California Institute
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Center for
Air Quality Analysis

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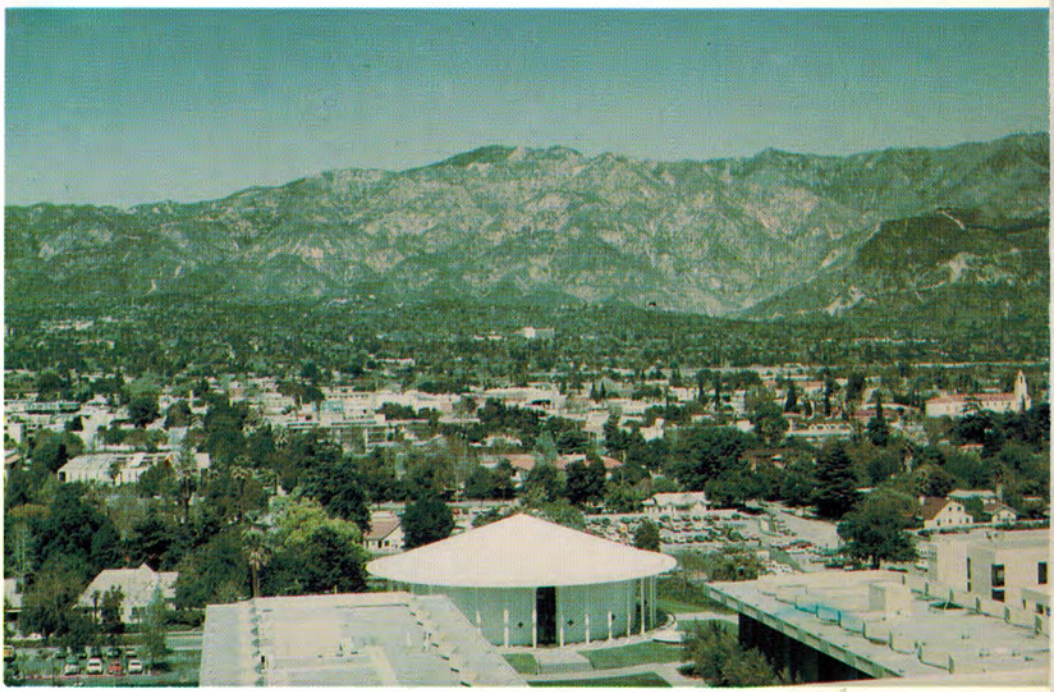

Tracking Down the Source of Contemporary Carbon Particles in the Atmosphere of Cities

The Center For Air Quality Analysis

The Caltech Center for Air Quality Analysis was initiated in 1990. Headed by Professors Glen R. Cass and John H. Seinfeld, and housed in Caltech's Environmental Quality Laboratory, the Center focuses on the development and use of air pollution models, which are critical to air quality analysis and control.

The Center aims to develop scientifically reliable environmental models, to conduct field experiments that test the accuracy of those models in order to better predict the air quality resulting from various emission control strategies, and to present analyses of the results to regulatory agencies governing environmental policy and to industry, in order to assist both sectors in devising and implementing controls for improving air quality.

The Center for Air Quality Analysis is housed in Lura House on the Caltech campus, which contains about 2000 square feet of space for offices, project rooms and computer facilities. Experiments are conducted in approximately 4000 square feet of fully equipped lab space in the W.M. Keck Engineering Laboratories. Experimental facilities include a 60 m^3 outdoor smog chamber; an artificially illuminated indoor smog chamber, and GC/MS facilities. Full capability exists for inorganic pollutant analyses by ion chromatography, atomic absorption spectrophotometry, and inductively coupled plasma mass spectrometry. A wide range of instruments for measurement of airborne and deposited particle size distributions are both in use and under development. Field experimental equipment includes a complete 10 station air monitoring network capability for particulate and some gaseous pollutants, along with dilution source testing systems.

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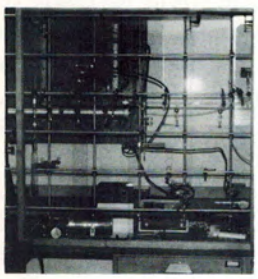

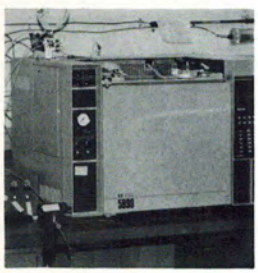

On the Cover:
On a clear day the San Gabriel Mountains are visible in this view from Caltech's Millikan Library, but on a smoggy summer day they disappear entirely.

Lura House*, at right, houses the Center for Air Quality Analysis.*

Inverse Air Pollution Modeling: A New Approach to Constructing Emissions Inventories

At present, air pollution emissions inventories are generally constructed from the "ground up" by assembling individual source information. Evaluating the accuracy of an emissions inventory is a particularly difficult task. One approach is to use the inventory as input to an air quality model and assess the degree of agreement between ambient concentrations predicted by the model and those measured. So-called *inverse air pollution modeling* asks the question – What is the source emissions distribution that produces the closest possible fit of observed and predicted concentrations?

Inverse Air Pollution Modeling attempts to use observations of airborne concentrations to deduce the location and strengths of sources. The improved source inventory that results from such a procedure then permits better estimates of the overall atmospheric concentration distribution.

One of the most pressing current problems in urban air quality modeling concerns the likely underestimation of CO and VOC emissions from motor vehicles in existing mobile source emissions inventories. Inverse air pollution modeling provides one approach to evaluating the question of how an existing inventory would need to be modified so that observed and predicted concentrations are in agreement.

The spatial and temporal variations of CO emissions in major urban areas are provided by appropriate air pollution control agencies in the format of a mobile source inventory. When performing inverse modeling, this CO emissions inventory can be considered as the starting point from which to determine how the CO source distribution needs to be altered so that observed and predicted CO concentrations at the monitoring sites are matched as closely as possible. Indeed, there is evidence that CO emissions from motor vehicles, particularly in the South Coast Air Basin, have been historically underestimated (Ingalls *et al.*, 1989; Pierson *et al.*, 1990; Fujita *et al.*, 1992). The inverse modeling approach provides a way to address the question – How should the CO emission inventory be adjusted to provide the best match of observed and predicted CO concentrations? The required adjustment then is indicative of the degree of under- (or over-) estimation inherent in the inventory.

In recent work, carried out by **Dr. Michael Mulholland** and **John H. Seinfeld** at the **Center for Air Quality Analysis**, inverse modeling has been applied to the August 27-29, 1987 episode of the Southern California Air Quality Study (SCAQS) to determine the spatial and temporal adjustments to the CO emissions inventory provided by the California Air Resources Board required to bring observed and predicted CO concentrations in as close agreement as possible.

