institute of Technology
Chiung-Ju Chen, Graduate Student
Wen-Chiun Ing, Graduate Student

Professors Joseph Bozzelli and Tsan Lay
New Jersey Institute of Technology
Satyen Amin, Undergraduate Student
Rajiv Berry, Research Staff
Chiung-Ju Chen, Graduate Student
Gem Patel, Undergraduate Student
Allan Petrin, Undergraduate Student
Ruth Wei, Graduate Student
Takahiro Yamada, Graduate Student

Professors William Carr and Kenneth Farmer
New Jersey Institute of Technology
Chao Sun, Graduate Student
Qi Xing Sun, Postdoctoral Student

Professor Glen Cass
California Institute of Technology
Jonathan Allen, Postdoctoral Student
Shohreh Ghari, Laboratory Research Engineer
Michael Hannigan, Graduate Student
Lara Hughes, Graduate Student
Robert Johnson, Undergraduate Student
Michael Kleeman, Graduate Student

Professor Wai Cheng
Massachusetts Institute of Technology
Thane Dewitte, Technical Support
Ioannis Kitsopanidis, Graduate Student
Susan Lutin, Administrative Support

Professor William Green
Massachusetts Institute of Technology
Preeti Aghalayam, Postdoctoral Student
Charles Boatin, Undergraduate Student
Hans-Heinrich Carstensen, Postdoctoral Student
Oleg Mazyar, Postdoctoral Student
Sumathi Raman, Postdoctoral Student

Professors John Heywood and Simone Hochgreb
Massachusetts Institute of Technology
Haissam Haidar, Graduate Student

Professor Simone Hochgreb
Massachusetts Institute of Technology
Kuochun Wu, Graduate Student
Ivan Oliveira, Graduate Student

Professors Simone Hochgreb and Arthur Lafleur
Massachusetts Institute of Technology
David Kayes, Graduate Student
Derek Kim, Graduate Student

Professor Jack Howard
Massachusetts Institute of Technology
Murray Height, Graduate Student
David Kronholm, Graduate Student
Stephen Lasher, Graduate Student
C. Pope, Research Associate
Henning Richter, Postdoctoral Student

Professors Barbara Kebbekus and Vladimir Zaitsev
New Jersey Institute of Technology and Moscow State University
Ashish Agrawal, Graduate Student

Professor Lev Kransoperov
New Jersey Institute of Technology

Sergey Grebenkin, Postdoctoral Student
Evgeni N. Chesnokov, Visiting Scientist

Professor Gregory McRae
Massachusetts Institute of Technology
Menner Tatung, Graduate Student
Betty Pun, Graduate Student

Professors Somenath Mitra and Barbara Kebbekus
New Jersey Institute of Technology
Yong Xu, Graduate Student

Somenath Mitra and Durgamadhab Misra
New Jersey Institute of Technology
Minhee Kim, Graduate Student

Professor Mario Molina
Massachusetts Institute of Technology
Keith Broekhuizen, Graduate Student
Christophe Guimbaud, Research Staff
Luisa Molina, Research Staff
Rafael Navarro-Gonzales, Research Staff

Professors Robert Pfeffer and Henry Shaw
New Jersey Institute of Technology
Istvan Bagyi, Postdoctoral Student
Ian Buedick, Graduate Student
Maria Rosa Diakno, Graduate Student
Kaiwan Ma, Graduate Student
Gui-Han Qian, Graduate Student
William Roy, Graduate Student
Wei Song, Graduate Student
John Stevens, Co-Principal Investigator
Shu Sun, Graduate Student
Shan Xiao, Graduate Student
Xiapong-Yong Tang, Graduate Student
Z. Zhao, Postdoctoral Student

Professors Adel Sarofim and Dr. William Peters
Massachusetts Institute of Technology
Jonathan Allen, Graduate Student
C. Feldermann, Postdoctoral Student
Angelo Kandas, Graduate Student

Arpád Palotás, Graduate Student
Lenore Rainey, Research Staff

Professors John Seinfeld and Richard Flagan
California Institute of Technology
Jean Andino, Graduate Student
Frank Bowman, Graduate Student
David Cocker, Graduate Student
Hali Forstner, Graduate Student
Robert Griffin, Graduate Student
Thorsten Hoffman, Postdoctoral Student
Tim Jungkamp, Postdoctoral Student
Markus Kalberer, Postdoctoral Student
Brian Mader, Postdoctoral Student
Jay Odum, Graduate Student
Manabu Shimada, Postdoctoral Student
Cecilia Tse, Graduate Student
Jian Yu, Postdoctoral Student
Hong Zhuang, Graduate Student

Professor John Vander Sande
Massachusetts Institute of Technology
David Bell, Postdoctoral Student
Arpád Pálotás, Postdoctoral Student
Lenore Rainey, Research Staff

Professor Paul Wennberg
California Institute of Technology
Coleen Roehl, Staff Scientist

Scientific Advisory Committee

Dr. Praveen Amar
NESCAUM
Expertise: Atmospheric chemical and physical processes modeling, air pollution policy, comustion sources control technology

Dr. Nancy Brown
Lawrence Berkeley Laboratory
Expertise: Combustion, chemical kinetics, modeling

