
Secondary Organic Aerosols

Research Strategy

To apportion biogenic/anthropogenic
sources of SOA

*An Outcome of the
First Secondary Organic Aerosols Workshop
February 4-5, 2002
Desert Research Institute
Reno, Nevada*

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Lead workshop presenters were:

- **Bill Malm**, Cooperative Institute for Research in the Atmosphere (CIRA), National Park Service
- **Jim Pankow**, Oregon Graduate Institute
- **Spyros Pandis**, Carnegie Mellon University
- **Jamie Schauer**, University of Wisconsin
- **Lynn Hildemann**, Stanford University
- **Richard Kamens**, University of North Carolina
- **Barbara Zielinska**, Desert Research Institute

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In addition to presentations made by lead presenters, nine guest presentations were made by the following: James Cowin, Pacific Northwest Research Center; Joellen Lewtas, EPA/ORD, Seattle; Paul Doskey, Argonne National Laboratory; Delbert Eatough, Brigham Young University; Judith Chow, Desert Research Institute, and; Gary Casuccio, Desert Research Institute.

Executive Summary

The first Secondary Organic Aerosols Workshop was unique because it was premised on what don't we know rather than what we do know about SOA. The workshop bears implications for future dialogue on research and policy development related to not only air quality in the United States, but significant to climate change, public health, and visibility and haze.

It has been a major goal of the first Secondary Organic Aerosols Workshop to provide opportunities for key researchers across the United States to contribute to developing a **Research Strategy** for the next 3-5 years that identifies where study is needed to advance knowledge associated with organic aerosols, particularly secondary organics aerosols. Bringing these key researchers together to discuss their work and share their recommendations about where research should be focused was a primary desired outcome of the workshop. Both the workshop and the strategy will contribute to enhancing interaction among researchers and federal agencies.

Rationale and need for studying SOAs

Secondary Organic Aerosol is important because:

1. it may contribute to large fraction of organic carbon, which in turn constitutes a large fraction of $PM_{2.5}$ that causes haze and adverse health effects;
2. it contains many water soluble compounds that may enhance light scattering at high humidities;
3. it is an end-product of photo chemical process that also create sulfate, nitrate, and ozone, and;
4. it is the least well-qualified and understood of the processes that form particles in the atmosphere.
5. some of it is natural and some is manmade
6. we may come to a point where it is a limiting unknown in achieving $PM_{2.5}$ standards and visibility goals.

The need for a rationale for studying secondary organic aerosols goes beyond the fact that very little is known about secondary organic aerosols and their precursors. A practical research plan and an underlying rationale is needed to justify studying secondary organic aerosols and to identify the benefits of characterizing ambient concentrations of secondary organic aerosols and their precursors. For example, what would be done with the information if it was discovered that secondary organic aerosols constitute 5 percent of the fine aerosol mass and 10 percent of the visibility extinction on an annual basis?

The importance of secondary organic aerosols related to haze, visibility, climate, and health has been recognized since the 1950s. A small community of researchers in the United States, as well as Europe, have persisted in sampling, measuring, improving the use of available technologies, analyzing and interpreting data. The problem is complex because there are hundreds, possibly thousands, of SOA precursors and end-products. Many of these remain to be identified and measured. Sampling, measuring, and defining SOAs is also recognized as being extremely difficult and challenging.

The Secondary Organic Aerosols Workshop, held February 4-5, 2002 in Reno, Nevada articulated the current context of SOA research and where knowledge gaps exist. Fifty-four workshop participants brainstormed and began to strategize research needs and identify funding sources for activating research of SOAs.

Lead workshop presenters and guest presenters made general recommendations about the directions in which research could and should go. Recommendations were drawn from the workshop's rather comprehensive articulation of the body of knowledge to enable us to begin categorizing areas for potential research.

Actual projects were not outlined. Some funding sources were listed.

Workshop Goals

The goals of workshop were to:

- 1) summarize existing knowledge of the extent to which chemical markers for secondary aerosol can be identified and measured at remote locations to determine their contributions to regional haze;
- 2) identify knowledge gaps and ways to fill them; and
- 3) specify projects, timelines, and approximate resources needed to demonstrate a source attribution of secondary organic aerosol at remote locations.

Each question was examined and addressed through each of these goals as a guide for formulating pre-workshop write-ups, workshop presentations, and guest presentations.

Statement of Problem

Potential Receptor-Oriented Methods to Identify and Quantify Contributions from Secondary Organic Aerosol to $PM_{2.5}$ and Light Extinction

Organic and elemental carbon constitute, on average, one-third of the average $PM_{2.5}$ mass and are estimated to contribute ~30% of particle light extinction at sites in remote locations such as national parks and wilderness areas. A large continuous database of carbon measurements has been acquired by the interagency monitoring of protected visual environment (IMPROVE) networks. Ammonium sulfate and geological material constitute the other two-thirds. For some 24-hour periods, carbon contributes more than half of the particle extinction. The major sources of this carbon are: 1) exhaust from gasoline and diesel powered vehicles, emitted locally and transported from distant sources; 2) formation during transport of secondary organic material from heavy hydrocarbon ($>C_8$) compounds originating from vegetation, industrial processes, and diesel combustion; 3) meat cooking, especially charbroiling over wood or natural gas; and 4)

vegetative burning emissions from wildfires, prescribed burns of forests and crops, and woodburning in campfires, fireplaces and wood stoves. Raw vegetative material from plant detritus, pollens, molds and spores also contributes to carbon, primarily in the coarse (PM_{10} minus $PM_{2.5}$) particle size fraction.

Thermal evolution carbon analysis protocols typically report organic carbon (OC) and elemental carbon (EC) fractions, sometimes with sub-fractions based on evolution temperature. These OC/EC mass ratios in urban areas are often found to range from 1 to 4, typical of ratios in primary emissions such as vegetative burning and vehicle exhaust. There are many examples at IMPROVE sites, however, where these ratios are much higher, indicating some source of OC that is not accompanied by EC. One interpretation of high OC/EC ratios is that additional OC is provided by secondary organic aerosol. Other interpretations are that remote sites are affected by primary emissions from sources with large organic carbon content (e.g., pollen and spores) and that organic vapors adsorbed onto quartz fiber filters used for sampling interfere with the particle measurements (despite subtraction of an average black from backup quartz filters).

Workshop Process for Answering Questions

The workshop centered on presentations addressing seven research questions about the overarching subjects of visibility, mechanisms and equilibrium, sampling methods, and analysis. In addition, two research implementation questions were posed to all workshop participants during a plenary session.

The key questions were assigned to seven lead workshop presenters who addressed key issues through presentations made to an audience of about 54 participants. A floor discussion, and questions and answers followed their presentations. Nine guest presentations were also made after selected lead presentations.

Goals and the questions were drafted and comments were solicited by lead presenters who examined recent literature relevant to each question, then recommended one or two articles for others to inform themselves. Lead presenters then composed their answers to questions in understandable terms, identifying knowledge gaps and how to fill them. These were distributed for general reading among core participants and discussed via a series of pre-workshop conference calls. Edited answers and workshop agenda were distributed to workshop registrants for the plenary session held on Feb. 5 in Reno. Lead presenters and workshop organizers met on February 4, 2002 in Reno to discuss answers to questions and prepare for plenary presentations. The workshop took place the next day in which about an hour was devoted to each question, followed by a question and answer discussion. Workshop facilitator, John Watson, assisted lead presenters and facilitated discussion. On Feb. 6, members of the organizing group edited answers, adding in other material presented by other participants, where necessary, into a draft Research Strategy that outlines the direction research could go in the next five years.

Outcomes

Nineteen recommendations for the near-, mid-, and long-term were listed by participants in a plenary brainstorming session in addition to several more recommendations made by individual presenters.

The workshop was an initial step towards developing relationships that will be needed to conduct appropriate and relevant research that expands on previously existing research, to develop significant new technologies, and to create concrete links to funding and other resources. It served to bring researchers closer together with potential funding sources and their representatives.

Opportunities

Workshop participants suggested additional topics that would merit separate and more tightly focused follow-up workshops. These included:

- 1) Specific needs of potential research sponsors with respect to organic particles and SOA;
- 2) fundamental causes of difference in carbon measurement methods;
- 3) development of measurement methods for polar compounds that constitute most of SOA, and;
- 4) quantification of fundamental physical and chemical parameters for SOA and precursor compounds.

Potential Future Directions

Phase I

This phase culminated in the completion of the Secondary Organic Aerosols Workshop, February 4-5, 2002, Reno, Nevada and in the preparation of the Research Strategy to guide SOA research in the near-, mid-, and long-term. Outcomes during this phase of initial development include: identifying interested parties, contacting them, and conducting a conversation about SOAs, particularly what can we do to address what we don't know about SOAs. Participants include university and EPA and NPS researchers, graduate students, corporate researcher/representatives, state agency staffs.

Numerous conference calls were held to formulate the conceptual approach, and to plan and prepare first workshop.

Fifty-four individuals attended the workshop.

Phase II

- Identify funding sources and raise dollars for continued communication among researchers and agency contacts.
- Identify and contact organizations and agencies for their potential involvement and support.
- Conduct second workshop as early as fall 2002.
- Determine which near-term research projects are most relevant, achievable within a realistic timeframe.
- Identify funding sources for conducting near-term research projects.

Summaries of Lead Presentations

Question #1

Where and when does the IMPROVE and other chemically-specified particle data bases show high OC/EC ratios that might indicate large contributions of secondary organic aerosol to light extinction?

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Introduction

Samples collected by the IMPROVE network at about 70 sites throughout the US for roughly the last 14 years have been analyzed by the IMPROVE thermal optical reflectance protocol. The IMPROVE protocol provides bulk carbon speciation based on the temperature and atmospheric conditions under which a species volatilizes. The carbon fractions which volatilize between 25°C and 550°C in a helium atmosphere are considered organic, and those which volatilize between 550°C and 800°C in a 98% helium/2% oxygen atmosphere are considered elemental. After an adjustment for charring that is measured by a reflected laser beam, a “backup”, “artifact”, or secondary filter is placed behind some of the primary filters to estimate the effects of gas sorption on the measurement.

Findings

- The highest fine organic mass concentrations are measured in the southeastern US, the southern Sierra Nevadas and the Pacific Northwest.
- The ratio of OC to EC at the Washington, D.C. urban site ranged from about 2 to 4. Non-urban eastern US sites had OC/EC ratios which varied between about 4 and about 10. Sites in the Western US generally had OC/EC ratios between 4 and 10 for low concentration days, but high concentration days tended to have OC/EC ratios closer to 10. There were anomalous sites, like Yosemite, with most of the OC/EC ratios near 10. Some published source profiles for OC/EC ratios include 2.66 for an urban tunnel and 11 for hardwood combustion, but these ratios are variable depending on the test and XXX.
- Organic mass accounts for a larger fraction of fine mass on high fine mass days in the Pacific Northwest, compared with median days. In the Eastern US, organic mass

accounts for a significantly lower fraction of fine mass on high fine mass days, compared with median days.

- OC measurements generally track wildfire emissions data for California and the Colorado Plateau.
- There is a noticeable discontinuity in the EC concentrations during 1995 at some sites. The discontinuity is also evident in some of the “backup” or secondary filter concentrations.
- 80th percentile OC concentrations have been increasing in the Inter-Mountain West, and generally decreasing elsewhere.
- Secondary filter or “artifact” values are similar across at least four sites. The secondary filter values are also very similar to field blank values. Field blanks are filters which are sent to the field with the regular samples, but have no air drawn through them.

Question #2—What organic particles should be included in the definition of secondary organic aerosol? Condensation of hot exhaust? Condensation of vapors on particles in the atmosphere? Equilibrium changes for volatile particles? Gas-phase transformations? Aqueous-phase transformations? Organic particle reactions with inorganic gases?

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Introduction

Definition of Secondary Organic Aerosol

For our purposes, *organic aerosols* are solid or liquid particles suspended in the atmosphere containing organic carbon. *Secondary organics* are the fraction of the organics which are not originally present in the aerosol soon after achieving equilibrium at atmospheric temperatures.

Secondary organic aerosols form through a variety of mechanisms.

- VOCs (precursors) react with O₃ and sunlight to form new compounds.
- For SOA formation to occur efficiently, high vapor pressure compounds need to convert to low vapor pressure compounds.
- The partitioning of these compounds between solid, liquid, and vapor state is driven by their activity coefficients and vapor pressures.
- Secondary compounds may be formed in liquid or solid particles.
- The mass concentration of particle-phase secondary compounds ($\mu\text{g}/\text{m}^3$) will depend on temperature, RH and water content, dilution, and age of the air parcel.

Findings

Partitioning matrix can be solved given activity coefficients and vapor pressures. The solution to this matrix would tell us the partitioning of each compound present.

Conclusions

1. SOA formation mechanics are coupled for multiple compounds.
2. Dilution tends to reduce the amount of condensation (non-linearly).
3. Presence of primary emitted compounds probably increases the condensation of secondary compounds.
4. Presence of water increases the condensation of primary and secondary compounds, though the opposite can also occur.
5. The thermodynamics of these aerosols is not adequately understood.

Question #3—What are the chemical mechanisms that create secondary organic aerosols, what are their precursors, what are the environmental conditions needed to create and sustain particles, and what are the organic substances in the particles?

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Introduction

The ability of a given volatile organic compound (VOC) to produce SOA during atmospheric oxidation depends on three factors:

- The volatility of its products
- Its emission rate (atmospheric abundance)
- Its chemical reactivity

Aromatics are by far the most significant anthropogenic SOA precursors.

Biogenic hydrocarbons emitted by trees are the most important natural source of SOA.

The incremental aerosol reactivity (IAR) is one approach to quantify the ability of a given precursor to the ambient organic aerosol concentration.

Formation —There are two important steps in the formation of SOA. The first is the chemical reactions in the gas phase leading to the production of the SOA compounds. These reactions involve the parent VOC, its products, and O₃, the OH radical, the NO₃ radical, NO_x, etc. The second step is the reversible partitioning of the produced SOA compounds between the gas and particulate phases.

Both the chemical mechanisms leading to the formation of SOA compounds and their partitioning have been studied in the laboratory for 20 years. Most of these have focused on the SOA production during the α -pinene reaction with ozone.

Developing detailed chemical mechanisms explaining the production of the SOA compounds is an ongoing process, but because of the chemical complexity, progress has been slow.

The partitioning of the SOA compounds between the gas and particulate phases is a critical step in the overall SOA formation process. Most of the SOA compounds have saturation vapor mixing ratios of the order of 1 ppb and are therefore semi-volatile. Quantifying the fraction of these compounds in the particulate phase under given conditions is a major challenge. The current approach suggested first by Pankow and co-workers and refined for SOA by Odum and co-workers assumes the formation of a solution by the SOA compounds.

There are several compounds that could be used to relate SOA compounds to precursor gases. Some (pinic acid, pinonic acid, norpinic acid, norpinonic acid, etc.) result from the oxidation of multiple precursors, but others (hydroxypinonaldehydes, hydroxypinaketones, sabinic acid, etc.) are unique products of a given precursor.

Several SOA compounds have been identified in laboratory studies but only a few (mostly biogenics) have been measured in ambient air.

SOA concentrations are expected to be sensitive to the ambient temperature, which will affect both the rates of the gas-phase reactions and the partitioning of the SOA compounds.

Findings

Anthropogenic and biogenic SOA compounds may interact. Increases in the production of one may lead to increased concentrations of the other by shifting their partitioning towards the particulate phase.