A new recursive least squares technique has been developed to give spatial and temporal definition to the adjustments necessary in an emission inventory, to fit ambient concentration observations optimally. The CIT Photochemical Airshed Model is used to compute CO concentration distributions arising from 29 separate source domains in the South Coast Air Basin of California. A Kalman filter integrated within the model matches predictions with CO observations at 27 locations by superposing the computed distributions with optimal weighting factors. The filter structure allows control of the extent to which adjusted emission inventories are allowed to deviate from a base-case, which already has high spatial and temporal definition. Applied to the Southern California Air Quality Study, August 27-29, 1987, strong temporal dependence was noted in the necessary adjustment to the available CO emission inventory, with a peak underestimation factor of 3.0 at midday on weekdays.

The division of the CO emission region into domains provided a degree of spatial resolution in the identification. In particular, for weekdays, a high-emission axis was found to extend from Pasadena through Pomona to San Bernardino, as well as an arc South of San Bernardino, extending from Riverside to Corona. On Saturday, a distinct high-emission pattern emerges along the coastline, probably due to recreational traffic. The necessary adjustment to the original emission inventory of Wagner and Allen (1990) also proved strongly time-dependent. The average factor by which the base inventory must be multiplied was found to peak at 3.0 at midday on the weekdays. This agrees with a general adjustment on mobile source emissions used by Harley *et al.* (1993) that was based on the results of motor vehicle emissions measurements made in a highway tunnel that also leads to agreement between O_3 predictions and observations. On the weekdays, the average factor then fell below unity from 9 PM to midnight, indicating that the current inventory may actually overestimate CO emissions at night. The factor climbed steadily through Saturday to reach a value of 10 at 9 PM. Even with this adjustment, however, Saturday's emissions of CO in the South Coast Air Basin are substantially lower than on weekdays.

Tracking Down the Source of Contemporary Carbon Particles in the Atmosphere of Cities

Airborne carbon particles typically account for 30% to 40% of the fine particulate matter in the atmosphere of cities. This is not surprising given the large amount of soot emitted from fossil fuel combustion, both from motor vehicle engines and from industrial processes and home heating.

However, for more than a decade, measurements of the carbon isotopes present in airborne particulate matter in Los Angeles and elsewhere have suggested that 23% to 52% of the fine particles in the urban atmosphere come from sources of modern carbon rather than from combustion of fossil fuel. These conclusions were reached by applying radiocarbon dating techniques to the atmospheric particulate matter samples. Interpretation of these results has been difficult. The first temptation might be to postulate a previously unknown biogenic source of carbonaceous particulate matter.

Over the past seven years, we have conducted a series of source tests designed to measure the mass emission rates and chemical composition of the organic compounds emitted from the major sources of carbon particle release to the Southern California atmosphere. Sources tested include motor vehicle exhaust, fuel oil combustion, natural gas combustion, fireplace combustion of wood, food cooking operations, roofing tar pots, paved road dust and many other sources. Atmospheric models also have been constructed that compute the incremental contribution of each of the major primary carbon particle emission sources to ambient air quality. Air quality modeling calculations have been verified by comparison to atmospheric samples taken during a year-long experiment.

The existence of these source samples, atmospheric samples and atmospheric models provides a unique opportunity to seek the explanation for the high contemporary (i.e. non-fossil) carbon loading in the atmospheric particles in Los Angeles. With support from the Center for Air Quality Analysis, a collaboration was developed between Professor Lynn Hildemann of Stanford University (formerly a graduate student at Caltech), Glen Cass at Caltech, and with Donna Klinedinst, Dr. George Klouda and Dr. Lloyd Currie at the National Institute of Standards and Technology (NIST). The NIST investigators are expert in accelerator mass spectrometry, a method for applying carbon dating techniques to extremely small samples. The NIST team measured the radiocarbon content of the source samples taken by Caltech investigators from the 15 most important sources of carbon particle emission to the Los Angeles area atmosphere, and also measured the radiocarbon content of quarter-year composites of airborne particulate matter collected by Caltech investigators at Long Beach and at Azusa, CA. These data were entered into existing Caltech atmospheric transport models and then used to predict the radiocarbon content expected at the community monitoring sites given the source composition, the location of the emission sources and the atmospheric transport patterns.

Examination of the isotopic composition of the emissions sources shows, not surprisingly, that purely fossil fuel combustion sources such as motor vehicle exhaust, and oil-fired boiler exhaust emit at most a few percent contemporary carbon. Asphalt roofing tarpot emissions are likewise purely fossil in nature. Conversely, food cooking operations, cigarette smoke, and fireplace combustion of natural wood contribute almost entirely contemporary carbon to the atmosphere. But there are other sources of mixed composition. One of the largest sources of urban particulate matter is paved road dust kicked-up by passing vehicle traffic. Paved road dust was found to consist of 49% contemporary carbon and 51% fossil carbon. Tire wear debris, vehicle brake lining dust, and combustion of synthetic logs likewise were found to emit a combination of fossil and contemporary carbon.

The source test data were used to construct emission inventories for fossil and contemporary carbon particle emissions in the Los Angeles area. These inventories indicate that wood smoke, meat cooking, paved road dust, cigarette smoke and brake lining wear particles are the most significant contributors to the contemporary carbon emissions in that locale. Analysis of the atmospheric particulate matter samples showed that the Long Beach aerosol contained 33-43% contemporary carbon, while the Azusa atmosphere contained 20-35% contemporary carbon. The emissions data were matched to an atmospheric transport model along with estimates of the contemporary carbon content of the background air upwind of the city. Model predictions were in reasonable agreement with the measured radiocarbon content of the atmospheric particulate matter samples. It is concluded that the high fraction of contemporary carbon in the Los Angeles atmosphere is not due to an undiscovered biogenic source; rather it is due to local man-caused sources of contemporary carbon emissions plus the contemporary carbon content of the marine background particulate matter advected into the city.