Dr. Larry Cupitt
US Environmental Protection Agency
Expertise: Atmospheric chemistry, air pollution monitoring and methods

Dr. Cliff Davidson
Carnegie Mellon University
Expertise: Atmospheric transport, deposition processes, aerosol behavior

Dr. Anthony Dean
Exxon
Expertise: Free radical kinetic, detailed kinetic modeling

Dr. John Holmes
California Air Resources Board
Expertise: Air pollution research on atmospheric chemical processes

Dr. Steven Japar
Ford Motor Company
Expertise: Atmospheric chemistry, aerosol optics, vehicle emissions

Mr. G. Blair Martin
US Environmental Protection Agency
Expertise: Combustion processes, acid gas control

Dr. Thomas Peterson
University of Arizona
Expertise: Chemical and environmental engineering, combustion-generated aerosols

Dr. Robert Sawyer
University of California at Berkeley
Expertise: Combustion-generated pollutants, regulatory policy, automotive emissions and control

Dr. Robert Slott
Shell Oil Company
Expertise: Vehicle emissions, control strategies for emission reduction, effects for gasoline composition on vehicle emissions

Total PIs: 24
Total Co-Is (from other institutions): 2
Total Postdoctoral students: 18
Total Graduate students: 42
Total Undergraduate students: 4
Total Research staff: 11

Table 1: Total Funding for Student as of 9/29/00 (Does not include supplemental funding awarded to chosen Center PIs for research completion during Center no-cost extension (2001-2002)

	Undergraduate	Graduate	Postdoctoral	Annual Total
1993-1994	$ 11,836.00	$ 192,181.00	$ 27,250.00	**$ 231,267.00**
1995	$ 5,906.00	$ 164,400.00	$ 28,743.00	**$ 199,049.00**
1996	$ 2,509.00	$ 217,456.33	$ 238,682.00	**$ 458,647.33**
1997	$ -	$ 237,536.00	$ 262,536.00	**$ 500,072.00**
1998	$ 4,000.00	$ 160,900.00	$ 28,300.00	**$ 193,200.00**
1999	$ 4,000.00	$ 87,100.00	$ 145,395.00	**$ 236,495.00**
2000	$ -	$ 60,400.00	$ 89,972.00	**$ 150,372.00**
Grand Total	**$ 28,251.00**	**$ 1,119,973.33**	**$ 820,878.00**	**$ 1,969,102.33**

Quality Assurance and Quality Control at the Center

The purpose of the quality assurance/quality control program or plan was to monitor the accuracy or precision, completeness, and comparability of the information produced within each project, thereby guaranteeing that the information was of sufficient quality to substantiate the conclusions of each research project and to provide the basis for further research. This plan was for all projects in the Center, including experiments and modeling, which may have produced experimental data or model predictions from which conclusions were or may have been drawn. The accuracy and precision of experimental data was determined by statistical means, i.e. multiple analyses of each sample were performed if sample quantity was sufficient. From the results of this data, a range of values would have been evident, and a statistical mean and standard deviation could be calculated. The accuracy of model predictions were to be computed based on uncertainties of input variables. If the uncertainties of inputs were unknown, then the accuracy of the predictions was unknown and so indicated.

The results of any project in the Center may eventually be used as a basis for further research or for policy decisions. Therefore, it was essential that the accuracy and precision of the results be included in the reports and publications of the work. It was also essential that notebooks and other records of the research be maintained so as to permit independent assessment and/or reproduction of the results.

Supplemental Keywords & Common Abbreviation

Caltech	California Institute of Technology
CAAA	Clean Air Act Amendments
CAO	Center on Airborne Organics
Center	Center on Airborne Organics
C_2H_2	Acetylene
CIMS	Chemical ionization mass spectrometer
CO	Carbon monoxide
CO_2	Carbon dioxide
DEMM	Deterministically Equivalent Modeling Method
DIT	Data incorporation technique
DOE	United States Department of Energy
EPA	United States Environmental Protection Agency
FID	Flame ionization detection
GDP	Gross domestic product
HAP	Hazardous air pollutant
HC	Hydrocarbons
HO_2	Hydroperoxy radical
LIF	Laser induced fluorescence
LII	Laser induced incandescence
MIT	Massachusetts Institute of Technology
MTBE	Methyl tert-butyl ether
N_2	Nitrogen
NAAQS	National Ambient Air Quality Standards
NJIT	New Jersey Institute of Technology
NO_x	Nitrogen oxides
NO	Nitric oxide
NO_2	Nitrogen dioxide
O_2	Oxygen
O_3	Ozone
OH	Hydroxyl radical

PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenols
PM	Particulate matter
$PM_{2.5}$	Particulate matter smaller than 2.5 microns
ppm	Parts per million
Pt	Platinum
RCM	Rapid compression machine
SAC	Scientific Advisory Committee of the Center on Airborne Organics
SAMP	Semiconductor-based adsorption-modified photosensitization
SI	Spark ignition
SO_2	Sulfur dioxide
TCD	Thermal conductivity detection
TID	Thermoionic ionization detector
UV	Ultra-violet
VOCs	Volatile organic compounds