A 10°C change in the ambient temperature can change SOA concentration in the α -pinene/ozone system by as much as a factor of two (Kamens and Jaoui 2001). Higher temperatures are expected to decrease the SOA yields in this system.

For the ambient atmosphere the increase in production rates with increasing temperature would partially offset the evaporation of SOA (Strader and Pandis 1999). Intermediate temperatures (around 20°C in their case) could be optimal for the SOA production. The change in partitioning of SOA at lower temperatures could lead to counterintuitive behavior of the SOA concentration during the day (Bowman and collaborators).

Relative humidity is a secondary factor to temperature to the formation of SOA, but its role in SOA production has yet to be elucidated. The lower the RH, the higher the OC/EC ratio.

The presence of aerosol liquid water does not significantly increase or decrease SOA yields during the photo-oxidation of toluene in the presence of NO_x (Edney et al. 2000). The same lack of sensitivity to relative humidity was reported for the α -pinene/ozone system (Kamens and Jaoui 2001). The partitioning of semi-volatile organic compounds (alkanes, alkanolic acids, PAHs, etc.) on secondary organic aerosol (formed from the α -pinene reaction with ozone) was not sensitive to relative humidity (Jang and Kamens 1998).

We don't see the amounts of SOA in forests that we expected to see. We are missing something: either the amount of time of the compounds in the atmosphere is significant factor and/or there are so many tracers that the amount of a single if minimal.

Conclusions

Our understanding of the ability of individual VOCs, at least at semi-quantitative level, to serve as SOA precursors appears to be satisfactory.

Our understanding of the physicochemical processes leading to the SOA formation has improved dramatically during the last decade. A number of models of variable complexity are now available.

The challenges in the effort to identify SOA compounds in laboratory studies are significant.

- 1) *The difficulty in measuring the concentrations of these compounds*—They are polar and their concentrations appear to be only a few nanograms per cubic meter.
- 2) *The partitioning of these compounds between the gas and particulate phases*—Most are semi-volatile and their aerosol fingerprints change continuously.
- 3) *The reactivity of these compounds*—Some of the most volatile ones have brief atmospheric lifetimes. The reactivity of the less volatile ones has not been investigated in any detail.
- 4) *An additional analytical pitfall*—Tobias et al. (2000) discovered that aerosol produced from the reactions of 1-tetradecene and ozone the hydroperoxides, peroxides, and secondary ozonides observed by thermal desorption particle beam mass spectrometry (TDPBMS) thermally decomposed to more volatile compounds including tridecanal, tridecanoic acid, and few unidentified products.

Nucleation of SOA could be a potentially important process for the aerosol number concentration, but is of negligible importance for the SOA mass concentration.

OC/EC ratio gives us a clue about the formation of SOA. When OC/EC ratio goes up, we can be sure that SOAs are formed. The ratio goes up the higher the temperature. “Photochemical activity drives the whole process.”

Recommendations

Develop chemical measurement methods that are appropriate depending on urban or non-urban conditions.

High time-resolution ambient measurements of OC and EC as well as of some of the major SOA components will be necessary for the improvement of our understanding of the role of environmental conditions in the SOA formation.

Extend techniques developed in smog chamber studies to field studies in order to get more reliable ambient measurements than current ones.

Continue evaluating and developing models of physicochemical processes leading to SOA formation against multiple smog chamber data and field observations.

Question #4—Which gas and particle end-products can best distinguish secondary organic aerosol from primary organic particles at receptor locations? How stable are these components and how consistent are their ratios to other components in the secondary organic aerosol “source profile?”

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Introduction

Speciation of the organic compounds present in the carbonaceous fraction of atmospheric particulate matter samples has been shown to provide powerful insight into the impact of primary air pollution sources on particulate matter concentrations in both the urban and remote locations.

Using gas chromatography mass spectrometry (GCMS) techniques, along with the rich knowledge of organic compound molecular markers, molecular marker chemical mass balance (CMB) models have been developed and applied to apportion the source contributions of direct primary sources of atmospheric particulate matter.

CMB models have been used to apportion the primary source contributions from diesel engine, gasoline-powered motor vehicles, hardwood combustion, softwood combustion, meat cooking operations, road dust, tire wear, vegetative detritus, natural gas combustion and coal combustion. These models are reasonably well developed and are currently being employed in a broad range of air quality studies.

Findings

- Molecular marker CMB models that explicitly apportion the direct primary source contributions to particulate organic carbon can be used to quantify an upper limit on secondary organic aerosols.
- Under conditions where there exists high confidence that all important direct primary sources of particulate matter are incorporated into the molecular marker CMB models, estimates of secondary organic aerosol contribution to particulate matter concentrations can be obtained.
- The direct apportionment of secondary organic aerosols would allow a direct mass balance check on particulate matter organic carbon concentrations.
- Three chemical analysis approaches have been used in the past to identify the organic constituents of secondary organic aerosols (SOA):
 - 1) chemical analysis of laboratory generated SOA formed in smog chamber experiments;
 - 2) analysis of atmospheric particulate matter samples collected in locations where high levels of SOA are expected;
 - 3) statistical analysis and chemical structural interpretation of organic compounds speciation measurements of atmospheric particulate matter.

- From a practical perspective, there are three criteria necessary for organic compounds to be useful as tracers for SOA:
 - 1) the source of these compounds in the atmosphere must be dominated by atmospheric chemical reactions and not primary source emissions;
 - 2) the compounds must be reasonably stable in the atmosphere after production;
 - 3) there must exist a quantitative relationship between SOA production from at least a class of SOA precursors and the tracer compound.
- The aliphatic and aromatic organic diacids are of specific interest in tracking SOA since these compounds have been identified in atmospheric particulate matter samples in both the urban atmosphere and remote locations marine environments.
- The multifunctional substituted carbonyls have been shown to be major components of SOA.
- Both nitrated mono-aromatic and nitrated polycyclic aromatic hydrocarbons have been identified as products of atmospheric chemical reactions that are contributors to SOA.
- Some of the potential tracers for SOA are semi-volatile organic compounds, which exist in both the gas and particle-phase at atmospheric conditions, while some have very low vapor pressures and reside almost entirely in the particle-phase.
- The development of source apportionment techniques that only utilize particle-phase measurements will need to exclusively utilize non-volatile tracers, such as the aromatic, aliphatic, and cycloalkyl diacids.
- Source apportionment strategies that take advantage of both non-volatile and semi-volatile tracers are still need to face the challenge of accurately measuring or effectively expressing the concentration of SOA in the particle-phase.

Recommendations

- Two different strategies for source apportionment of SOA are needed: One that can be applied to routine filter based samples, and; one that can fully exploit advanced sampling techniques that are likely to be employed in selected field studies.
- Identify molecular markers for secondary organic aerosols and develop source profiles for secondary organic aerosols that can be incorporated in CMB models.
- Field studies should be conducted that make adequate measurements of likely SOA tracers and known primary source tracers that can be used in an advanced positive matrix factorization (Ramadan et al., 2001) such that effective profiles for different sources of SOA can be identified. Field studies should be implemented in both regions that are likely impacted by SOA originating from both biogenic and anthropogenic sources.
- Smog chamber studies should be conducted to identify the atmospheric reactions and precursors for secondary aromatic diacids.
- Additional smog chamber experiments should be conducted to further investigate the stability of potential tracers for SOA, with specific attention to diacids, multifunctional substituted carbonyls, and nitrated aromatics.

- Better integration of analytical techniques among atmospheric measurements, primary source measurements and laboratory smog chamber experiments to help assess the uniqueness of proposed SOA tracers.
- More advanced analytical techniques need to be tested to identify novel SOA tracers including isotopic fractionation during SOA production, physical properties, nitrogen containing compounds, and polar organic compounds.

Question #5—What are the size, composition, and hygroscopic properties of secondary organic particles that are most likely to affect light extinction? Which end-products and formation mechanisms are likely to cause the largest and smallest effects on regional haze?

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Findings

- Secondary organic compounds condense on the surface of suspended particles, thereby increasing their size. This growth is usually toward particle sizes ($\sim 0.5 \mu\text{m}$) that scatter light more efficiently than the original particles.
- Many secondary organic compounds absorb water as relative humidity increases. This causes particles to grow toward sizes that scatter light more efficiently than the original particles. This growth is not as much as that observed for inorganic compounds such as ammonium sulfate and ammonium nitrate at $\text{RH} > 70\%$. This effect has been observed in non-urban areas.
- Some secondary organic compounds may cause particles containing ammonium sulfate, ammonium nitrate, and other water-absorbing inorganic compounds to grow less than expected as humidity increases. This may be due to organic surface films that inhibit the interaction of water vapor with the inorganic salt. This effect has been observed in urban areas.
- Organic compounds must have a low enough vapor pressure to condense at ambient temperatures of 10 to 30 °C. They must be water-soluble to affect light extinction. Potential compound groups include diacids, polyols, and amino acids. These are rarely quantified in ambient air and can arise from both primary emissions and secondary formation.
- Particles that include secondary organic compounds may be non-spherical and of inhomogeneous composition. Extinction efficiencies determined by models of uniform spherical particles may misrepresent actual efficiencies. Descriptions of particle structures and models to approximate their effects on light extinction are currently unavailable.
- For the few water-soluble organic compounds that have been examined, a widely-used chemical model (UNAFAC, not intended for water mixtures, but the only model available) does not estimate water activities that are consistent with measurements. This lack of information frustrates efforts to mathematically model water uptake.
- Typical urban mitigation strategies focus on very small or vary large particles may increase the effect of condensed secondary organic compounds because the remaining particles ($0.3\text{-}0.7 \mu\text{m}$) will collect more of the condensable secondary organic material, thereby enhancing its light scattering efficiency.
- Secondary organic compounds will have the largest visibility effect when sulfate levels are low and relative humidities are 50% to 70%. Sulfate dominates light extinction at higher humidities and when it dominates $\text{PM}_{2.5}$ mass.

Question #6—What are the precursor compounds for secondary organic aerosols? What are the types of vegetation, vehicle exhaust, and burning that emit these precursors and under what conditions?

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Introduction

The environmental chamber work of many investigators clearly demonstrates that aromatics and naturally emitted terpenes have the potential to generate secondary aerosol material. The primary atmospheric reactions of these compound classes involve the hydroxyl (OH) radical, ozone, and the nitrate radical (NO_3). These reactions produce a host of low volatility dicarbonyls, carboxylic acids, hydroxy carbonyl and organic nitrate compounds that can exist both in the gas and aerosol phase.

As reported by Went^[i], Leonardo Da Vinci described haze over cities and thought that water emissions from plants were its source. We know today that the relative importance of precursors to secondary aerosol formation will depend on their overall aerosol potential, atmospheric emissions, and the presence of other initiating reactants (O_3 , OH, NO_3 , sunlight, acid catalysts). Over 40 years ago, Went posed the question, “What happens to 17.5×10^7 tons of terpene-like hydrocarbons or slightly oxygenated hydrocarbons once they are in the atmosphere?” Went^[i] suggested that terpenes are removed from the atmosphere by reaction with ozone and demonstrated “blue haze” formation by adding crushed pine or fir needles to a jar with dilute ozone. Monoterpenes ($\text{C}_{10}\text{H}_{16}$) represent about 10% of the natural non-methane hydrocarbon (NMHC) emitted by vegetation to the atmosphere^[iii]. α -pinene tends to be the most ubiquitous terpene, and may account for about 20-25% of the potential secondary aerosol mass from terpenoid type compounds^[iii,iv]; d-limonene may be as high as 20% and β -pinene from 7-15%.

Sesquiterpenes ($\text{C}_{15}\text{H}_{24}$) are also released from vegetation and they may contribute as much as 9% to the total biogenic emissions from plants^[v]. Other estimates are both higher and lower. The sesquiterpenes β -caryophyllene and α -humulene have very short life times in the presence of representative global average concentrations of O_3 or the nitrate radical (NO_3), which have life times on the order of minutes. These two compounds on a reacted mass basis have 3-5 times the aerosol potential of either α - or β -pinene. In addition to monoterpenes and sesquiterpenes, a number of oxygenates are emitted by vegetation. These include alcohols, carbonyls, acetates and organic acids. Of significance is that in many instances the oxygenate emissions may be higher, depending on the plant species, than monoterpene emissions.

Some recent examples of ambient terpene concentrations are given in Table 2. Yu et al^[vi] reported terpene concentrations for San Bernardino National Forest, California, USA. Sampling was for an evening to the next midday. On average, terpene concentrations ranged from 10 to 63 pptV.

Hannele et al^[vii] have reported similar concentrations in an open field near a forested area in Finland.

Globally, about 25 Tg yr⁻¹ of toluene and benzene are emitted with fossil fuels contributing ~80% and biomass burning another 20 %^[viii]. Volatile aromatic compounds comprise a significant part of the urban hydrocarbon mixture in the atmosphere, up to 45% in urban US and European locations^[ix,x,xii]. Toluene, m- and p-xylenes, benzene and 1,2,4-trimethyl benzene, o-xylene and ethylbenzene make up 60-75% of this load.

In the rural setting, the picture is quite different. At a rural site in Alabama in the summer of 1990, aromatics contributed ~1.7 % to the overall VOCs^[xiii]. Alkenes were the major category, with isoprene and α -pinene and β -pinene making up 37, 3.5, and 2% of the VOCs. Alkanes made up 9% and oxygenates 46%.

Hydrocarbon emissions from two tunnels in the US showed that aromatic emissions comprised 40-48% of the total nonmethane hydrocarbon emissions for light and heavy duty vehicles^[xiii]. On a per mile basis heavy-duty trucks emit more than twice the aromatic mass, than light-duty vehicles emit, and the distribution of aromatic is different between these two classes. The six aromatic compounds mentioned above comprised ~60% of the light-duty emissions, but only about 27% of the heavy-duty emissions.

Definitions

For the purposes of this discussion secondary organic aerosol (SOA) material will be defined as organic compounds that reside in the aerosol phase as a function of atmospheric reactions that occur in either the gas or particle phases

Findings

Natural and anthropogenic fine aerosol emissions to the atmosphere are on the order of 200 to 300 Tg yr⁻¹. Biogenic aerosols represent ~10% of this figure. A modeling estimate by Griffin et al. for biogenic aerosols emissions is 13 to 24 Tg y⁻¹; this is on the same order of magnitude for predictions of anthropogenic soot, and natural or anthropogenic nitrates, but much less than sea salt or natural or anthropogenic sulfate aerosols. If more realistic and lower average global temperatures were used, other existing aerosol surfaces were considered and possible particle reactions proposed by Jang and Kamens^[xiv], this emission rate estimate may be much higher.

The chamber work of many investigators clearly demonstrates that terpenoid and aromatics have potential to generate secondary aerosol material^[xv,xvi,xvii,xviii,xix,xx,xxi,xxii,xxiii]. For aromatic systems with TSP concentration of 100 μ g/m³, and using the Pankow relationship for absorptive partitioning^[xxiv], 0.1% of a multi carbonyl-OH product, 0.06% of a buten-al-oid product, and 15% of a dicarbonyl-alcohol-carboxylic acid product would be in the aerosol phase. A host of new ring-opening products, which include oxo-butenoic, dioxo-pentenoic, methyl-oxo-hexendienoic, oxo-heptadienoic and trioxohexanoic carboxylic acids, as well as similar analog aldehydes were recently identified by Jang and Kamens^[xiv], along with chemical mechanisms to explain their formation have recently been reported. Many of these products were major components in the particle phase. Very few of these products have been observed in ambient samples, although the under predicted receptor modeling of dicarboxylic acid aerosol content by Schauer et al.^[xxv] may be a result of these processes.