Faculty

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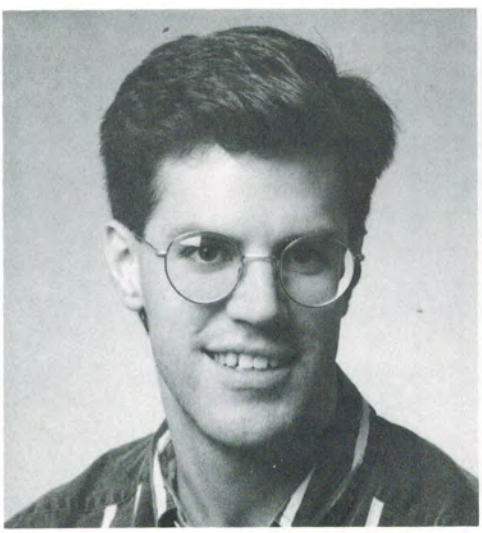
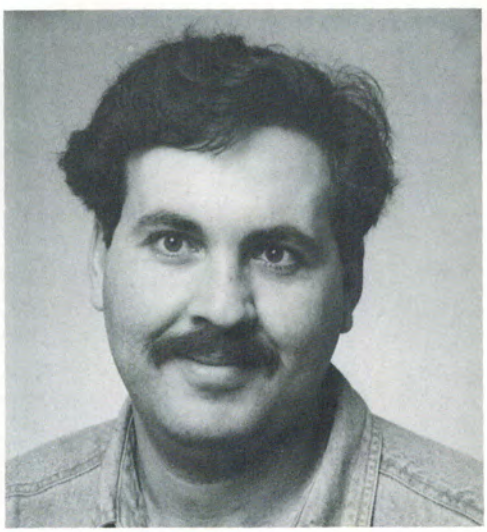
Investigators

DR. YOSHIAKI AKUTSU received a Ph.D. at the University of Tokyo, Japan in 1985. He worked for Seikei University as a research associate from 1985 to 1988, and currently is a research associate of the University of Tokyo. He is currently a Visiting Associate at Caltech. His major research interests are atmospheric chemistry and safety of reactive chemicals.

JEAN ANDINO was born and raised in the Bronx, New York. After receiving her B.S. degree in Engineering Sciences from Harvard-Radcliffe in 1988, she worked as a Research Scientist in the Atmospheric Chemistry group at Ford Motor Company. She received a M.S. in Chemical Engineering from Caltech in 1993. Jean is investigating the gas-phase mechanisms of anthropogenic hydrocarbons through both predictive modeling and controlled experiments.

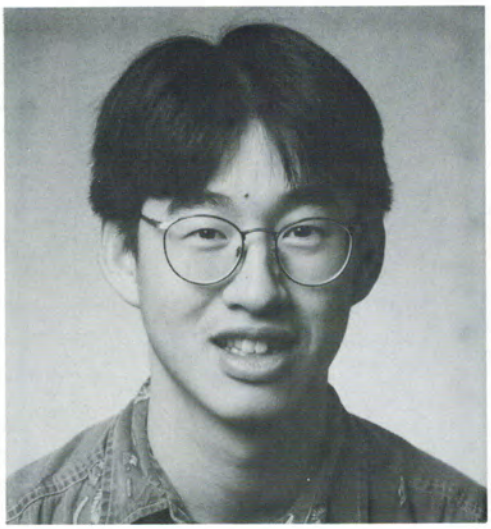


FRANK BOWMAN is a graduate student at Caltech from Midland, Michigan. He received his B.S. in Chemical Engineering in 1991 from Brigham Young University. His Ph.D. research is focused on understanding the atmospheric reaction mechanisms of organic compounds.

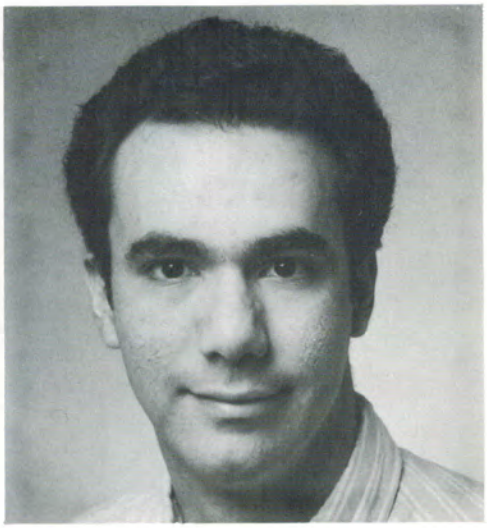


CHRISTOS CHRISTOFOROU, a citizen of Cyprus, is a Ph.D. student in Mechanical Engineering at Caltech. He holds a B.S. degree from Rice University (1988) and a M.S. degree from Caltech (1989), both in Mechanical Engineering. His research interests include methods for measurement of airborne and deposited particle size distributions, modeling of air flows and particle mechanics inside buildings, and control of indoor air quality.

Investigators



PATRICK CHUANG graduated from the University of Alberta with an undergraduate degree in Chemical Engineering. He is currently a Ph.D. student in Environmental Engineering Science. For his thesis, he is planning to build an instrument to classify aerosols by size for particles roughly 1 μm in diameter. The main application for this instrument is studying the role of aerosols in air pollution.



DONALD DABDUB was born in Masaya, Nicaragua. He received a B.S. degree at Lehigh University (1990) and a M.S. degree from Caltech (1992), both in Chemical Engineering. Currently he is enrolled in the doctoral program at Caltech. His academic interests focus on mathematical modeling of photochemical air pollutant formation on massively parallel computers.

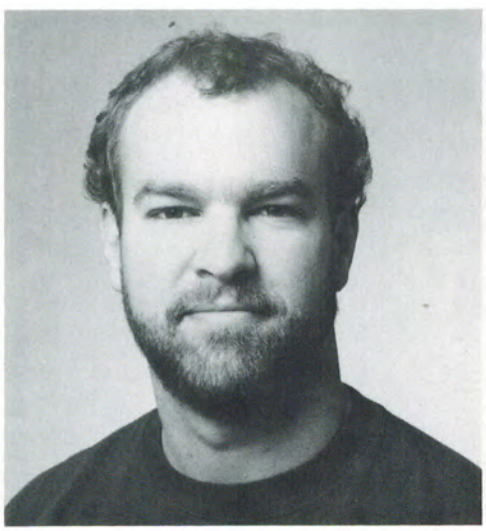
ANNMARIE ELDERING is a Ph.D. student in Environmental Engineering Science at Caltech. She holds a B.E. in Chemical Engineering from the Cooper Union (1988). Her work has focused on visibility models, including models that create simulated photographs showing the effects of air pollution on visibility and models that track the emissions, formation, and transport of particulate air pollutants and their resulting effects on visibility.

HALI FORSTNER was born and raised in Calgary, Alberta. She received her B.S. with Honors in Chemical Engineering (1991) from the University of Calgary, and her M.S. from Caltech (1993). Her Ph.D. research at Caltech involves determining the molecular composition of secondary organic aerosol resulting from the atmospheric reaction of various hydrocarbons in a smog chamber and elucidating the chemical mechanisms by which the aerosol forms.

Investigators

MATT FRASER entered the Environmental Engineering Science Ph.D. program at Caltech after receiving his B.S. degree in Chemical Engineering from Carnegie Mellon University in 1991. He was awarded his M.S. degree in 1993, and his Ph.D. research interests include measurement and modeling of the atmospheric concentrations of organic air pollutants.