Of the major SOA products observed in toluene and α -pinene outdoor smog chamber experiments^[xiv,xxvi], the experimental partitioning coefficients between the gas and the particle phases (K_p) of aldehyde products were much higher and deviated more from predicted K . This is an extremely important result, because it suggests that aldehyde products can further react through heterogeneous processes and may be a very significant SOA generation mechanism for the oxidation of aromatics in the atmosphere. As product, aldehydes become incorporated into larger molecules in the particle phase, more parent aldehydes partition from the gas to the particle phase. A very recent study reported that inert particles acidified with sulfuric acid can promote these reactions and form much higher yields of secondary products than when acid is not present^[xxvii]. This study also shows that dialdehydes such as glyoxal, as well as hexanal and octanal can directly participate in secondary aerosol formation, but this process is significantly enhanced by the presence of an acid seed aerosol. The same phenomena was observed for the reaction of aldehydes and alcohols. The products of particle phase aldehyde reactions that lead to this SOA increase are probably thermally unstable and do not usually survive the workup procedure for traditional analysis techniques.

Conclusions

- Sesquiterpenes are important to some currently unknown level in SOA formation.
- The description and understanding of chemical mechanisms for the production of SOAs from biogenics and aromatic precursors are critical.
- Many of the techniques used to detect and quantify particle phase reactions are too harsh. We are destroying, or at least changing, the compounds that we are attempting to find.
- Some uncertainty exists in the area of impacts caused by humidity and drought stress on biogenic emissions, such that emission models can accurately reflect their input.
- Carboxylic acids may be very good candidates to look at as tracer compounds (agreeing with J. Schauer), while aldehydes may not, because of their reactivity.

Recommendations

- Determine the importance of particle phase reactions as a source of SOA.
- Determine the importance of sesquiterpenes in SOA formation.
- Clarify the impact of drought and relative humidity on biogenic emissions so that these factors can be incorporated into emission models.
- Define the integrated chemical mechanisms necessary to predict SOA from biogenics and aromatic precursors
- Develop new analytical techniques to detect and quantify particle phase reactions. These need to be non-invasive or “chemically soft” so that complex particle phase reaction products are not decomposed.

References

- ¹ Went, F.W, Organic Matter in the Atmosphere, and its possible Relation to Petroleum Formation, Proc National Academy of Sciences, Botany, 212-221, 1959.

- ² Guenther, A.B.; Monson, R.K.; Fall, R.; Isoprene and Monoterpene Emission Variability: Observation with Eucalyptus and Emission rate Algorithm Development, *J. Geophys. Res.*, 96, 10799-10808, 1991
- ³ Griffin, R. J.; Cocker, D. R., III; Flagan, R. C.; Seinfeld, J. H. Organic Aerosol Formation from the Oxidation of Biogenic Hydrocarbons. *J. Geophys. Res.*, 104, 3555-3567. 1999
- ⁴ Andersson-Sköld Y. and Simpson D., Secondary Organic Aerosol Formation in Northern Europe: a Model Study, *J. Geophys. Res.*, 106, 7357-7374, 2001
- ⁵ Helmig D., L ; Klinger, L.F.; Greenberg, J.; Zimmermann, P.; Emissions and Identification of Individual Organic Compounds From Vegetation in Three Ecosystems in the U.S., 207 ACS Meeting Am. Chem. Soc., San Diego, California, 13-18, March 1994.
- ⁶ Yu, J.; Griffin, R.J.; Cooker III, D.R.; Flagan, R.C.; Seinfeld, J.H.; Observations of Gaseous and Particulate Products of MonoTerpene Oxidation in Forested Atmospheres, *J. Geophys. Res. Let.*, 26, 1145-1148, 1999
- ⁷ Hannele, H.; Laurila, T.; Rinne, L.; Puhto, K.; The Ambient Concentration of Biogenic Hydrocarbons at a Northern European, Boreal Site, *Atmos. Environ.*, 4971-4982, 2000.
- ⁸ Ehhalt, D.H. Gas phase chemistry of the troposphere, pp. 21-109, in R. Zellner (edit.), *Global Aspects of Atmospheric Chemistry*, Steinkopff-Verlag, Darmstadt, and Springer-Verlag, New York, 1999.
- ⁹ Kurtenbach, R.; K.J. Brockmann, J. ; J. Lorzer; A. Niedojadlo; K. H. Becker |VOV-Measurements in Urban Air of the City of Wuppertal, in TFS-LT3 annual Report (German), K.H. Becker editor, 1998.
- ¹⁰ Fujita, E.M.; Z. Lu; L. Sheetz; G. Harshfeld; B. Zilinska Determination of Mobile Source Emissions Fraction Using Ambient Field Measurements, Report to the Coordinating Research Council (CRC), 215 Perimeter Center Parkway, Atlanta, GA, 1997.
- ¹¹ Ciccioli, R.; E. Brancaleoni; M. Frattoni The Reactive Hydrocarbons in the Atmosphere at Urban and Regional Scales, in Reactive Hydrocarbons in the Atmosphere, C.N. Hewitt(editor) Academic Press, San Diego, 1999.
- ¹² Goldan, P.D., Kuster, W.C. ; Fehsenfeld, F.C.; Montzka, S.A.; Hydrocarbon Measurements in the Southeast United States: the Rural Oxidants in the Southern Environment (ROSE) Program 1990, *J. Geophys. Res.*, 100, 259454-25963, 1995.
- ¹³ Sagebiel, J.C.; Zielinska, B.; Rierson, W.P.; Gertler, A.W.: Real-World Emissions and Calculated Reactivities of Organic Species from Motor Vehicles, *Atmos. Environ.*, 30, 2287-2296, 1996.
- ¹⁴ Jang, M.; Kamens, R.M.; Characterization of Secondary Aerosol from the Photooxidation of Toluene in the Presence of NO_x and 1-Propene, *Environ. Sci. Technol.*, 35, 3625-3639, 2001
- ¹⁵ Prager, M. J.; Stephens, E. R.; Scott, W. E.; Aerosol Formation for Gaseous Air Pollutants, *Ind. Eng. Chem.* 52, 521-524, 1960
- ¹⁶ Izumi, K.; Fukuyama, T.; Photochemical Aerosol Formation From Aromatic Hydrocarbons in the Presence of NO_x, *Atmos. Environ.* 241, 1433-1441, 1990
- ¹⁷ Hatakeyama, S.; Izumi, K.; Fukuyama, T.; Akimoto, H. ; Reactions of ozone with α -pinene and β -pinene in air: yield of gaseous and particulate products. *J. Geophys. Res.* 20, 13013-13024, 1989.
- ¹⁸ Yu, J., Flagan R. C.; Seinfeld, J.; Identification of products Containing -COOH, -OH, -C=O in Atmospheric Oxidation of Hydrocarbons, *Environ. Sci. and Technol.*, 32, 2357-2370, 1998.
- ¹⁹ Jang, M., and R. M. Kamens, Newly characterized products and composition of secondary aerosols from reaction of α -pinene with ozone, *Atmos Environ.*, 33, 459-474, 1999.
- ²⁰ Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/Particle Partitioning and Secondary Organic Aerosol Yields, *Environ. Sci. Technol.*, 30, 2580-2585, 1996.
- ²¹ Glasius, M., Lahaniati, M.; Caligirou, A.; Di Bella, D.; Jensen, N. R.; Hjorth, J.; Duane M. J.; Kotzias, D.; Larsen B. R.; Carboxylic Acids in Secondary Aerosols from Oxidation of Cyclic Monoterpenes by Ozone, *Environ. Sci. and Technol.* 34, 1001-1010, 2000.
- ²² Hull, L. A. Terpene Ozonolysis Products. In Atmospheric Biogenic Hydrocarbons; Bufalini, J. J.; Arnts, R. R., Eds.; Ann Arbor Science: Ann Arbor, MI, 1981; Vol. 2, 161-186, 1981
- ²³ Griffin, R. J.; Cocker, D. R., III; Flagan, R. C.; Seinfeld, J. H. Organic Aerosol Formation from the Oxidation of Biogenic Hydrocarbons. *J. Geophys. Res.*, 104, 3555-3567. 1999
- ²⁴ Pankow, J. F. An absorption model of gas/particle partitioning of organic compounds in the atmosphere *Atmos. Environ.* 28, 185-188, 1994.
- ²⁵ Schauer, J.J.; Rogge, W.F.; Hildemann, L. > M.; Mazurek, M.; Cass, G.R.: Source Apportionment of Airborn Particulate Matter Using organic Compounds as Tracers, *Atmos. Environ.*, 30, 3837-3855, 1996.

- ²⁶ Kamens, R. M., and Jaoui, M., Modeling aerosol formation from α -pinene + NO_x in the presence of natural sunlight using gas phase kinetics and gas-particle partitioning theory, *Environ. Sci. Technol.* 35, 1394-1405, 2001.
- ²⁷ Jang, M., Kamens; R.M, Atmospheric Secondary Aerosol Formation by Heterogeneous Reactions of Aldehydes in the Presence of a Sulfuric Acid Aerosol Catalyst *Environ. Sci. Technol.*, 35, 4758-4766, 2001.

Question #7—What current sampling and measurement technologies are available to measure marker components? How can they be practically applied at urban and remote locations?

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Sampling

At present the most commonly used method is filter collection of ambient aerosol, followed by laboratory analyses. Since organic compounds, including secondary organics, are associated with fine particles (i.e. below 2.5 μm aerodynamic diameter), the use of an appropriate cut-off inlet is necessary. From the point of view of a sample size, a cyclone, which allows for higher sampling flow, is recommended. The selection of a filter depends on the type of analysis that will be run on the sample later. For thermal carbon analysis, a quartz fiber filter is appropriate, since it withstands temperatures up to 1000 °C. However, due to the large specific surface area, a quartz filter is prone to positive sampling artifact, i.e. adsorption of organic gases during sample collection. Teflon membrane filters have much smaller exposed surface area and are thought not to adsorb organic gases, but they are not thermally stable and not easy to use for extraction. Teflon-coated glass fiber filters (TIGF) are not stable enough in high temperatures to be used for carbon analyses, but they are an excellent choice for the collection of samples to be used for organic solvent extraction. The effectiveness of Teflon coating in reducing adsorption has not been studied; however, our data (B.Zielinska, unpublished results) indicate that the adsorption is not significant for these types of filters.

Impactors can be used to obtain size-segregated samples of organic aerosol, however due to the small sample sizes, their application to the detailed chemical speciation of organic aerosol is still limited. Particles collected in impactors are usually subjected to smaller pressure drops than filter-collected samples, resulting in lower losses due to volatilization. Particle bouncing may be a problem, especially at low humidity, since organic analysis excludes the use of grease.

The denuder strips the gas-phase species from the air stream by diffusion to an adsorbent surface (e.g. activated carbon, XAD resins, etc.) before collection of the particles on a filter. Since the removal of gas-phase organics disturbs the gas-particle equilibrium and drives the volatilization of the particulate material from the filter, an adsorbent bed (such as polyurethane foam, XAD resins, etc) should be used downstream of the filter to capture any particle-phase organics volatilized from the filter. To obtain meaningful data from the denuder sampling, the collection efficiency of the denuder should be either 100% or be accurately known for the species to be measured under variety of ambient conditions. It has been shown (R. Rasmussen, private communication) that the efficiency of activated charcoal denuders is greatly influenced by ambient humidity.

Analyses

A variety of methods are used to characterize organic carbon in atmospheric PM samples. The methods may be divided into “total” or “bulk” methods that characterize only certain properties of organic PM (such as organic carbon content, functional groups, isotope ratios, etc) and molecular-level methods that characterize individual organic compounds.

“Bulk” Methods

The “bulk” methods include thermal/optical carbon analysis (TOC) and various spectroscopic methods. TOC allows for measuring and separating total amount of organic and elemental carbon (OC/EC). The definition of OC and EC is operational only and it is tied to the method of carbon measurement and do not necessary correspond to a physical meaning of “organic” or “elemental” carbon. For obtaining the estimation of organic compound mass concentration, the OC concentration is generally multiplied by values ranging from 1.2 to approximately 1.8 to account for hydrogen, oxygen and other elements that constitute organic molecules. However, this factor itself is a source of uncertainty, since it depends on organic compound composition, which may be different in different locations. In remote locations, the higher contribution of secondary organic aerosol, which contains higher proportion of oxygenated (oxidized) compounds, would result in a higher average molecular weight per carbon weight ratio.

Fourier transform infrared (FTIR), Raman, nuclear magnetic resonance (NMR) and other spectroscopic methods provide functional group and bond information. FTIR spectra can be obtained directly from ZnSe impactor substrates, without extraction. The methods do not provide quantitative information, or the information concerning individual compounds.

Molecular Level Methods

Organic compound speciation provides the most valuable information about organic aerosol composition, sources, and atmospheric transformation processes. Presently it is not possible to completely resolve all organic carbon mass into concentrations of specific organic compounds and no single analytical technique is capable of analyzing the entire range of organics. The molecular level methods usually require extraction of a sample with organic solvent(s), followed by analysis by gas chromatography/mass spectrometry (GC/MS), GC/FTIR/MS, GC with various detectors, HPLC/MS and other methods.

The most widely used analysis method for complex mixtures of organic compounds is high-resolution capillary gas chromatography with mass spectrometric detection (GC/MS). However, GC/MS methods have typically resolved only 10-15% of the organic mass into specific compounds. This is because high-molecular organics (>C40) and highly polar compounds (especially multifunctional) do not elute through a GC column. Polar organic compounds require derivatization prior to analysis, to convert them into less polar and more volatile derivatives that will elute through a GC column. However, the derivatization techniques are compound-class specific and thus several different methods may be required for a comprehensive analysis of one ambient sample. The derivatization reagent by-products, the complexity of derivatization products, lack of standards, and limited mass spectral libraries makes these analyses difficult and time consuming.

HPLC coupled with a mass spectrometer or a photodiode array detector seems to be especially suitable for the analysis of polar organic compounds. Aqueous solutions can be injected into reverse-phase columns, and polar compounds do not need a derivatization step in order to elute from most of the LC columns. However, LC columns offer less resolving power than GC columns and are usually designed for a narrower compound class. In addition, although several LC/MS systems are commercially available, they are not necessarily optimized for atmospheric research. Further development of separation methods and mass spectral libraries is also needed.

Several new and promising methods have recently been proposed for a molecular-level organic aerosol characterization. For example, flash evaporation by Curie point pyrolysis coupled with GC/MS (CPP-GC/MS) was used for direct analysis of atmospheric semi-volatile organic compounds (Neususs et al., 2000). The advantage of this method is that only a few micrograms of sample is needed (thus it could be used with size-segregated sampling) and no sample preparation is necessary. The disadvantage is that very polar compounds may either not elute from a GC column, or be destroyed during a flash evaporation process.

Capillary electrophoresis (CE) was recently used (Neususs et al., 2000) for analysis of dicarboxylic and hydroxy dicarboxylic acids, as well as the common inorganic ions and methanesulfonate. In CE, ions are separated in a strong electric field, because of their different electrophoretic mobilities. The advantage of this method over ion chromatography and GC or HPLC is that inorganic and organic ions can be analyzed in a single run. Also, the separation efficiency is higher than in LC and the required sample amount is very low.

***In situ* analysis techniques**

An automated carbon analyzer with 1 hour resolution time is now commercially available from Sunset Laboratory, Inc. However, since it uses a quartz filter as a substrate, it does not resolve the problem of positive/negative filter artifacts.

Single particle mass spectrometry is a promising technique for a real time characterization of individual particles. Although there are some differences between various instruments, the principle of operation is to fragment each particle into positive and/or negative ions using either a high-power laser or a heated surface and to measure the ions by a time-of-flight mass spectrometer. At present, quantitative determinations are difficult (or not possible) for this technique, and the instruments are generally more suitable for inorganic than organic species, but the future development of this technique could overcome these challenges.

Summary and Recommendations

Although size-selective and denuder sampling methods are certainly very useful for investigating the property of organic aerosol, a filter sampling method is presently the main method for ambient PM sample collection, due to its simplicity, relatively low cost and a large sample size. To account for semi-volatile organic compounds (SVOC), the filter should be followed by a solid adsorbent, such as PUF plugs, XAD resins, or "sandwich" type PUF/XAD/PUF cartridges. Use of a cut-off inlet (e.g. 2.5 μm) is also recommended.

Research is needed to:

- simplify and standardize derivatization procedures; develop more universal derivatization reagents, standards, and MS libraries;

- further develop HPLC methods, especially LC/MS;
- develop methods that do not require extraction, can be used on-site, and offer better temporal and particle size resolution.

References

Neusüss, C., Pelzing, M., Plewka, A., and Herrmann, H. (2000): A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles: Methods and first results. *Journal of Geophysical Research*, 105, 4513-4527.

Research Recommendations

The following 19 research recommendations are divided into near- (1 to 2 years), middle- (3 to 5 years), and long- (5 to 10 years) time periods. Most recommendations cut across the different topics addressed at the workshop. The recommendations emerged out of the plenary brainstorming session at the end of the workshop in which each participant present shared their thoughts on what needs to be done.

Ideally, each recommendation specifies an expected product, an approach to obtaining that product, and a summary of how the product might be used to support other research recommendations and practical applications.

Near-Term Recommendations

Identify primary and secondary organic compounds and their properties.

This project would produce a data base of specific organic compounds and compound groups along with important properties. The data base would include Chemical Abstract Service and common names for identified compounds, references to reports of their detection, reported concentration ranges, water activities, melting point, boiling point, vapor pressures, codes indicating primary or secondary or both, codes indicating potential sources of precursors, potential quantification methods, and detection limits. The data base would be updatable as new information became available and downloadable from a central location. Queries would allow users to extract data and to place it into usable formats. This data base would be assembled from existing tables created by atmospheric organic chemistry researchers via a survey of these researchers. It would be used to identify which compounds are lacking data that need to be quantified in subsequent experiments. It could also be used by decision-makers to determine organic compounds that might result from different source emissions (John Watson).

Specify thermal evolution carbon temperature fractions that separate organic compounds into more logical groupings than currently applied carbon fractions.

Review, evaluate, and compare light scattering and absorption models.

Document and evaluate procedures for detection of secondary organic compound quantification.

Define reporting conventions, data base, and priorities for aerosol smog chamber experiments and results.

This project would provide a consistent set of reporting conventions for smog chamber secondary organic aerosol experiments. Currently smog chamber experiments tend to fall into two groups, those characterizing the dynamics of aerosol formation and those emphasizing aerosol chemical speciation. Data acquired during these experiments are not always presented in a consistent format. Possible common reported data might include the following information: temperature, type of lightsource, NO₂ photolysis rate, humidity, seed particle concentration and type, chamber volume, material and surface/volume ratio, initial and final concentrations of VOC, NO, NO₂, O₃ and aerosol . If a public database becomes available, it could also include detailed particle distribution and speciation data and intermediate data in addition to the initial and final values. The establishment of smog chamber research priorities would provide direction for experiments leading to a better understanding of the origins of secondary organic aerosol formation and the atmospheric conditions that affect aerosol growth. The goals of this project could be accomplished by surveying current investigators in the field, however a meeting of these individuals would also prove valuable (Michael Hurley).

Evaluate methods to measure black carbon as a normalization for primary and secondary organic carbon.

Define and organize follow-on topical workshops on organic aerosol issues.

Evaluate national networks for optimal resource allocation.

Middle-Term Recommendations

Measure and tabulate vapor pressures and water activities.

Most of the SOA compounds have intermediate volatilities and therefore exist in both the gas and particulate phases in the atmosphere. Their fraction in the particulate phase depends strongly on temperature and on the concentrations of other organic PM components, and also somewhat on relative humidity. While the framework for understanding these partitioning processes exists, there is little information about the physical properties of the SOA compounds (volatility, behavior in organic and aqueous solutions, etc.). We recommend the measurement of these parameters and their dependence on temperature and composition. A variety of approaches can be used including the investigation of individual compounds, or the analysis of appropriate smog chamber measurements.

Determine shapes, sizes, and surface reaction properties of particles.

Create and disseminate calibration and performance testing standards.

Develop and apply extraction and derivatization procedures that optimize organic aerosol recovery and quantification.

Organic compound speciation provides the most valuable information about organic aerosol composition, sources, and atmospheric transformation processes. The molecular level methods usually require extraction of a sample with organic solvent(s), followed by analysis by gas chromatography/mass spectrometry (GC/MS), GC/FTIR/MS, GC with various detectors, HPLC/MS and other methods. Sequential extractions with solvents of increasing polarity and liquid chromatographic separations are frequently used prior to GC/MS analysis to simplify complex organic mixtures. There is a need to optimize the selection of solvents and extraction procedures to assure the integrity of less stable organic compounds, as well as a need for development of more selective separation methods (particularly solid phase extraction methods).

Highly polar compounds (especially multifunctional) do not elute through a GC column. They require derivatization prior to analysis, to be converted into less polar and more volatile derivatives that will elute through a GC column. The derivatization techniques are compound-class specific and thus several different methods may be required for a comprehensive analysis of one ambient sample. The derivatization reagent by-products, the complexity of derivatization products, lack of standards, and limited mass spectral libraries makes these analyses difficult and time consuming. Since the derivatization methods are currently the main tool for polar compound analysis, research is needed to simplify and standardize the derivatization procedures. There is a need for better and more universal derivatization reagents and less laborious procedures.

Field measurements of secondary precursors and end-products in locations with contrasting source emissions and meteorology.

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Monoterpenes, which are emitted by vegetation, and aromatic compounds, originating from the production and consumption of petroleum fuels, are two classes of gas-phase organic compounds that have been found to produce high aerosol yields in chamber experiments. Aerosol formation events should be investigated in locations where emission rates of these precursors and levels of atmospheric oxidants are expected to be large. Monoterpene emission rates in the United States are greatest in the southeast, northeast Texas, central and northern California, the Pacific Northwest, and high elevations of the Southwest. Forested ecosystems in the southeast, northeast Texas, central California, and the southwest are likely receptors of a complex mixture of atmospheric oxidants from major urban areas. Aromatic compound emissions in Houston and Mexico City are large and produce ambient levels in air that frequently exceed 5 ppbv. These urban areas would be good locations for studies of aerosol formation from anthropogenic precursors. Field experiments should focus on measuring precursors, oxidants, and the likely products of the chemical oxidations to generate data for aerosol model evaluation. Meteorological measurements to support the chemical measurements are essential. It would be desirable to have surface sites established at the candidate locations for long-term monitoring and for conducting intensive field campaigns when, e.g., measurements from aircraft could supplement the surface observations.

Field and laboratory measurements of particulate hygroscopic properties.

Characterize primary emissions of secondary organic precursors and primary oxygenated compounds.

Source types of particulate carbon in the majority of field studies have not been characterized very well. For example, in one recent source apportionment study from Los Angeles, only two medium-duty (rather low mileage) diesel vehicles were used to collect source samples to construct a source signature to represent diesel exhaust.

It is critical to adequately sample the most important source types of primary (and emissions of secondary organic) precursors from the sources thought to be most important contributors to ambient PM_{2.5}. To do so, examine the data from the NFRAQS (<http://www.nfraqs.colostate.edu>) for mobile sources, and the new Gasoline/Diesel PM Split Study in Los Angeles, to get an idea of what sample sizes and characteristics are needed to represent the on-road mobile fleet. In addition, samples from important off-road sources are needed; for example, from locomotives and ship emissions, as well as maybe some data from other source types. We need to understand the relative importance of on- and off-road mobile source contributions to ambient data. This previous discussion covered only mobile sources; what's also important are the other contributors, which may already be sufficiently characterized. One could examine the source profiles from the most recent PM blame apportionment studies to see whether there are chemical differences between similar sources from different studies.

Regarding oxygenated compounds, this whole issue became very much more complicated once the regulators started mandating oxygen contents of fuels. We know already, for example, that diesels are important sources of primary formaldehyde, and once oxygenates were added to gasoline, formaldehyde and acetaldehyde became important emissions from spark ignition vehicles.

From Eric Fujita's work in the NFRAQS, we learned that along with PM, we need to pay special attention to SVOC measurement and characterization, not only because these are important emission species, but we don't know how to apportion them between particle and vapor phase, and therefore, we don't know well how to apportion them in ambient studies. So the best approach is to collect the total exhaust as the sum of PM and SVOCs.

IMPROVE EC/OC data hinted that SOA might not be very important once one understands the importance of smoke and other primary emission sources at the regional sites.

Because the source selection and exhaust collection is so costly, I recommend sacrificing some of the ambient measurements in favor of adequate/sufficient source collection for development of source profiles. We will not be able to do apportionment properly, and thereby properly characterize the relative importance of primary and secondary organic aerosols, until this is done correctly.

Develop improved information extraction methods for current analytical methods.

Develop and test operational mechanisms for secondary aerosol formation for forecasting models.

Aerosol extinction and other optical properties affect the photolysis rate parameters. For example, the presence of soot particles may decrease photolysis rates by absorbing solar radiation. On the other hand, the presence of other types of particles, particularly fine particles, could increase photolysis rates through increases in radiation scattering. The effect of aerosol particles on photolysis rates is especially important with respect to the formation of secondary organic aerosols because these aerosols are formed through photochemically driven processes. Measurements of spectrally resolved actinic flux should be made in conjunction with other aerosol optical properties. Photolysis rate parameters could then be directly calculated under different aerosol containing atmospheric conditions. Comparison of these kinds of measurements made in urban areas such as Los Angeles in the United States with those made in much more polluted regions such as Mexico City or Shanghai would be helpful in determining the effects of aerosols on photolysis rates.

Long-Term Recommendations

Develop measurement methods that minimize changes in organic composition from that in the atmosphere.

Develop and apply analytical methods to identify and quantify a larger fraction of organic compounds and groups of compounds in suspended particles.

Develop detailed mechanisms and models for secondary organic aerosol formation.

While the description of the formation of the SOA compounds with a constant yield (e.g., 2% of the oxidized precursor) is a first step it is an oversimplification of the chemical processes leading to these products. Several reaction steps are, in general, needed for the formation of the SOA species. Development and testing of the chemical mechanisms leading to these compounds based on smog chamber work will be necessary for the efficient control of these compounds (for example for understanding the effect of NO_x on the formation rates of SOA). The corresponding detailed models should be evaluated against field measurements of the concentrations of these compounds.

STRATEGY FRAMEWORK

Key Organizations for Future Involvement

Future involvement of key organizations and agencies would include funding, expertise, resources, communication and dissemination of information.

- National Science Foundation
- National Park Service
- Environmental Protection Agency
- National Oceanic Atmospheric Administration
- Western Regional Air Program (WRAP)
- Department of Energy
- Ford Foundation
- American Petroleum Institute
- Coordinating Research Council (www.crcao.com)
- Additional Automobile Manufacturers
- Additional Energy Corporations
- Additional Government Agencies
- State Agencies
- Advocacy Organizations

Workgroup Development

Form a group of multi-disciplinary and multi-representational members to build greater capacity to research SOAs. Goals would include developing concrete steps and actions to achieve substantive results in research methods, more effective technologies, measurements, analysis and interpretation.

Early goal: Provide concrete rationale for the study of SOA that links research with policy development

Members of workgroup:

- Agency representatives, including EPA, NPS, USFS, and perhaps relevant state agencies such as the California Air Resources Board;
- Western Regional Air Partnership, as well as the Western Governor's Association;
- Educational and research institutions, (including Desert Research Institute, Reno; Fort Lewis College, Durango, CO; the University of Wisconsin; Carnegie-Mellon University; University of North Carolina; the Oregon Graduate Institute; Stanford University);

- Non-governmental organizations (none have been actively, nor directly, involved to date); Environmental consultants involved as participants in the workshop, many of which have been involved in research for many years.
- Corporations such as Ford and Texaco that have demonstrated interest in the subject of SOAs and the topics discussed at the SOA Workshop 2001.

Meeting Development

Future discussions, meetings, and workshops should emphasize the development of concrete steps and actions to achieve substantive results in research methods, technologies, measurements, analysis and interpretation.

Conference calls have been occurring on a regular basis since August 2001 among core organizers of the Secondary Organic Aerosols Workshop 2001. Intermittent calls had been taking place for as much as three before August 2001. The core organizers include representatives from the EPA, NPS, Fort Lewis College in Durango, Colorado, Desert Research Institute in Reno. Several other individuals joined conversations irregularly. Since August 2001, the calls have been hosted by the NPS, Denver.

The conference call approach allows interested members from several timezones to participate in discussing ideas and issues related to the subject of organic aerosols. Each meeting includes an update of activities occurring related to efforts to improve research potential.

The SOA workshop that took place in Reno was considered by many, if not most, participants to be very successful. There appears to be interest in conducting another one within a year of the February 2002 workshop.

Science Proposals

Description of Selected Proposals Funded by the California Air Resources Board

(Provided by Dongmin Luo, ARB)

Thermodynamics of Organic Atmospheric Aerosols," California Institute of Technology, \$299,122, Contract 98-314

Particulate matter has been implicated in human morbidity and mortality and many researchers suspect that the organic fraction is more potent in terms of adverse health effects. It is now well recognized that primary and secondary organic matter contribute significantly to the particulate burden in the urban atmosphere. The earliest attempts to model the organic fraction of the ambient aerosol assumed that primary emitted organic compounds are inert, totally nonvolatile, and do not interact with other species in the aerosol. The results of more recent studies show that many primary organics are semi-volatile, and interact with other species in the aerosol or gas phases.

This air quality-modeling project includes, for the first time, treatment of inorganic and organic components simultaneously. It addresses the effects of organic constituents on the hygroscopic behavior of aerosols as well as the gas-aerosol equilibrium of secondary organic aerosol components. The basic thermodynamics was formulated based on information in the literature and on data from detailed outdoor smog chamber experiments at Caltech that were incorporated into the current state-of-the-art inorganic equilibrium model known as "SCAPE2". The sensitivity of the model to variations in key atmospheric parameters was also investigated, as was issues of computational efficiency. The two three-dimensional models were tested individually on two episodes in the South Coast Air Basin: Models-3/CMAQ on the August 27-28, 1987 SCAQS episode and CIT on the September 8, 1993 episode. The two components of secondary organic aerosol (SOA), hydrophilic and hydrophobic, were predicted to exhibit quite different behavior. The formation of aqueous-phase SOA was probably limited by partitioning during the day; higher concentrations were predicted at night when relative humidity is high. Despite the formation of secondary species, primary organic carbon represents the dominant component of organic carbon in the South Coast Air Basin. The results of this project are absolutely crucial to our ability to model both the inorganic and organic fractions of PM_{2.5} and therefore to construct comprehensive gas/aerosol photochemical models for SIP applications. Information of this type plays a vital role in the design of emissions control programs that reduce airborne particle concentrations in California.