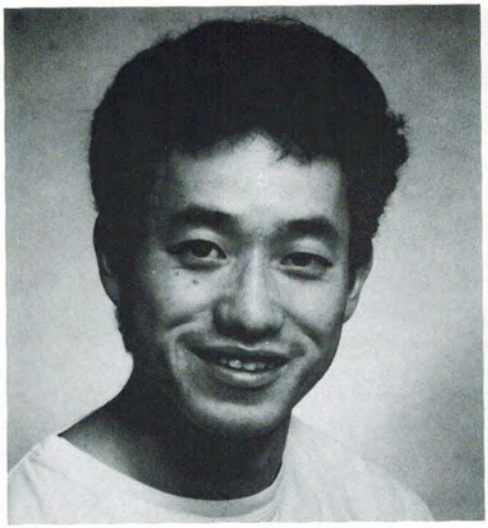
SHOHREH GHARIB is a Research Engineer at the Environmental Quality Laboratory. She received a B.S. degree from Tehran University in Iran (1975) and an M.S. degree from Syracuse University (1978), both in Chemical Engineering. She has worked at EQL (1978-1984) , at UCSD as a lecturer/research staff, and at the San Diego APCD as an engineer (1984-1992). At Caltech she is working on atmospheric monitoring experiments.



MIKE HANNIGAN is a graudate student in Environmental Engineering Science at Caltech. He holds a B.S. in Civil Engineering from Southern Methodist University and a M.S. in Environmental Engineering Science from Caltech. His Ph.D. thesis research focuses on the chemical character of airborne particles and their effects in producing mutations in biological systems.

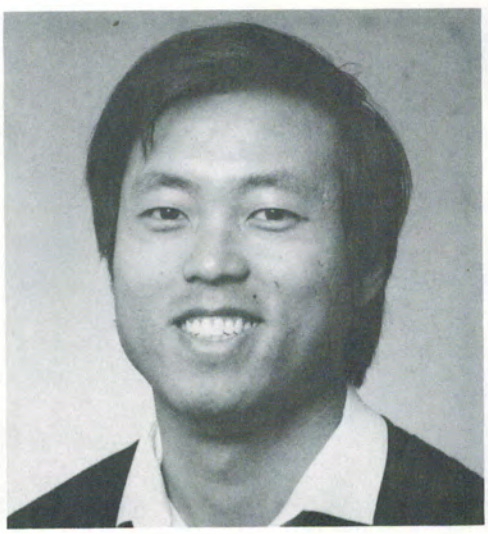
DR. ALEX KUKLIN was born in 1960 in Kiev, Ukraine. He received a B.S. in Computer Science in 1981 and a M.S. in Mechanical Engineering in 1983 from the Kiev Polytechnic Institute. In 1989 he obtained a Ph.D. from the Academy of Sciences Gas Institute, Kiev. Alex joined the Center for Air Quality Analysis in January 1993 as a Research Fellow in Environmental Engineering Science.

Investigators

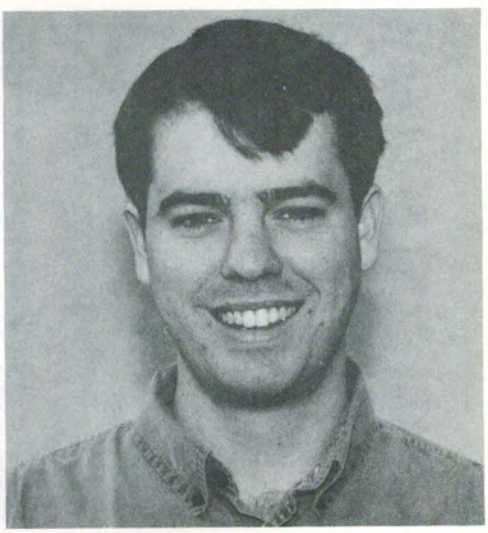


ISAMU KUSAKA is a graduate student in Chemical Engineering at Caltech. His research interest is in nucleation theory. He received a B.S. degree (1988) and M.S. degree (1990) in Precision Mechanics from the University of Tokushima in Japan.

DR. KENNETH MCCUE is a Research Scientist at the Environmental Quality Laboratory at Caltech. He received a Ph.D. from Caltech in Social Sciences and a M.S. in Mathematical Statistics from the University of Kansas. His research interests include spatial modeling of ambient chemical species and statistical analysis in the context of photochemical air pollution formation.



ZHAOYUE MENG is from Beijing, China. He obtained his B.S. in 1986 from the Department of Geophysics of Beijing University in China, and his M.S. in 1991 from the Department of Atmospheric Sciences at UCLA. He is now a Ph.D. candidate in the Department of Environmental Engineering Science, working on aerosol modeling and thermodynamics.



CHRIS NOLTE received a B.S. degree in Physics from Stanford University in 1991, and is now a Ph.D. student in Environmental Engineering Science at Caltech. He is interested in determining and quantifying the various natural and anthropogenic sources of atmospheric organic acids.

Investigators

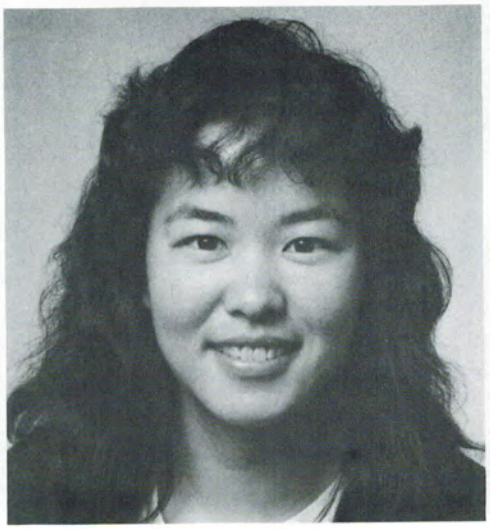
Born in Greece in 1961, DR. CHRIS PILINIS received his Diploma in Chemical Engineering in 1983 from the National Technical University of Athens. He received both his M.S. and Ph.D. degrees at Caltech from the Department of Environmental Engineering Science, the latter degree in 1988. After periods at AeroVironment and ENSR, Chris returned to Caltech in 1993 as a Senior Scientist in the Center for Air Quality Analysis.

LYNN RUSSELL came to Caltech to study the atmospheric chemistry and physics of the marine boundary layer in Chemical Engineering. She completed her A.B. in International Relations and her B.S. in Chemical Engineering at Stanford University(1991) and-received a M.S. in Chemical Engineering at Caltech(1993). Her research focus is reconciling mathematical models of tropospheric aerosol evolution over the ocean with observations.

LYNN SALMON received a S.B. degree in Materials Science from MIT and a M.S. degree in Engineering from UCLA. Since 1986 she has been a Research Engineer at Caltech, where she specializes in the study of effects of atmospheric pollution on works of art. Her research projects have included fading of artists' colorants and numerous studies of airborne pollutants in national parks, museums, and archaeological sites around the world.