"Quantitative Analysis of Aerosol Time-of-Flight Mass Spectrometry Data using YAADA," Arizona State University, \$50,000.

Researchers are now able to measure the size and composition of single aerosol particles using instruments like the Aerosol Time-of-Flight Mass Spectrometry (ATOFMS) instruments developed by Prof. Kimberly Prather and others. Complete mass spectra are collected on individual particles at a rate of approximately one per second. Thus very large data sets (approximately 200 Megabytes per day) can be collected during a multi-day, multi-instrument experiment. These data sets are too large for ad hoc data analysis techniques. YAADA is a software package of data management and analysis that can be used to process these large data sets. YAADA includes functions to import, plot, and quantitatively analyze ATOFMS data. The import module rapidly converts data from the common ATOFMS data acquisition software and performs quality control checks on the data.

This research project will develop and test a quantification module for the existing program, YAADA, which will allow users to perform quantitative comparisons of ATOFMS and reference sampler data. This will be accomplished by comparison of ATOFMS data and collocated impactor measurements of aerosol mass to determine particle detection efficiencies for the modified ATOFMS design used in the Bakersfield study. It will also compare ATOFMS data and collocated impactor measurements of aerosol carbon to determine chemical sensitivity of ATOFMS instruments for organic and elemental carbon. The resulting software will allow for a much wider analysis of the ATOFMS data collected under other ARB contracts. Quantitative aerosol measurements are needed to better understand the sources, transformations, and fate of ambient particles in order to understand the effects of particulate matter on global climate, human health, and regional visibility.

"Impact of NO_x Surface Reactions on the Formation of Particles and Ozone, and the Development of Control Strategy Options," University of California, Irvine, \$400,003

The development of effective control strategies for ozone, particles, and associated photochemical air pollutants depends on an accurate description of the atmospheric chemistry of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in air quality models. While the gas-phase chemistry is reasonably well understood, the heterogeneous gas-liquid chemistry, especially for NO_x is still not understood. As a result, current air quality models either do not

include heterogeneous NO_x chemistry at all, or treat it inaccurately. This project will address two key heterogeneous NO_x reactions that are likely to be important in polluted airsheds in California: the hydrolysis of nitrogen dioxide (NO₂) on wet surfaces and the reaction of nitric oxide (NO) with nitric acid on wet surfaces. The first reaction plays a pivotal role in the initiation of smog formation by producing nitrous acid, which is the major source of ozone-forming hydroxyl radicals at dawn. The second reaction reactivates deposited nitric acid back into photochemically active forms.

Previously, the formation of nitric acid was believed to be an end product of the oxidation processes of NO_x in the atmosphere. This "renoxification" of nitric acid could alter the relative effectiveness of VOC and NO_x controls on the photochemical air pollutant levels. The investigators will quantify the kinetics and mechanisms of the heterogeneous NO_x reactions described above and incorporate these descriptions into air quality models. The improved models will allow accurate assessments of the impact of heterogeneous NO_x chemistry on the formation of photochemical air pollutants and further the development of effective air pollution control strategies.

"Source Apportionment of Fine and Ultrafine Particles in California," University of California, Davis, \$315,000

Airborne particulate matter (PM) has been implicated in increased mortality. A recent estimate is that approximately 20,000 Californians die prematurely each year due to PM. Reducing fine particulate pollution is one of the most difficult environmental challenges facing California because of the great diversity of sources and chemical species involved. Developing a technically defensible PM control program requires identifying the contribution of each source type to the measured PM concentrations, and then estimating the air quality benefits associated with implementing a suite of emission controls. Source apportionment techniques calculate the contribution that different sources make to airborne particulate matter concentrations. In this project, the investigator will perform source apportionment of fine particles (PM_{2.5}), including ultrafine particles. Particle samples collected during several major ambient field monitoring and source sampling studies will be analyzed for the quantity of unique chemical tracers that can be used in a source apportionment analysis. Apportionment of the particulate matter collected from these studies would effectively reveal the contribution that different sources make to fine and ultrafine particle concentrations. Because fine particles have been implicated in serious health effects, a better understanding of source contributions to fine particle concentrations will enable decision-makers to formulate effective control strategies to protect public health.

"Determination of the Contributions of Light-duty and Heavy-duty Vehicle Emissions to Ambient Particles in California," University of California, Riverside, \$333,790

California needs to develop controls to reduce ambient concentrations of aerosols in order to attain the National Ambient Air Quality Standards for particulate matter (PM). Research is required so that a scientific foundation can be created for future PM controls. This research will need to include characterizing directly emitted "primary" aerosols in sufficient detail to link them to particular sources studying the dynamics of particle aging in ambient air, and investigating "secondary" particle formation from gaseous precursors in direct gas-to-particle, droplet, and condensation processes. The principal investigator's previous work with Aerosol Time of Flight Mass Spectrometry (ATOFMS) has demonstrated that ATOFMS can overcome many of the limitations of conventional aerosol analysis. It provides real-time data. Real-time data eliminates problems of long-time sample integration, lags between sample collection and data availability, and positive and negative chemical artifacts. It also provides unprecedented specificity regarding particle size and composition within a heterogeneous mix of particles in ambient air. This proposal will address issues regarding the sampling of motor vehicle aerosols in both semi-

controlled (tunnel experiment) and ambient settings. The results will be used to support emission inventory, aerosol modeling, risk assessment and health effects research programs.

Funding

The first phase of efforts to improve research resources related to secondary organic aerosols culminated in the Secondary Organic Aerosols Workshop, February 4-5, 2002, in Reno Nevada. The following matrix outlines the costs and activities utilized to carry out the project.

It is suggested that Phase II be characterized by continuing communication of issues, methods, and other activities identified during the workshop.

Phase I: August 2001 through March 2002, DRI, Reno, NV

Activity	Cost
Workshop Coordinator	\$
Workshop Emcee	
Lead Presenter Honoraria	
Proceedings Report/Research Strategy	
Indirect Costs	
Staff Support	
Materials	
Match	
TOTAL	\$30,000

Proposed Phase II: 5/02 to 2/02 - Ft. Lewis College, Durango, CO

Activity	Cost
Strategy Implementation Coordination	\$
Workshop Coordinator	
Workshop Emcee	
Honoraria	
Proceedings Report	
Indirect Costs	
Staff Support	
Materials	
Match	
TOTAL	

Potential Funding Sources

National Science Foundation
 Coordinating Resource Council (www.crao.com).
 WRAP, Western Governor's Association
 Office of Federal Activities

Communication

Define and design messages

- That stimulate awareness in key audiences.
- That describe and establish the importance of issues related to secondary organic aerosols.
- That show the significance in tangible ways of secondary organic aerosols.
- That create understanding in laypeople.
- That create interest and involvement of key members of the research community.

Define audiences

- Develop mail lists of key members of educational institutions, organizations, agencies involved in air quality issues, research, policy development, legislative staffs.
- Identify grant and funding sources, then develop a mail list of key contacts and addresses and other information for contacting and building relationships.
- Determine where message should be distributed spatially; i.e., local, state, national levels (internationally?).
- New research participants who are available to become actively and productively involved in efforts.

Identify and design methods of dissemination

Media

- Written
- Oral
- Video
- Visiting presenter to local events.
- Face-to-face presentations upon request by interested organizations.
- Media event displays, presentations.
- Workshop and conference presentations.
- Capitol Hill testimony.

Determine timeframes and key timepoints for distributing messages on short-term and long-term timescales.

- Immediate information that builds awareness.
- Timely delivery associated with legislative activities, benchmarks.
- Funding cycles.

Milestones & Measures

- Dissemination of initial round of RFPs.
- Proposals prepared and accepted.
- Completion of projects.
- Demonstrated implementation of methods, techniques, technology among selected key stakeholders.
- Increase in requests for information from state and national sources.
- Dissemination of key information and products such as reports, experimental technologies.
- Regular, timely discussions through a variety of media, including workshops, online discussions, television and radio, etc.

Appendices

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**February 4-5, 2002
Reno, Nevada**

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Workshop Presentations

**Provided on a Compact Disk in electronic format
Available on Website**

Pre-Workshop Lead Presentation Writeups to the Secondary Organic Aerosols Workshop

Where and when does the IMPROVE data base show high OC/EC ratios that might indicate large contributions of secondary organic aerosol to light extinction?

Dr. William Malm, CIRA, National Park Service

Outline

1. Review geographic extent of IMPROVE network
2. Monitoring methodologies used in the IMPROVE network with an emphasis on Thermal Optical Reflectance (TOR) carbon measurement.
3. General spatial trends in elemental and organic carbon.
4. Literature review of OC/EC source profile measurements using TOR analytic technique.
5. Review of OC/EC measurements found in the IMPROVE monitoring network
 - a. Seasonality of OC, EC, and OC/EC ratios – If biogenic emissions increase during summer months as well as photochemical processes enhanced one might expect seasonal variability in OC and OC/EC ratios.
 - b. Review other mechanisms for seasonal variability in carbon based measurements such as transport and mixing depths. Do we see evidence of these effects in the IMPROVE network.
 - c. Examine OC, EC, and OC/EC ratios in geographic regions known to have significant wild and prescribed fire contributions.
 - d. Examine OC, EC, and OC/EC ratios in urban areas such as Washington DC.
6. From a qualitative perspective rural regions of the eastern United States may have approximately enhanced OC/EC ratios of about a factor of 3-4 suggesting that secondary organics are about a factor of 3-4 greater during summer season compared to winter.
7. Other areas of the United States such as the west coast have OC/EC summer vs winter enhancements that are almost negligible.
8. The north central US appear to be dominated by fire emissions in that the OC/EC ratios are near that for fire related activity and show less seasonal variability than typical eastern sites.
9. Examine long term trends in OC, EC, and OC/EC ratios

10. What role does changes in TOR analytic methodology and artifact corrections play in observed trends in OC, EC and OC/EC ratios?

What are the chemical mechanisms that create secondary organic aerosols, what are their precursors, what are the environmental conditions needed to create and sustain particles, and what are the organic substances in the particles?

Dr. Spyros Pandis, Carnegie Mellon University

1. Precursors

The ability of a given volatile organic compound (VOC) to produce SOA during its atmospheric oxidation depends on three factors:

- The volatility of its products
- Its emission rate (atmospheric abundance)
- Its chemical reactivity

Most VOCs do not form aerosol under atmospheric conditions due to the high vapor pressure of their products. As a result of the above constraints, VOCs that for all practical purposes do not produce organic aerosol in the atmosphere include all alkanes with up to six carbon atoms (from methane to hexane isomers), all alkenes with up to six carbon atoms (from ethane to hexene isomers), benzene and many low-molecular weight carbonyls, chlorinated compounds, and oxygenated solvents.

Aromatics are by far the most significant anthropogenic SOA precursors (Grosjean and Seinfeld, 1989). Compounds like toluene, xylenes, trimethyl-benzenes, etc., have been estimated to be responsible for 50-70% of the secondary organic aerosols in urban areas. The experimental work of Odum et al. (1997) showed that the secondary organic aerosol formation potential of gasoline could be accounted for solely in terms of its aromatic fraction. The rest of the anthropogenic hydrocarbons (alkanes, paraffins, etc.) have been estimated to contribute 5-20% to the SOA concentration depending on the urban area.

Biogenic hydrocarbons emitted by trees are expected to be also an important source of secondary organic particulate matter. Isoprene emitted mainly by deciduous trees does not form organic aerosol under ambient conditions (Pandis et al., 1991) but terpenes (α - and β -pinene, limonene, carene, etc.) and the sesquiterpenes are expected to be major contributors to SOA in areas with significant vegetation cover. In the southeast US α -pinene and β -pinene seem to dominate the monoterpene emissions, while in the northern forests emissions are distributed more evenly among these two pinenes and β ³-carene, d-limonene, camphene, and myrcene (Geron et al., 2000). In some parts of western forests, β -pinene and β ³-carene can be more abundant than α -pinene.

The incremental aerosol reactivity (IAR) is one of available approaches to quantify the ability of a given precursor to the ambient organic aerosol concentration. The IAR is defined as the change in the secondary organic aerosol mass concentration per unit of parent organic reacted. Griffin et al. (1999a) estimated the IARs of some typical SOA precursors for typical atmospheric conditions

(Table 1). The calculated reactivities varied from a fraction of a $\mu\text{g m}^{-3}$ per ppb reacted for the aromatics to several $\mu\text{g m}^{-3}$ for limonene and caryophyllene (a sesquiterpenes).

Table 1. Estimated Incremental Reactivities for Selected VOCs for Typical Atmospheric Conditions (Griffin et al., 1999a)

Precursor	Incremental Reactivity ($\mu\text{g m}^{-3} \text{ppb}^{-1}$)
m-xylene	0.1-0.2
low-yield aromatics	0.25
high-yield aromatics	0.3-0.4
methylpropylbenzene	0.4-0.5
terpinolene	0.4-0.5
ocimene	0.5-0.6
linalool	0.5-0.7
α -pinene	0.5-0.8
diethylbenzene	0.7-0.8
Δ -carene	0.5-1.1
Sabinene	1-1.2
Terpinenes	0.8-1.3
β -pinene	0.8-1.5
Limonene	1.4-2.4
Caryophyllene	6-9

Our understanding of the ability of individual VOCs, at least at semi-quantitative level, to serve as SOA precursors appears to be satisfactory.

2. Formation

There are two important steps in the formation of SOA. The first is the chemical reactions in the gas phase leading to the production of the SOA compounds. These reactions involve the parent VOC, its products, and O_3 , the OH radical, the NO_3 radical, NO_x , etc. The second step is the reversible partitioning of the produced SOA compounds between the gas and particulate phases. A number of processes are involved in this second step including dissolution in the particulate aqueous or organic phase, adsorption, condensation, etc. Small amounts of SOA may also nucleate forming new ultrafine particles. Nucleation of SOA could be a potentially important process for the aerosol number concentration, but is of negligible importance for the SOA mass concentration.

Both the chemical mechanisms leading to the formation of SOA compounds and their partitioning have been the topic of numerous laboratory studies during the last twenty years. The majority of the work has focused on the SOA production during the α -pinene reaction with ozone (there are roughly 20 published studies for this system). Other systems investigated in some detail include the reactions of selected other biogenics with ozone (see for example Yu et al., 1999, Koch et al., 2000, Hoffmann et al., 1998; Glasius et al., 2000; Griffin et al., 1999), α -pinene photo-oxidation in the presence of NO_x , (Kamens and Jaoui, 2001), monoterpene reaction with the NO_3 radical (Hallquist et al., 1999), toluene photo-oxidation (Edney et al., 2000; Hurley et al., 2001), 1-

tetradecene and ozone reaction (Tobias and Ziemann, 2000; Tobias et al, 2000), methylene-cyclohexane and methyl-cyclo-hexene and ozone reaction(Koch et al., 2000), etc.

Development of detailed chemical mechanisms explaining the production of the SOA compounds is an ongoing process (for a review see Calogirou et al., 1999). Because of the chemical complexity, progress has been slow. A good example of this process is the work of Jenkin et al. (2000) on the development of a “possible” mechanism for the production of cis-pinic acid from the ozonolysis of α and β -pinene. Additional work in the development of these mechanisms is necessary as well as evaluation of the results against multiple smog chamber experiments from different laboratories.