JAMIE SCHAUER holds a B.S. degree in Chemical and Petroleum Refining Engineering from the Colorado School of Mines and a M.S. degree in Environmental Engineering from UC Berkeley. Jamie has eight years of industrial experience in the petroleum refining industry and is currently a Ph.D. student in Environmental Engineering Science at Caltech.

Investigators



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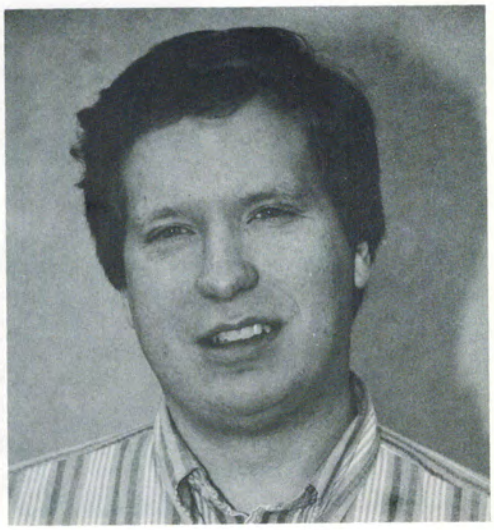


DARRELL WINNER is a Ph.D. student in the Environmental Engineering Science program at Caltech. He holds a B.S. degree in Chemical Engineering from Carnegie Mellon University (1989) and a M.S. degree in Environmental Engineering Science from Caltech (1990). His research interests include the modeling of photochemical air pollutants, evaluation of control strategies for pollutant abatement, and meteorology.

MASARU YARIME is studying Chemical Engineering as a graduate student at Caltech. He graduated from the University of Tokyo with a B.S. degree in Chemical Engineering in 1993.

DR. SHOUHUA ZHANG, Senior Scientist, was born in Shanghai (China) in 1942. He received a B.S. from East China Institute of Chemical Technology (ECICT) in 1964 and a Ph.D. from ECICT in 1984. Both degrees are in Chemical Engineering. Dr. Zhang is a principal scientist in our research on aerosol dynamics and instrumentation.

Aerosol Dynamics

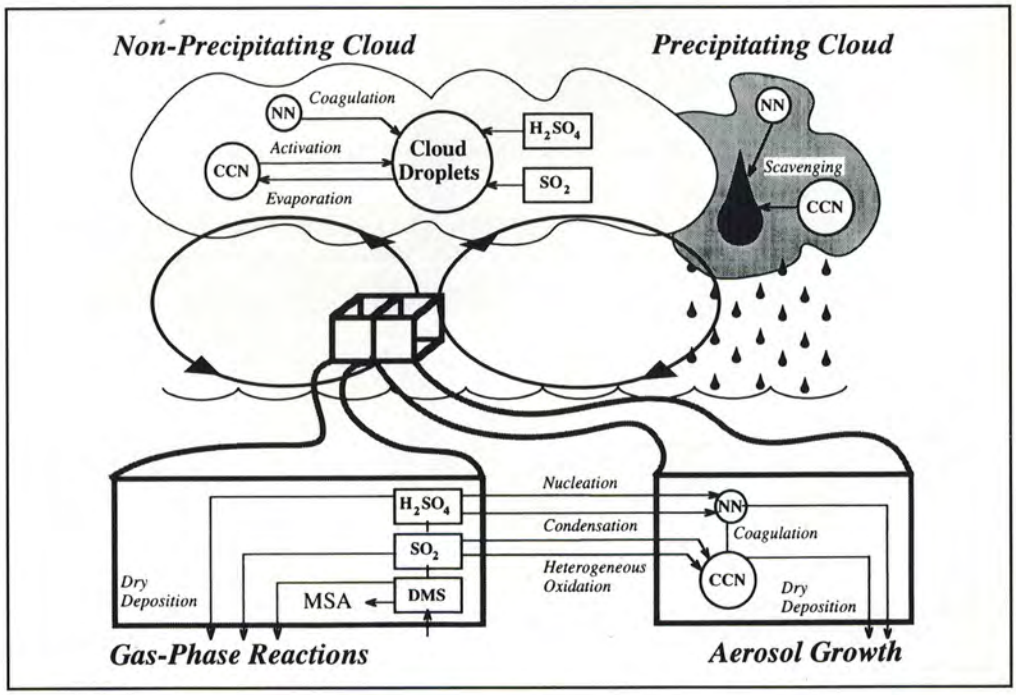
Aerosol Dynamics in the Marine Atmosphere

Stratus clouds in the marine boundary layer play an important role in the earth's climate system since they govern the albedo over large areas of the oceans. In fact, some investigators have estimated that if the amount of ocean covered by clouds is increased by just 4%, the consequent cooling effect could offset the amount of warming that would result from a doubling of atmospheric CO_2. The microphysical processes controlling marine stratus clouds depend in part on the size-dependent physical chemistry of marine aerosols. One of our goals in this research is to collect data illustrating the key processes in the remote marine boundary layer. To this end, we are developing instrument capabilities to probe the fast dynamics and low concentrations of remote aerosols.

A critical role for dimethyl sulfide (DMS) emitted from metabolic processes of phytoplankton has been suggested in determining the radiation balance through the atmosphere by regulating aerosol growth and cloud formation. In the atmosphere, oxidation of DMS can serve as a source of non-sea salt sulfate which contributes to the marine aerosol by the processes of nucleation and condensation. One eventual goal of our research is to incorporate these processes into a mathematical model of marine aerosols capable of predicting both the size distribution and chemical composition and including state-of-the-art treatments of homogeneous nucleation, condensation and evaporation, and liquid phase thermodynamics and chemistry.

Investigators:
Lynn Russell
Spyros Pandis
Richard C. Flagan
John H. Seinfeld

Support:
Office of Naval Research
National Science Foundation



The dynamics of dimethyl sulfide (DMS) and aerosols in the marine boundary layer. DMS oxidation leads to sulfuric acid that is ultimately a source of cloud condensation nuclei (CCN). This process plays a role in regulating the generation of stratus clouds over the ocean, a principal factor in the earth's albedo.

Gas Phase Photooxidation Chemistry

Gas-Phase Photooxidation Chemistry

We have established a new indoor photochemical reactor, designed to investigate gas-phase atmospheric chemistry. Briefly, the system is composed of a 1 m^3 batch reactor made of 2 mil FEP Teflon, surrounded by ultraviolet lamps. There are a total of 48 lamps which are mounted on a specially designed reflective surface to allow for uniformity in irradiation. The system is coupled to NO_x and ozone analyzers, and has an additional port for GC or GC-MS sampling.