The partitioning of the SOA compounds between the gas and particulate phases is a critical step in the overall SOA formation process. Most of the SOA compounds have saturation vapor mixing ratios of the order of 1 ppb and are therefore semi-volatile. Quantifying the fraction of these compounds that is in the particulate phase under given conditions is a major challenge. The current approach suggested first by Pankow and co-workers and refined for SOA by Odum and co-workers assumes the formation of a solution by the SOA compounds. The predicted SOA concentration in this framework is sensitive to the vapor pressures of the SOA compounds, and their temperature dependence, and to the activity coefficient of these compounds in solution. While these physical properties can be calculated by group contribution methods (Jang et al., 1997) or can be estimated by fitting the smog chamber results (Kamens et al., 1999), the uncertainty of the estimated values can be as high as a factor of ten. The success of efforts like the one by Kamens and Jaoui (2001) in reproducing not only the SOA mass concentration time evolution but also of the major gas and aerosol products is encouraging. Similar experiments and theoretical work will be necessary for the reduction of the uncertainty of these models. Measurements of the physical properties of the major SOA components will assist these efforts.

The anthropogenic and biogenic SOA compounds may interact. Increases in the production of one of them may lead to increases in the concentrations of the other by shifting their partitioning towards the particulate phase. Kanakidou et al. (2000) suggested that the increase in anthropogenic SOA since pre-industrial times has resulted in a threefold increase of the biogenic SOA concentrations globally.

Our understanding of the physicochemical processes leading to the SOA formation has improved dramatically during the last decade. A number of models of variable complexity are now available. Evaluation and continued development of these models against multiple smog chamber data and ultimately field observations is the next necessary step in this effort.

3. Composition

Numerous SOA compounds have been identified in laboratory studies (Table 2) but only a few of them (mostly biogenics) have been identified in ambient air. The few field studies that identified unique SOA tracer compounds were designed specifically to achieve this objective and took place mostly in forests.

The list includes a number of unique compounds that could be used as tracers for the quantification of the contribution of selected SOA precursors. Some of these compounds (pinic acid, pinonic acid, norpinic acid, norpinonic acid, etc.) are the result of the oxidation of multiple precursors, but others (hydroxypinonaldehydes, hydroxypinaketones, sabinic acid, etc.) are unique products of a given precursor.

Table 2. SOA Compounds Identified in Laboratory and Field Studies

Precursor	SOA Compound	Ambient Air	Field Studies
a-pinene	Pinic acid Norpinic acid Hydroxypinonaldehydes Pinonic acid Norpinonic acid Pinonaldehyde Norpinonaldehyde Hydroxy-pinonic acid	Yes Yes Yes Yes Yes Yes Yes	Yu et al. (1999) Kavouras et al. (1998;1999)
β -pinene	Pinic acid Norpinic acid Pinonic acid Norpinonic acid Hydroxypina ketones Hydroxy-norpinic acid Hydroxy-pinonic acid	Yes Yes Yes	Yu et al. (1999) Kavouras et al. (1998;1999)
sabinene	Pinic acid Sabinic acid Norsabinic acid Norsabinonic acid Hydroxy-sabina-ketones Sabine ketone	Yes	Yu et al. (1999) Kavouras et al. (1998;1999)
Δ^3 -carene	Pinic acid 3-caric acid hydroxy caronaldehydes 3-caronic acid nor-3-caronic acid caronaldehyde hydroxy-3-caronic acid	Yes	Yu et al. (1999) Kavouras et al. (1998;1999)
Cyclohexene	Adipaldehyde 6-oxohexanoic acid adipic acid glutaraldehyde 5-oxopentanoic acid glutaric acid succinic acid	Yes Yes Yes	
Limonene	Limonic acid Limononic acid Hydroxy-limononic acids		
1-tetradecene	a-hydroxytridecyl hydroperoxides secondary ozonides		

The challenges in this effort are significant. First, there is the difficulty in measuring the concentrations of these compounds. They not only are polar but their concentrations appear to be only a few nanograms per cubic meter. Techniques that have been developed in smog chamber studies can probably be extended to field studies. The second difficulty is the partitioning of these compounds between the gas and particulate phases. As most of them are semi-volatile their

aerosol fingerprint changes continuously. The third difficulty is the reactivity of these compounds. Some of the most volatile ones (pinonaldehyde, nopinone, etc.) have been shown to have atmospheric lifetimes of the order of a few hours. The reactivity of the less volatile ones has not been investigated in any detail. Finally, there is an additional analytical pitfall. Tobias et al. (2000) discovered that when they analyzed the aerosol produced from the reactions of 1-tetradecene and ozone the hydroperoxides, peroxides, and secondary ozonides observed by thermal desorption particle beam mass spectrometry (TDPBMS) thermally decomposed to more volatile compounds including tridecanal, tridecanoic acid, and few unidentified products.

4. Environmental Conditions

The SOA concentrations are expected to be sensitive to the ambient temperature, which will affect both the rates of the gas-phase reactions and the partitioning of the SOA compounds. According to Kamens and Jaoui (2001), a 10°C change in the ambient temperature can change the SOA concentration in the α -pinene/ozone system by as much as a factor of two. Higher temperatures are expected to decrease the SOA yields in this system. Strader and Pandis (1999) suggested that for the ambient atmosphere the increase in production rates with increasing temperature would partially offset the evaporation of SOA. They suggested that intermediate temperatures (around 20°C in their case) could be optimal for the SOA production. Bowman and collaborators proposed that the change in partitioning of SOA at lower temperatures could lead to counterintuitive behavior of the SOA concentration during the day, e.g., a maximum during the night even without any nighttime production.

The role of relative humidity in the SOA production has yet to be elucidated. Edney et al. (2000) argued based on their laboratory measurements that the presence of aerosol liquid water does not significantly increase or decrease SOA yields during the photo-oxidation of toluene in the presence of NO_x. The same lack of sensitivity to relative humidity was reported for the α -pinene/ozone system by Kamens and Jaoui (2001). Jang and Kamens (1998) estimated that the partitioning of a variety of semi-volatile organic compounds (alkanes, alkanolic acids, PAHs, etc.) on secondary organic aerosol (formed from the α -pinene reaction with ozone) was not sensitive to relative humidity. On the other hand, water vapor was found to be an important reactant during the reactions of 1-tetradecene and ozone (Tobias et al., 2000). Seinfeld et al. (2001) estimated that the SOA concentration formed in the α -pinene ozone system increases by roughly 25% as the relative humidity increases from 0 to 90%. The corresponding changes for the other biogenics were 40% for β -pinene/ozone, and 10% of carene. A much larger change (around a factor of 2) was predicted for the cyclohexene/ozone and sabinene/ozone SOA because of the hydrophilicity of their products.

SOA production usually requires sunlight. However, reaction between the nitrate radical and β -pinene, Δ^3 -carene, and sabinene leads to high conversion to aerosol, indicating probable ambient aerosol formation at night when monoterpenes continue to be emitted and the nitrate radical concentration increases (Griffin et al., 1999b; Hallquist et al., 1999). Even if the chemical production of SOA were slow during the night, the SOA concentration could increase during the nighttime by condensation of the SOA compounds that may exist in the gas phase.

High time resolution ambient measurements of OC and EC as well as of some of the major SOA components will be necessary for the improvement of our understanding of the role of environmental conditions in the SOA formation.

References

- Calogirou A., B. R. Larsen, and D. Kotzias (1999) Gas-phase terpene oxidation products: A review, *Atmos. Environ.*, 33, 1424-1439.
- Edney E. O., D. J. Driscoll, R. E. Speer, W. S. Weathers, T. E. Kleindienst, W. Li, and D. F. Smith (2000) Impact of aerosol liquid water on secondary organic aerosol yields of irradiated toluene/propylene/NO_x/(NH₄)₂SO₄/air mixtures, *Atmos. Environ.*, 34, 3907-3919.
- Geron C., R. Rasmussen, R. A. Arnts, and A. Guenther (2000) A review and synthesis of monoterpene speciation from forests in the United States, *Atmos. Environ.*, 34, 1761-1781.
- Glacius M., M. Lahaniati, A. Calogirou, D. Di Bella, N. R. Jensen, J. Hjorth, D. Kotzias, and B. R. Larsen (2000) Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone, *Environ. Sci. Technol.*, 34, 1001-1010.
- Griffin R. J., D. R. Cocker, and J. H. Seinfeld (1999a) Incremental Aerosol Reactivity: Application to aromatic and biogenic hydrocarbons, *Environ. Sci. Technol.*, 33, 2403-2408.
- Griffin R. J., D. R. Cocker, R. C. Flagan, and J. H. Seinfeld (1999) Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, 104, 3555-3567.
- Grosjean D. and J. H. Seinfeld (1989) Parameterization of the formation potential of secondary organic aerosols, *Atmos. Environ.*, 23, 1733-1747.
- Hallquist M., I. Wangberg, E. Ljungstrom, I. Barnes, and K. H. Becker (1999) Aerosol and product yields from NO₃ radical-initiated oxidation of selected monoterpenes, *Environ. Sci. Technol.*, 33, 553-559.
- Hoffmann T., R. Bandur, U. Marggraf, and M. Linscheid (1998) Molecular composition of organic aerosols formed in the a-pinene/ozone reaction: Implications for new particle formation processes, *J. Geophys. Res.*, 103, 25569-25578.
- Hurley M. D., O. Sokolov, T. L. Wallington, H. Takesawa, M. Karasawa, B. Klotz, I. Barnes, and K. H. Becker (2001) Organic aerosol formation during the atmospheric degradation of toluene, *Environ. Sci. Technol.*, 35, 1358-1366.
- Jang M., R. M. Kamens, K. B. Leach, and M. R. Strommen (1997) A thermodynamic approach using group contribution methods to model the partitioning of semivolatile organic compounds on atmospheric particulate matter, *Environ. Sci. Technol.*, 2805-2811.
- Jang M. and R. M. Kamens (1998) A thermodynamic approach for modeling partitioning of semivolatile organic compounds on atmospheric particulate matter: Humidity effects, *Environ. Sci. Technol.*, 32, 1237-1243.
- Jenkin M. E., D. E. Shallcross, and J. N. Harvey (2000) Development and application of a possible mechanism for the generation of cis-pinic acid from the ozonolysis of a- and b-pinene, *Atmos. Environ.*, 2837-2850.
- Kamens R., M. Jang, C. J. Chien, and K. Leach (1999) Aerosol formation from the reaction of a-pinene and ozone using a gas-phase kinetics-aerosol partitioning model, *Environ. Sci. Technol.*, 33, 1430-1438.
- Kamens R. M. and M. Jaoui (2001) Modeling aerosol formation from a-pinene and NO_x in the presence of natural sunlight using gas-phase kinetics and gas-particle partitioning theory, *Environ. Sci. Technol.*, 35, 1394-1405.
- Kanakidou M., K. Tsigaridis, F. J. Dentener, and P. J. Crutzen (2000) Human-activity-enhanced formation of organic aerosols by biogenic hydrocarbon oxidation, *J. Geophys. Res.*, 105, 9243-9254.
- Koch S., R. Winterhalter, E. Uherek, A. Koloff, P. Neeb, and G. K. Moortgat (2000) Formation of new particles in the gas-phase ozonolysis of monoterpenes, *Atmos. Environ.*, 4031-4042.
- Odum J. R., T. P. W. Jungkamp, R. J. Griffin, R. C. Flagan, and J. H. Seinfeld (1997) The atmospheric aerosol-forming potential of whole gasoline vapor, *Science*, 276, 97-99.
- Pandis et al. (1991) Aerosol formation in the photooxidation of isoprene and b-pinene, *Atmos. Environ.*, 25, 997-1008.

- Seinfeld J. H., G. B. Erdakos, W. E. Asher, and J. F. Pankow (2001) Modeling the formation of secondary organic aerosol (SOA). 2. The predicted effects of relative humidity on aerosol formation in the a-pinene, b-pinene, sabinene, carene, and cyclohexene systems, in press.
- Tobias H. J. and P. J. Ziemann (2000) Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and ozone in the presence of alcohols and carboxylic acids, Environ. Sci. Technol., 34, 2105-2115.
- Tobias H. J., K. S. Docherty, D. E. Beving, and P. J. Ziemann (2000) Effect of relative humidity on the chemical composition of secondary organic aerosol formed from reactions of 1-tetradecene and ozone, Environ. Sci. Technol., 34, 2116-2125.
- Yu et al. (1999) Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products, J. Atmos. Chem., 34, 207-258.
- Yu et al. (1999) Observations of gaseous and particulate products of monoterpene oxidation in forest atmospheres, Geophys. Res. Lett., 26, 1145-1148.

Which gas and particle end-products can best distinguish secondary organic aerosol from primary organic particles at receptor locations? How stable are these components and how consistent are their ratios to other components in the secondary organic aerosol “source profile?”

Molecular Marker Tracers for Secondary Organic Aerosols (SOA)

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Background

Speciation of the organic compounds present in the carbonaceous fraction of atmospheric particulate matter samples has been shown to provide powerful insight into the impact of primary air pollution sources on particulate matter concentrations in both the urban and remote locations (Simoneit, 1985; Simoneit, 1986; Simoneit, 1999; Simoneit, et al., 1991). Using gas chromatography mass spectrometry (GCMS) techniques, along with the rich knowledge of organic compound molecular markers, molecular marker chemical mass balance (CMB) models have been developed and applied to apportion the source contributions of direct primary sources of atmospheric particulate matter (Manchester, et al., 2001; Schauer and Cass, 2000; Schauer, et al., 1998; Schauer, et al., 1996; Watson, et al., 1998). These CMB models have been used to apportion the primary source contributions from diesel engine, gasoline-powered motor vehicles, hardwood combustion, softwood combustion, meat cooking operations, road dust, tire wear, vegetative detritus, natural gas combustion and coal combustion. Although these models are still undergoing refinement to reduce apportionment uncertainties and to incorporate additional primary particulate matter sources, these models are reasonably well developed and are currently being employed in a broad range of air quality studies.

Molecular marker CMB models that explicitly apportion the direct primary source contributions to particulate organic carbon (Schauer and Cass, 2000; Schauer, et al., 1998; Schauer, et al., 1996) can be used to quantify an upper limit on secondary organic aerosols. Under conditions where there exists high confidence that all important direct primary sources of particulate matter are incorporated into the molecular marker CMB models, estimates of secondary organic aerosol contribution to particulate matter concentrations can be obtained. However, in many remote locations only limited information on primary sources exists such that secondary organic aerosol estimates of this nature have very high uncertainties. Likewise, all molecular marker models would be greatly enhanced in source profiles for secondary organic aerosols were developed and incorporated in these models. The direct apportionment of secondary organic aerosols would allow a direct mass balance check on particulate matter organic carbon concentrations. For these reasons, there is a great need to identify molecular marker tracers for secondary organic aerosols and develop source profiles for secondary organic aerosols that can be incorporated in CMB models.