As with any new system, experiments to verify the performance of the system had to be conducted. We chose to repeat the t-butyl alcohol photooxidation study conducted at Ford Motor Company by Japar et al. because of its simplicity. When t-BA reacts with hydroxyl radicals (or chlorine atoms), acetone is formed in a 1:1 ratio to the t-BA consumed. When comparing our results to those of Japar et al. (and references therein), we found our results to be consistent, thus verifying our system. With this system, our group at Caltech is now equipped to study the mechanisms of gas-phase reactions of organics in photochemical smog.

Investigations over the past year have included the gas-phase reactions of hydroxyl radicals with 2,2,4 trimethylpentane and 2,2,5 trimethylhexane. Primary products identified from the photooxidation of 2,2,4 trimethylpentane include isobutyraldehyde, formaldehyde, acetone, and acetaldehyde; and from the photooxidation of 2,2,5 trimethylhexane include 3,3 dimethylbutyraldehyde, trimethylacetaldehdye, acetone, formaldehyde, and acetaldehyde. The information gained in this study adds to the mechanistic database for the reactions of large alkanes.

We are currently embarking on a program to study the gas-phase photooxidation mechanisms of aromatic compounds such as toluene and m- and p-xylene. The goal of this program is to accurately determine the effect of NO_x on these systems, while attempting to elucidate the subsequent reactions of the aromatic-OH adducts.

Investigators:
Jean Andino
Richard C. Flagan
John H. Seinfeld

Support::
Coordinating Research Council
U.S. Environmental Protection Agency

Caltech's new 1 m^3 indoor photochemical reactor for the study of gas-phase mechanisms of atmospheric reactions. The reactor, constructed by graduate student Jean Andino, is being used to study the atmospheric chemistry of aromatics.

Parallel Airshed Model

Atmospheric Modeling Algorithms for Massively Parallel Architectures

The use of parallel computers for air quality modeling is addressed in this project. This work focuses on the study of algorithms, the determination of new parallel computational methods, and the evaluation of architectures to improve the modeling tools available to the air pollution community. In particular, the following objectives are proposed to be accomplished:

- To develop a parallel implementation of an urban scale photochemical model under Multiple Instruction Multiple Data (MIMD) architectures such as are used by the Intel Touchstone Delta or a network of optically interconnected workstations.
- To study a variety of gas-phase chemistry solvers in a parallel environment. We have developed a new integration algorithm based on Richardson extrapolation to solve the chemical kinetics in air quality models. In addition, we have compared the performance and accuracy of other commonly used integrators such as the Hybrid method and the QSSA solver.
- To study the parallel implementation and accuracy of different transport solvers used in air quality models. We are currently studying transport solvers that were dismissed in the past due to their high computational demand but provide great improvements in accuracy despite their expense. The use of the accurate space derivative (ASD) method to solve air quality transport computations is being investigated. We have also evaluated the performance of finite elements, finite differences, numerical method of lines, and semi-Lagrangian algorithms.
- To study different approaches to decompose the computational domain used by the models. The implementation of different numerical techniques in the model requires different domain decompositions to achieve near optimal performance. Our goal is to implement decomposition strategies that provide the best performance while maintaining the modularity of the model.
- To design a cluster of IBM workstations to fit the needs of air pollution computations. The cluster is connected using a high speed fiber network.

In brief, we intend to make use of new developments in computer hardware and more robust mathematical techniques to produce parallel implementations of air quality models to be used as a research or application tool.

Investigators:
Donald Dabdub
John H. Seinfeld

Support:
This project was initiated with funding by the Center for Air Quality Analysis and is now supported by the U.S. Environmental Protection Agency and IBM.

Organic Compound Emissions

Comprehensive Characterization of Organic Compound Emissions from Air Pollution Sources

Adoption of the toxic substances provisions of the 1990 Clean Air Act amendments has focused attention on the characterization and control of individual organic compounds that are emitted from air pollution sources. The nearly 200 substances slated for control under that act include most of the abundant aromatic hydrocarbons in the atmosphere, aldehydes, chlorinated organics, and polycyclic organic compounds that are distributed between the gas-phase and the particle-phase in the atmosphere. Information on the emissions of many of these substances from sources are incomplete, especially for the semi-volatile organics and oxygenated organics that are seldom measured during source tests intended only to establish VOC compliance or particulate matter mass emission rate compliance.

A series of source tests is being planned that is intended to measure as many of the single organic compounds as possible that are present in the emissions from several important classes of air pollution sources. Sources to be examined include gasoline-powered and diesel-powered motor vehicle exhaust, natural gas combustion, fireplace combustion of wood, and food cooking operations, among others. Simultaneous measurements will be made of volatile organic species, semi-volatile organic species, particle-phase organic species, aldehydes and organic acids using a dilution source sampling system that we have previously developed for measuring particle-phase organic compound emissions from sources.

Investigators:
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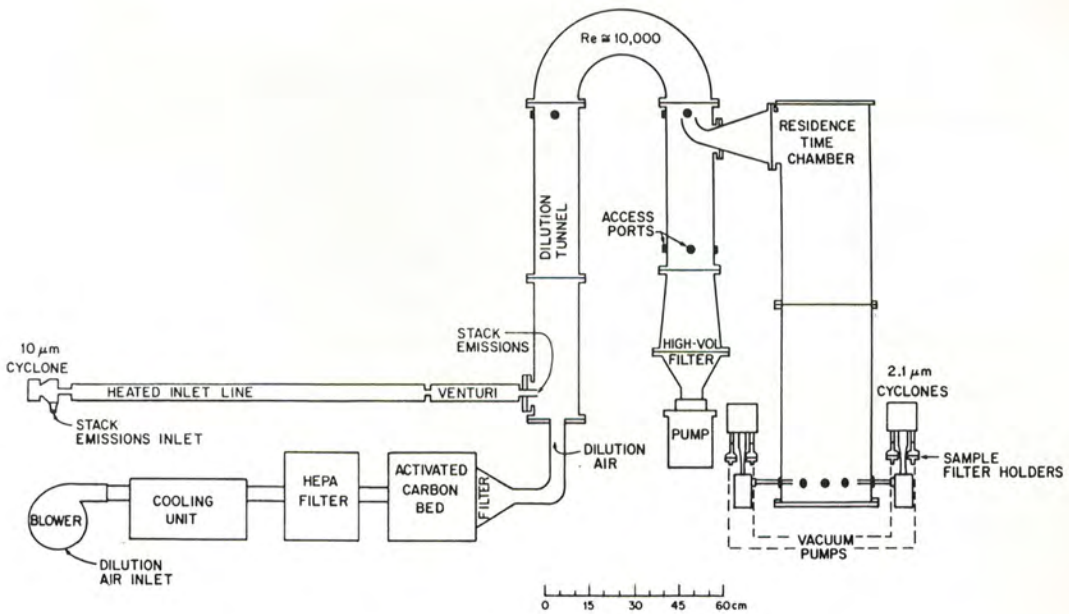
Lynn Hildemann
Glen R. Cass