Potential Tracers of SOA

Three chemical analysis approaches have been used in the past to identify the organic constituents of secondary organic aerosols (SOA): 1) chemical analysis of laboratory generated SOA formed in smog chamber experiments (Forstner, et al., 1997a; Forstner, et al., 1997b; Glasius, et al., 2000; Jang and Kamens, 2001; Tobias and Ziemann, 2000; Yu, et al., 1999a), 2) analysis of atmospheric particulate matter samples collected in locations where high levels of SOA are expected (Kavouras, et al., 1999; Yu, et al., 1999b), and 3) statistical analysis and chemical structural interpretation of organic compounds speciation measurements of atmospheric particulate matter (Kawamura and Sakaguchi, 1999; Rogge, et al., 1993; Schauer, et al., 1996). Clearly, all three strategies have advantages and disadvantages such that we ultimately seek to have all approaches converge together to identify the organic compounds, which comprise SOA. Table 1 summarizes some of the key classes of compounds that have been identified as contributors to SOA, which may be useful as tracers for SOA. It is important to recognize that within each of these compound classes there exists a broad range of organic compounds with very different chemical structures and likely very different atmospheric precursors. With this said, however, Table 1 does provide a basis to identify potential analytical methods, sampling techniques, and research needs to better prioritize critical uncertainties in the development of SOA tracers. Clearly, on going and future research will be able to add more compound classes to Table 1 and will be able to better link laboratory smog chamber experiments and field measurements.

From a practical perspective, there are three criteria necessary for organic compounds to be useful as tracers for SOA: 1) the source of these compounds in the atmosphere must be dominated by atmospheric chemical reactions and not primary source emissions, 2) the compounds must be reasonable stable in the atmosphere after production, and 3) there must exist a quantitative relationship between SOA production from at least a class of SOA precursors and the tracer compound. Since the chemical structures of SOA precursors have a broad range of chemical structures, it is reasonable to assume that SOA formed from different classes of compounds will have different tracer compounds. The potential compounds classes listed in Table 1 need to be assessed based on the criteria listed above.

Table 1. Selected Classes of Organic Compound Present in SOA Generated in Smog Chamber Experiments, Which Are Potential Tracers for SOA

Compound Class	Precursors in Smog Chamber	Example References	Observed in Atmos.	Example References
Cycloalkyl Diacids	Biogenics	Glasius et al. (2000)	Yes	Kavouras et al. (1999)
Aliphatic Diacids	Cycloalkenes	(Kalberer, et al., 2000)	Yes	Rogge et al. (1993) Kawamura & Sakaguchi (1999)
Aromatic Diacids			Yes	Rogge et al. (1993) Schauer & Cass (2000)
Hydroxy Acids	Cycloalkenes Biogenics Aromatics	Kalberer et al. (2000) Glasius et al. (2000) Jang & Kamens (2001)		
Keto Acids	Cycloalkenes Biogenics Aromatics	Kalberer et al. (2000) Glasius et al. (2000) Jang & Kamens (2001)	Yes	Kavouras et al. (1999) Yu et al. (1999)
Oxo Acids	Cycloalkenes Biogenics Aromatics	Kalberer et al. (2000) Glasius et al. (2000) Jang & Kamens (2001)	Yes	Yu et al. (1999)
Dicarbonyls	Cycloalkenes Biogenics Aromatics	Kalberer et al. (2000) Yu et al. (1998) Jang & Kamens (2001)	Yes	Kavouras et al. (1999) Yu et al. (1999)
Nitrates	PAH Aromatics	Kames et al. (1999) Jang & Kamens (2001)	Yes	Feilberg et al. (2001)

The compound class listed in Table 1 can be divided into three groups: organic diacids, multifunctional carbonyls, and nitrated compounds. The aliphatic and aromatic organic diacids are of specific interest since these compounds have been identified in atmospheric particulate matter samples in both the urban atmosphere (Rogge, et al., 1993) and remote locations marine environments (Kawamura and Sakaguchi, 1999). These measurements suggest that these compounds are relatively stable and may represent near final end product of atmospheric processing. In addition, the primary emissions of many of these compounds are expected to be relatively small (Schauer, et al., 1996). Very little is known about the distribution and atmospheric stability of the cycloalkyl diacids, which are products of atmospheric reactions of biogenics, since these compounds have only been measured in forested regions and in smog chamber experiments. As a result, there is a great need to look for these compounds in other regions, such as downwind of forested regions. If these compounds are reasonably stable in the atmosphere, or if they degrade to other relatively unique compounds, the diacids could be important tools to track SOA since the distribution of diacids may be related to the SOA precursors. Rogge et al. (Rogge, et al., 1993) suggested that the aromatic diacids might result from the degradation of PAH in the atmosphere. Although direct primary emissions of aromatic diacids have been reported (Fraser, et al., 1998; Kawamura and Kaplan, 1987; Simoneit, 1985), it is unclear if the direct primary emissions of these compounds are important contributors to their atmospheric concentrations. Likewise, the exact precursors for these compounds have not been identified in laboratory smog chamber experiments.

The multifunctional substituted carbonyls have been shown to be major components of SOA (Glasius, et al., 2000; Jang and Kamens, 2001; Kalberer, et al., 2000; Yu, et al., 1999a). Since these compounds are likely to undergo further chemical reactions at reasonable high reaction rates, due to their carbonyl functional groups, these compounds may be very difficult to use as tracers for SOA under conditions of long-range transport. Under conditions of near field SOA

production, however, these carbonyl compounds may provide important information on SOA sources and production rates. Further investigations of the stability of these compounds will be needed to better assess their viability as tracers for SOA.

Both nitrated mono-aromatic and nitrated polycyclic aromatic hydrocarbons have been identified as products of atmospheric chemical reactions that are contributors to SOA. Nitrated aromatic compounds may be useful as tracers for SOA produced from mono-aromatic hydrocarbons that result from reactions with nitrogen oxides (Jang and Kamens, 2001). It is important to recognize that different chemical mechanisms will yield different product distribution and likely different amounts of SOA. To this end, tracers for different SOA formation mechanisms from the same SOA precursors may be needed for accurate apportionment of SOA. For this reason, the ability to use nitrated mono-aromatic compounds as tracers for SOA should be further investigated. Feilberg et al. (Feilberg, et al., 2001) investigated the relative primary and secondary contributions to atmospheric contributions of nitro-PAH and that specific nitro-PAH, including 1-nitropyrene and 3-nitrofluoranthene, are dominated by direct primary emissions while other nitro-PAH are dominated by atmospheric chemical reactions. This work further supports the notion that some nitro-PAH could be used as tracers for some SOA reaction mechanisms.

Strategies for SOA Apportionment

It is important to note that some of the potential tracers for SOA are semi-volatile organic compounds, which exist in both the gas and particle-phase at atmospheric conditions, while some have very low vapor pressures and reside almost entirely in the particle-phase. Clearly, the requirements of sampling strategies that seek to collect the semi-volatile compounds and the compounds, which are only present in the particle-phase, will be very different. Although quantitative collection of both semi-volatile and particle-phase organic compounds is desirable for tracing SOA, it is important to note that many existing sampling networks are not equipped with capabilities for semi-volatile organic compounds. Although these sampling networks could be retrofitted, it is important to recognize that the great advantage of these networks is that they are able to efficiently collect a large number of routine samples that can be analyzed retrospectively. Addition of semi-volatile organic compound sampling capabilities on these networks would have significant cost and is not practical. To this end, two different strategies for source apportionment of SOA need to be developed: 1) a strategy that can be applied to routine filter based samples and 2) a strategy that can fully exploit advanced sampling techniques that are likely to be employed in selected field studies. Clearly, SOA contains significant amounts of semi-volatile organic compounds, which needs to be properly addressed in both cases.

The development of source apportionment techniques that only utilize particle-phase measurements will need to exclusively utilize non-volatile tracers, such as the aromatic, aliphatic, and cycloalkyl diacids. Ultimately, these tracers will need to be related to the total non-volatile and semi-volatile SOA concentrations present in the atmospheric particulate matter samples. Potentially, these tracers may be related to an effective SOA concentration that is expressed as an SOA concentration at standardized temperature, humidity, organic particulate matter concentrations. Source apportionment strategies that take advantage of both non-volatile and semi-volatile tracers will still need to face the challenge of accurately measuring or effectively expressing the concentration of SOA in the particle-phase.

Recommendations

- 1) Field studies should be conducted that make adequate measurements of likely SOA tracers and known primary source tracers that can be used in an advanced positive matrix factorization (Ramadan et al., 2001) such that effective profiles for different sources of SOA can be identified. Field studies should be implemented in both regions that are likely impacted by SOA originating from both biogenic and anthropogenic sources.
- 2) Additional smog chamber experiments should be conducted to further investigate the stability of potential tracers for SOA, with specific attention to diacids, multifunctional substituted carbonyls, and nitrated aromatics.
- 3) Better integration of analytical techniques among atmospheric measurements, primary source measurements and laboratory smog chamber experiments to help assess the uniqueness of proposed SOA tracers.
- 4) Smog chamber studies should be conducted to identify the atmospheric reactions and precursors for secondary aromatic diacids.
- 5) More advanced analytical techniques need to be tested to identify novel SOA tracers including isotopic fractionation during SOA production, physical properties, nitrogen containing compounds, and polar organic compounds.

References

- Feilberg A, Poulsen MWB, Nielsen T, Skov H. 2001. Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. *Atmospheric Environment*. 35: 353-366.
- Forstner HJL, Flagan RC, Seinfeld JH. 1997a. Molecular speciation of secondary organic aerosol from photooxidation of the higher alkenes: 1-octene and 1-decene. *Atmospheric Environment*. 31: 1953-1964.
- Forstner HJL, Flagan RC, Seinfeld JH. 1997b. Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: Molecular composition. *Environmental Science & Technology*. 31: 1345-1358.
- Fraser MP, Cass GR, Simoneit BRT. 1998. Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. *Environmental Science & Technology*. 32: 2051-2060.
- Glasius M, Lahaniati M, Calogirou A, Di Bella D, Jensen NR, Hjorth J, Kotzias D, Larsen BR. 2000. Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone. *Environmental Science & Technology*. 34: 1001-1010.
- Jang MS, Kamens RM. 2001. Characterization of secondary aerosol from the photooxidation of toluene in the presence of NO_x and 1-propene. *Environmental Science & Technology*. 35: 3626-3639.
- Kalberer M, Yu J, Cocker DR, Flagan RC, Seinfeld JH. 2000. Aerosol formation in the cyclohexene-ozone system. *Environmental Science & Technology*. 34: 4894-4901.
- Kavouras IG, Mihalopoulos N, Stephanou EG. 1999. Secondary organic aerosol formation vs primary organic aerosol emission: In situ evidence for the chemical coupling between monoterpene acidic photooxidation products and new particle formation over forests. *Environmental Science & Technology*. 33: 1028-1037.
- Kawamura K, Kaplan IR. 1987. Motor Exhaust Emissions as a Primary Source for Dicarboxylic Acids in Los-Angeles Ambient Air. *Environmental Science & Technology*. 21: 105-110.
- Kawamura K, Sakaguchi F. 1999. Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics. *Journal of Geophysical Research-Atmospheres*. 104: 3501-3509.

- Manchester JB, Schauer JJ, Cass GR. The Distribution of Particle-Phase Organic Compounds in the Atmosphere and Source Contributions to Atmospheric Particulate Matter Concentrations During the Southern California Children's Health Study California Air Resources Board Report 98-320: University of Wisconsin-Madison, 2001.
- Rogge WF, Mazurek MA, Hildemann LM, Cass GR, Simoneit BRT. 1993. Quantification of Urban Organic Aerosols at a Molecular-Level - Identification, Abundance and Seasonal-Variation. Atmospheric Environment Part a-General Topics. 27: 1309-1330.
- Schauer JJ, Cass GR. 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. Environmental Science & Technology. 34: 1821-1832.
- Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. Characterization and Control of Airborne Particles Emitted from Air Pollution Sources. Ph.D. Thesis: California Air Resources Board, 1998.
- Schauer JJ, Rogge WF, Hildemann LM, Mazurek MA, Cass GR. 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. Atmospheric Environment. 30: 3837-3855.
- Simoneit BRT. 1985. Application of Molecular Marker Analysis to Vehicular Exhaust for Source Reconciliations. International Journal of Environmental Analytical Chemistry. 22: 203-233.
- Simoneit BRT. 1986. Characterization of Organic-Constituents in Aerosols in Relation to Their Origin and Transport - a Review. International Journal of Environmental Analytical Chemistry. 23: 207-237.
- Simoneit BRT. 1999. A review of biomarker compounds as source indicators and tracers for air pollution. Environmental Science and Pollution Research. 6: 159-169.
- Simoneit BRT, Sheng GY, Chen XJ, Fu JM, Zhang J, Xu YP. 1991. Molecular Marker Study of Extractable Organic-Matter in Aerosols from Urban Areas of China. Atmospheric Environment Part a-General Topics. 25: 2111-2129.
- Tobias HJ, Ziemann PJ. 2000. Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O-3 in the presence of alcohols and carboxylic acids. Environmental Science & Technology. 34: 2105-2115.
- Watson JG, Fujita EM, Chow JC, Zielinska B, Richards LW, Neff WD, Dietrich D. Northern Front Range Air Quality Study (NFRAQS) Final Report, Chapter 4. Reno: DRI, 1998.
- Yu JZ, Cocker DR, Griffin RJ, Flagan RC, Seinfeld JH. 1999a. Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products. Journal of Atmospheric Chemistry. 34: 207-258.
- Yu JZ, Griffin RJ, Cocker DR, Flagan RC, Seinfeld JH, Blanchard P. 1999b. Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. Geophysical Research Letters. 26: 1145-1148.

What are the size, composition, and hygroscopic properties of secondary organic particles that are most likely to affect light extinction? Which end-products and formation mechanisms are likely to cause the largest and smallest effects on regional haze?

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It is clear on a theoretical basis that condensed organics which are moderately to highly polar will take up water under elevated relative humidity conditions. Moderately polar compounds with limited solubility in water will exhibit deliquescence behavior similar to what has been predicted and observed for inorganic compounds like ammonium sulfate: that is, no water uptake will occur

until a minimum relative humidity is reached; at this deliquescence point, substantial water uptake will suddenly occur. More highly polar organic compounds having very high aqueous solubilities should take up water over the entire range of relative humidities (e.g., Saxena and Hildemann, 1997).

Relatively little is known about the composition of potentially hygroscopic organics in the atmosphere, because traditional extraction and derivatization techniques have focused on the recovery of relatively nonpolar compounds. To be potentially hygroscopic aerosol components, organic compounds must have a low enough vapor pressure to partition into the condensed phase under typical ambient conditions, and they must have enough polar substituents to be significantly soluble in water. Candidate hygroscopic organic aerosol components hypothesized to be of potential importance include multifunctional species such as diacids, polyols, and amino acids (Saxena and Hildemann, 1996). Organics with single polar substituents are not of interest: if they are small enough to be relatively polar, they are too volatile to occur in the condensed phase, and if they are of a high enough molecular weight to be condensable, they will be relatively nonpolar despite the hydroxyl or carboxyl group. Since analytical methods for reliably preparing, identifying, and quantifying complex mixtures of polar organic species are not yet well established, only very limited data on polar atmospheric aerosol species are available.

Both primary emission sources and secondary organic aerosols can generate polar organics. For primary aerosol emissions, the more efficient the combustion process, the more nonpolar the organic aerosols emitted. Thus, emissions from diesel combustion only take up 2-3% water as the relative humidity increases from 40 to 90%, whereas wood smoke takes up about 10% water over the same change in relative humidity (McDow et al., 1994). It has also been reported that the aerosol oxidation products of monoterpenes take up 10% water at a relative humidity of 84% (Virkkula et al., 1999).