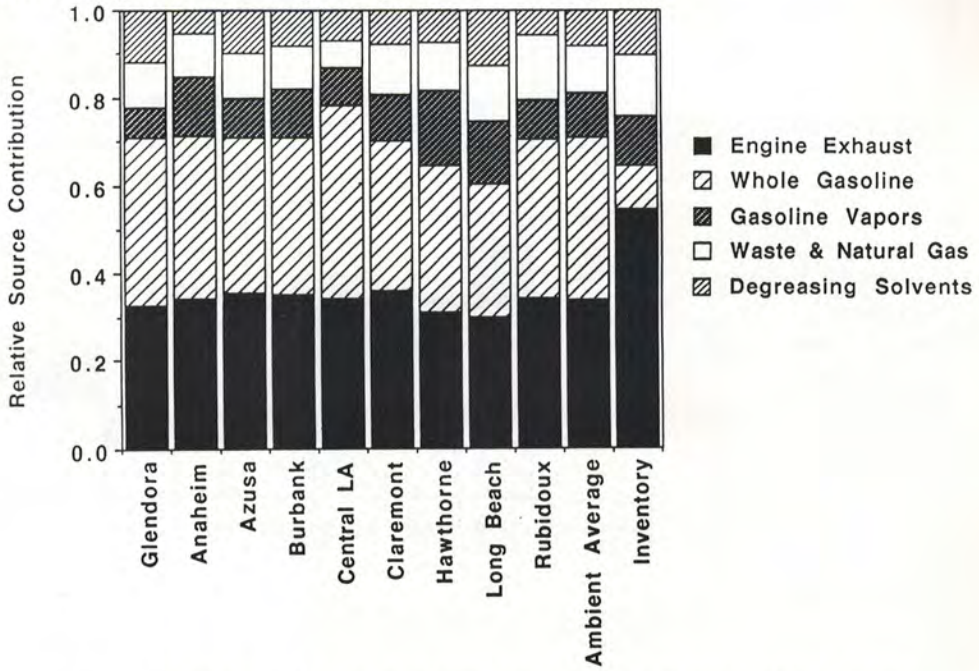
Dilution stack sampler schematic diagram.

Source/Receptor Modeling for Gas-Phase Organics

Source/ Receptor Reconciliation of Gas-Phase Organic Air Pollutants

An accurate organic gas emissions inventory is an essential component of photochemical modeling calculations, and is also a necessary basis for programs designed to control the emissions of toxic air contaminants. There has been considerable debate about the accuracy of current emission estimates for the South Coast Air Basin. One way to diagnose errors in the emission inventory and to gain insight into the relative importance of different source types is to reconcile ambient measurements of organic gas species concentrations with representative speciation profiles for selected source categories.

A revised set of organic gas speciation profiles has been developed for Southern California. Respeciation of the organic gas emissions resulted in large changes in the basinwide emissions estimates for many individual organic species, including 1,3-butadiene, ethylene glycol, methanol, and cyclohexane. Significant changes were observed in the reactivity of the chemical composition profiles for individual source categories, especially for surface-coating activities and associated thinning solvent use. Receptor-modeling methods have been used to identify the relative importance of major sources that contribute to atmospheric organic gas concentrations in Southern California. The receptor modeling results indicate a key discrepancy between the emission inventory and ambient data: there is much more unburned gasoline in the atmosphere than is indicated in the emission inventory. These excess unburned gasoline emissions may be coming from a combination of sources including tailpipe emissions, hot-soak evaporative emissions, and fuel spillage.



Relative source contributions to non-methane organic gas concentrations at various receptor monitoring sites in Southern California.

Investigators:
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Support:
Electric Power Research Institute

Thermodynamics of Atmospheric Aerosols

Thermodynamics of Atmospheric Aerosols

A rigorous and computationally efficient thermodynamics model, SCAPE, that estimates the state and composition of atmospheric inorganic species between gas and aerosol phases has been developed. With incorporation of the up-to-date thermodynamic data and optimal approaches in the routine, SCAPE (Simulating Composition of Atmospheric Particles at Equilibrium) represents a state-of-the-art gas/aerosol equilibrium model. The current version of SCAPE can use data on the total concentrations (gas and aerosol phases) of sulfate, nitrate, ammonia and ammonium, sodium, and chloride as well as data on relative humidity and temperature. Other species, such as calcium, potassium, magnesium, and carbonate, are being added to the model to include all the important inorganic species.

One application of SCAPE is to calculate water content and acidity associated with atmospheric aerosols. We have estimated water content associated with the inorganic fraction of $PM_{2.5}$ and PM_{10} mass at San Nicolas Island, Long Beach, Burbank, and Riverside using SCAPE and the measured aerosol composition data from the 1987 Southern California Air Quality Study (SCAQS). We have found that from midnight to the early morning, when the temperature is low and relative humidity high, water is usually the predominant aerosol substance. Particulate water in the winter was estimated to be considerably larger than in the summer at each of the four sites. Aerosol acidity for SCAQS was estimated for all the considered sampling sites, with the highest pH values at Riverside (2-4.5) and lowest at Long Beach and San Nicolas Island (-0.8-3.3) in the summer. Wintertime particles were estimated to be less acidic than those in the summer.

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AEROSOL EQUILIBRIUM MODELS

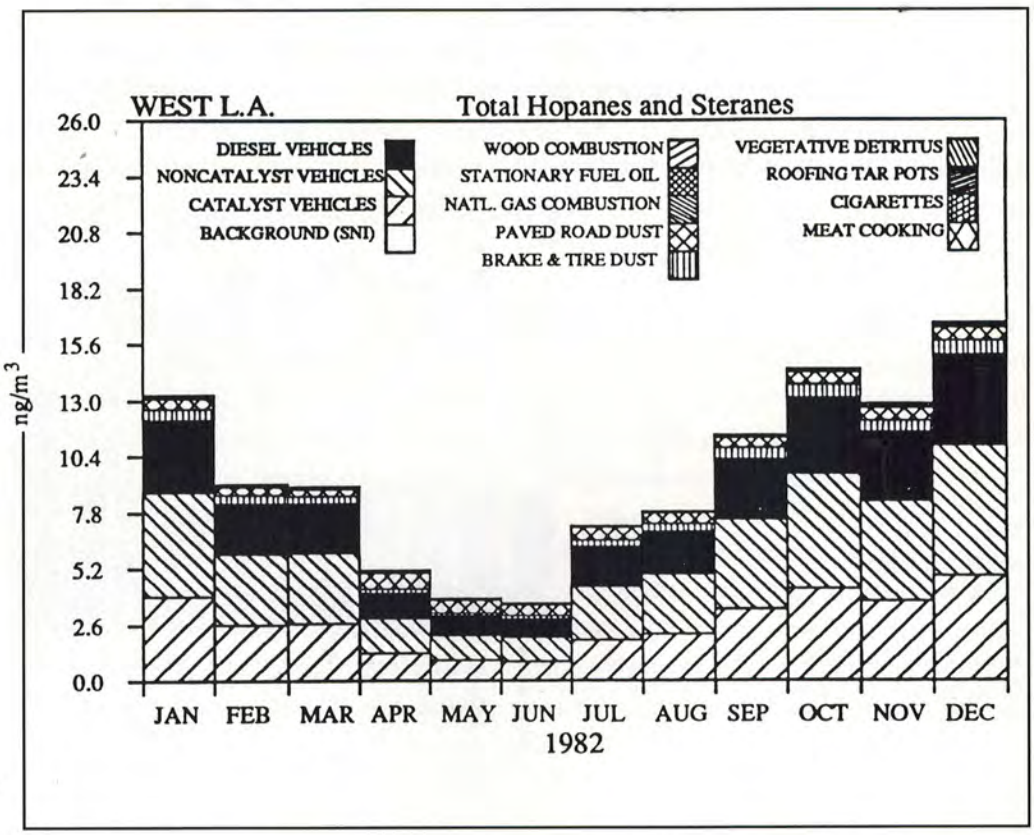
Species	Reference	Gas Phase	Aerosol Phase	Comments
Ammonium Nitrate	Stelson and Seinfeld(1982), Russell et al.(1983)	NH_3, HNO_3	NH_4NO_3	No sulfate
Ammonium Nitrate and Sulfate	Bassett and Seinfeld(1984)-EQUIL, KEQUIL	NH_3, HNO_3	NH_4NO_3, $(NH_4)_2SO_4$, Mixed salts	Rigorous, Computationally demanding, Size segregation
Same as above	Saxena et al. (1986)-MARS	Same as above	Same as above	Approximations, Fast
Ammonium Nitrate, Sulfate, Sodium, Chloride	Pilinis and Seinfeld(1987)-SEQUILIB	NH_3, HNO_3, HCl	Various salts(9)	Approximations, Fast, Size segregation
Same as above	Wexler and Seinfeld(1991)-AIM	Same as above	Same as above	Including transport, Rigorous
Same as above	Kim et al. (1992)-SCAPE	Same as above	Same as above	Rigorous, Fast

Source/Receptor Modeling for Particulate Organics

Source/ Receptor Modeling for Fine Particulate Organic Matter Characterized on a Molecular Level

The purpose of this research is to provide a molecular characterization of the primary organic particulate matter emitted from urban air pollution sources, and to test new methods for relating emissions to air quality for many organic compounds. A dilution source sampling system has been employed to collect primary fine particulate matter emissions from 15 major urban sources contributing close to 80% of the fine organic aerosol emitted in the Los Angeles area. Ambient fine particle samples were collected for one entire year at four urban locations and at one remote offshore sampling site. Organic compound identification and quantification is conducted by high resolution GC and GC/MS techniques. The identification of organic marker compounds that are characteristic of particular source types is emphasized. Such compounds are very helpful for confirming and modeling source/receptor relationships.

The emission data have been matched to atmospheric transport models, which then were used to compute source contributions to atmospheric compound concentrations at community monitoring sites. Predictions in general are in good agreement with measured atmospheric concentrations.



Air Quality model predictions of the monthly mean total hopanes and steranes concentrations at West Los Angeles (1982) based on measured emissions from sources combined with atmospheric transport calculations.

Investigators:
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Electric Power Research Institute

Visualizing the Effect of Air Pollution

Development of Improved Image Processing Based Visibility Models

Light scattering and absorption by airborne particles can lead to pronounced visibility reduction, in both urban and remote wilderness areas. In cities such as Los Angeles and Denver, visibility can be reduced to only a few kilometers by relatively high concentrations of air pollutants. In national parks, wilderness areas and other remote parts of the globe, small increments to the ambient fine aerosol concentration can shorten visual range by tens of kilometers.

Since many of these remote areas are valued for their scenic beauty, even a small level of air pollutant intrusion can noticeably degrade the quality of the scenic view.

A mathematical model has been developed that uses simulated photographs to display the effect of atmospheric aerosols on visibility. Synthetic photographs of the predicted appearance of a heavy smog event have been compared to actual photographs of the event being simulated. The appearance of objects in the scene, including buildings, landscape elements and mountains in the distance, were reproduced quite accurately by an image processing-based visibility model. Recent work has remarkably improved the appearance of the sky in the synthetic images.

Work is continuing on further development of a version of this model that is driven by data taken from earth orbiting satellites that can be applied at any location of interest.

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Support:
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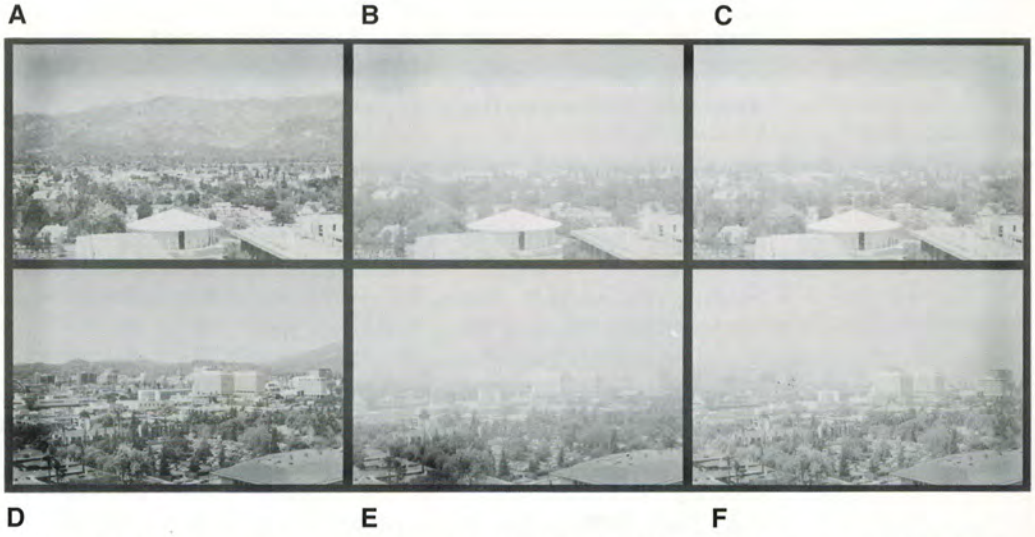

Actual photographs and synthetic images: April 7, 1983, clear day photograph of the San Gabriel Mountains scene (a) and downtown Pasadena scene (d); August 25, 1983 smoggy day photographs for the same scenes (b and e, respectively); visibility model synthetic images of the predicted appearance of the smoggy day (c and f respectively) computed from the clear day photographs.