There is currently substantial disagreement among researchers regarding how much of haze formation may be attributable to water uptake by organics. Some ambient measurements have been published in which a tandem differential mobility analyzer (TDMA) was used to measure the increase in diameter that particles of a given size undergo when exposed to a high relative humidity. Based on thermodynamic calculations using these data, some researchers have reported that ambient organics at certain rural locations may contribute substantially to total water uptake (e.g., Saxena et al., 1995; Dick et al., 2000). However, other researchers measuring increases in light scattering at elevated relative humidities in a rural area have reported that all of the measured increases can be satisfactorily attributed to water uptake by the inorganic species present (Waggoner et al., 1983, Malm and Day, 2001). For one urban area, analysis of TDMA data suggested that the organic aerosol can retard or inhibit water uptake (Saxena et al., 1995).

Despite this disagreement, a conclusion which can be drawn from the currently available evidence is that the relative contribution of organics to water uptake should be most significant under lower relative humidity conditions (Saxena and Hildemann, 1997; Ansari and Pandis, 2000), that is, below the deliquescence points of inorganic hygroscopic species. In addition, the contribution of polar organics to haze formation should be most noteworthy in regions where the ambient aerosol is not dominated by highly hygroscopic inorganic species like ammonium sulfate species.

Organics can span the full range from highly nonpolar (hydrophobic) to highly polar, and they are expected to exist in the atmosphere mainly (i) as coatings on insoluble inorganic cores, and (ii) as solution mixtures with inorganic compounds. Several laboratory-scale research efforts have attempted to examine whether organic coatings can alter the hygroscopic behavior of the core.

Some researchers have seen no measurable changes in the behavior of a hygroscopic core for hydrophobic coatings (e.g., Hansson et al., 1990; Hameri et al., 1992; Cruz and Pandis, 1998; Kleindienst et al., 1999), while others have seen retardation or suppression of water uptake (Andrews and Larson, 1993; Xiong, 1998). For solution mixtures, one research group reported an averaging effect for water uptake by mixtures of hygroscopic organics and inorganics (Virkkula et al., 1999), while another group reported that the extent to which organics enhanced or inhibited water uptake depended on the inorganic salt tested and the fraction of organic material present (Cruz and Pandis, 2000). Thus, substantial additional research is needed to understand what factors (such as particle size, composition of the inorganic component, composition of the organic component, and the thickness of the coating or the relative volume of organic) may influence the rate and amount of water uptake.

For inorganic compounds, a theoretical construct has been developed for predicting hygroscopic behavior as a function of factors like relative humidity, temperature, and composition. For aqueous mixtures of organics and inorganics, the vapor pressure and the activity coefficient will play major roles in determining partitioning and water uptake (Saxena and Hildemann, 1997; Hemming and Seinfeld, 2001). Current methods of estimating these measures via group contribution methods (such as UNIFAC) have not been found to be very precise for the limited number of organic compounds for which measurements are available for comparison. Thus, this is another area where additional research is needed, both to determine these properties under typical ambient conditions for atmospherically-relevant organics, and to develop or refine a group contribution method to more accurately represent the interactions between functional groups on the organic molecules.

In summary, the polar organic compounds in aerosols are most likely to significantly affect light extinction. These can originate from certain primary sources (e.g., wood burning), as well as from the generation of secondary organic aerosol species. Since low volatility organic species will condense onto existing particles, the size distribution of the ambient aerosol will strongly influence the impact of hygroscopic organics on light extinction. It has been pointed out that in urban areas, some common strategies for reducing the mass of airborne particulate matter could paradoxically lead to further degradation in visibility (Kleeman and Cass, 1999). Typical urban mitigation strategies focus on combustion particles (typically less than 0.3 μm) and on sources of dust (typically greater than 2.5 μm); however, this would increase the relative importance of particles between 0.3 and 2.5 μm in size. This remaining "background" aerosol, with sizes that scatter light in an especially efficient manner, will collect more of the condensable secondary organic material, thereby enhancing its ability to generate visible haze.

References

- Andrews, E., and S.M. Larson (1993). Effect of Surfactant Layers on the Size Changes of Aerosol Particles as a Function of Relative Humidity. *Environmental Science & Technology* 27:857-865.
- Ansari, A.S., and S.N. Pandis (2000). Water Absorption by Secondary Organic Aerosol and Its Effect on Inorganic Aerosol Behavior. *Environmental Science and Technology* 34:71-77.
- Cruz, C.N., and S.N. Pandis (1998). The Effect of Organic Coatings on the Cloud Condensation Nuclei Activation of Inorganic Atmospheric Aerosol. *Journal of Geophysical Research* 103:13,111-13,123.
- Cruz, C.N., and S.N. Pandis (2000). Deliquescence and Hygroscopic Growth of Mixed Inorganic-Organic Atmospheric Aerosol. *Environmental Science & Technology* 34:4313-4319.

- Dick, W.D., P. Saxena, and P.H. McMurry (2000). Estimation of Water Uptake by Organic Compounds in Submicron Aerosols Measured during the Southeastern Aerosol and Visibility Study. *Journal of Geophysical Research* 105:1471-1479.
- Hameri, K., M.J. Rood, and H.-C. Hansson (1992). Hygroscopic Properties of a NaCl Aerosol Coated with Organic Compounds. *Journal of Aerosol Science* 23:S437-S440.
- Hansson, H.-C., A. Wiedensohler, M.J. Rood, and D.S. Covert (1990). Experimental Determination of the Hygroscopic Properties of Organically Coated Aerosol Particles. *Journal of Aerosol Science* 21:S241-S244.
- Hemming, B.L., and J.H. Seinfeld (2001). On the Hygroscopic Behavior of Atmospheric Organic Aerosols. *Ind. Eng. Chem. Res.* 40:4162-4171.
- Kleeman, M.J., and G.R. Cass (1999). Effects of Emissions Control Strategies on the Size and Composition Distribution of Urban Particulate Air Pollution. *Environmental Science & Technology* 33:177-189.
- Kleindienst, T.E., D.F. Smith, W. Li, E.O. Edney, D.J. Driscoll, R.E. Speer, and W.S. Weathers (1999). Secondary Organic Aerosol Formation from the Oxidation of Aromatic Hydrocarbons in the Presence of Dry Submicron Ammonium Sulfate Aerosol. *Atmospheric Environment* 33:3669-3681.
- Malm, W.C., and D.E. Day (2001). Estimates of Aerosol Species Scattering Characteristics as a Function of Relative Humidity. *Atmospheric Environment* 35:2845-2860.
- McDow, S.R., M. Vartianen, Q. Sun, Y. Hong, Y. Yao, and R.M. Kamens (1994). Combustion Aerosol Water Content and its Effect on Polycyclic Aromatic Hydrocarbon Reactivity. *Atmospheric Environment* 29:791-797.
- Saxena, P., L.M. Hildemann, P.H. McMurry, and J.H. Seinfeld (1995). Organics Alter Hygroscopic Behavior of Atmospheric Particles. *Journal of Geophysical Research* 100:18,755-18,770.
- Saxena, P., and L.M. Hildemann (1996). Water-Soluble Organics in Atmospheric Particles: A Critical Review of the Literature and Application of Thermodynamics to Identify Candidate Compounds. *Journal of Atmospheric Chemistry* 24:59-109.
- Saxena, P., and L.M. Hildemann (1997). Water Absorption by Organics: Survey of Laboratory Evidence and Evaluation of UNIFAC for Estimating Water Activity. *Environmental Science & Technology* 31:3318-3324.
- Virkkula, A., R. Van Dingenen, F. Raes, and J. Hjorth (1999). Hygroscopic Properties of Aerosol Formed by Oxidation of Limonene, alpha-Pinene, and beta-Pinene. *Journal of Geophysical Research* 104:3569-3579.
- Wagoner, A.P. R.E. Weiss, and T.V. Larson (1983). In-Situ Rapid Response Measurement of H₂SO₄/(NH₄)₂SO₄ Aerosols in Urban Houston: a Comparison with Rural Virginia. *Atmospheric Environment* 17:1723-1731.
- Xiong, J.Q., M. Zhong, C. Fang, L.C. Chen, and M. Lippmann (1998). Influence of Organic Films on the Hygroscopicity of Ultrafine Sulfuric Acid Aerosol. *Environmental Science & Technology* 32:3536-3541.

What are the precursor compounds for secondary organic aerosols? What are the types of vegetation, vehicle exhaust, and burning that emit these precursors and under what conditions?

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Summary

For the purposes of this discussion secondary organic aerosol (SOA) material will be defined as organic compounds that reside in the aerosol phase as a function of atmospheric reactions that occur in either the gas or particle phases. Monoterpenes ($C_{10}H_{16}$), that are emitted from vegetation, have long been implicated in secondary aerosol formation since Went published a paper on the subject in 1960. Monoterpenes represent about 10% of the natural non-methane hydrocarbon (NMHC) emitted by the vegetation to the atmosphere. Terpenes react in the atmosphere with hydroxyl radicals (OH), nitrate radicals (NO_3) and ozone (O_3). Recent measurements of individual terpene concentrations suggest ranges from 10 to 63 pptV. α -pinene tends to be the most ubiquitous terpene. Given its average ambient concentration, and aerosol potential, on a reacted mass basis, it may account for about 20-25% of the potential secondary aerosol mass from terpenoid type compounds; d-limonene may be as high as 20% and α -pinene from 7-15%.

Sesquiterpenes are a class of unsaturated $C_{15}H_{24}$ biogenic compounds also released from vegetation. There is a dearth of data on the emissions strength of sesquiterpenes, although it has been estimated by Helmig et al. that sesquiterpenes may contribute as much as 9% to the total biogenic emissions from plants. Other estimates are much lower. Lifetimes in the presence of a night time average background of NO_3 (5×10^8 molecules cm^{-3}), for all of the sesquiterpenes, with the exception of longifolene, are in the range of 1-5 minutes. In the presence of 30 ppb of O_3 α -caryophyllene and α -humulene have life times on the order of minutes. These compounds on a reacted mass basis have 3-5 times the aerosol potential of either α or β pinene. In addition to monoterpenes and sesquiterpenes, a number of oxygenates are emitted by vegetation. These include alcohols, carbonyls, acetates and organics acids. Of significance is that in many instances the oxygenate emissions may be higher, depending on the plant species, than monoterpene emissions.

Natural and anthropogenic fine aerosol emissions to the atmosphere are on the order of 200 to 300 Tg yr^{-1} . Biogenic aerosols represent ~10% of this figure. A modeling estimate by Griffin et al. for biogenic aerosols is 13 to 24 Tg yr^{-1} ; it is on the same order of magnitude for predictions of anthropogenic soot, and natural or anthropogenic nitrates, but much less than sea salt or natural or anthropogenic sulfate aerosols.

According to the USEPA the major atmospheric sources of aromatics in the US from 1988 to 1998 were solvent utilization and transportation sources. Volatile aromatic compounds comprise a significant part of the urban hydrocarbon mixture in the atmosphere, up to 45% in urban US and European locations. Toluene, m- and p-xylenes, benzene and 1,2,4-trimethyl benzene, o-xylene and ethylbenzene make up 60-75% of this load. In the rural setting the picture is quite different. At a rural site in Alabama in the summer of 1990, aromatics contributed ~1.7% to the overall VOCs. Alkenes were the

major category, with isoprene and α -pinene and β -pinene making up 37, 3.5, and 2% of the VOCs. Alkanes made up 9% and oxygenates 46%. In a recent study on the hydrocarbon emissions from two tunnels aromatic emissions comprised 40-48% of the total nonmethane hydrocarbon emissions for light and heavy duty vehicles. On a per mile bases heavy duty trucks emit more than twice the aromatic mass, that light duty vehicles emit, and the distribution of aromatic is different between these two classes. The six aromatic compounds mentioned above comprised ~60% of the light duty emissions, but only about 27% of the heavy duty emissions.

The chamber work of many investigators clearly demonstrate that aromatics have to potential to generate secondary aerosol material. The primary atmospheric reaction of gas phase aromatics involves the OH radical. This reaction produces a host of dicarbonyls, carboxylic acids, and hydroxy carbonyl compounds. At a TSP concentration of $100 \mu\text{g}/\text{m}^3$, and using the Pankow relationship for absorptive partitioning, 0.1% of the multi carbonyl-OH compound, 0.06% of a buten-al-oic compound, and 15% of a dicarbonyl-alcohol-carboxylic acid would be in the aerosol phase. A host of new ring-opening products, which include oxo-butenoic, dioxo-pentenoic, methyl-oxo-hexendienoic, oxo-heptadienoic and trioxohexanoic carboxylic acids, as well as similar analog aldehydes were recently identified by Jang and Kamens, along with chemical mechanisms to explain their formation have recently been reported. Many of these products were major components in the particle phase. Very few of these products have been observed in ambient samples, although the under predicted receptor modeling of dicarboxylic acid aerosol content by Schauer et al., may be a result of these processes.

Of the major SOA products observed in the Jang and Kamens toluene experiment, the experimental partitioning coefficients between the gas and the particle phases (K_p) of aldehyde products were much higher and deviated more from predicted K_p . This has also been observed with α -pinene systems for product aldehydes such as pinonaldehyde and pinic acid. This is an extremely important result, because it suggests that aldehyde products can further react through heterogeneous processes and may be a very significant SOA generation mechanism for the oxidation of aromatics in the atmosphere. As product aldehydes become incorporated into larger molecules in the particle phase, more parent aldehydes partition from the gas to the particle phase. In a very recent study it has just been reported that inert particles acidified with sulfuric acid can promote these reactions and form much higher yields of secondary products than when acid is not present. This study also shows that dialdehydes such as glyoxal, as well as hexanal and octanal can directly participate in secondary aerosol formation, but this process is significantly enhanced by the presence of an acid seed aerosol. The same phenomena was observed for the reaction of aldehydes and alcohols. The products of particle phase aldehyde reactions that lead to this SOA increase are probably thermally unstable and do not usually survive the workup procedure for traditional analysis techniques.

Based on the above summary of the literature the following research needs are:

1. Determine the importance of particle phase reactions as a source of SOA.
2. Determine the importance of sesquiterpenes in SOA formation.
3. Clarification of the impact of drought and relative humidity on biogenic emissions is needed so these factors can be incorporated into emission models.

4. Integrated chemical mechanisms for predicting SOA from biogenics and aromatic precursors.
5. New analytical techniques to detect and quantify particle phase reactions. These need to be non-invasive or “chemically soft” so that complex particle phase reactions products are not decomposed.

What current sampling and measurement technologies are available to measure these marker components (i.e. of secondary aerosol)? How can these be practically applied at remote locations in pristine environments?

Dr. Barbara Zeilinska

1. Sampling

Organic species are the most numerous class of chemicals, and in the atmosphere each individual compound is generally present as a small proportion of the total amount of organic carbon. In remote locations, where particle concentrations are low, a long sampling time may be necessary, on the order of days, to collect enough sample to satisfy the detection limits of analytical methods. The long sampling time may increase sampling artifacts and limit the information concerning temporal resolution.

1.1 Filter Sampling

At present the most commonly used method is filter collection of ambient aerosol, followed by laboratory analyses. Since organic compounds, including secondary organics, are associated with fine particles (i.e. below 2.5 μm aerodynamic diameter), the use of an appropriate cut-off inlet is necessary. From the point of view of a sample size, a cyclone, which allows for higher sampling flow, would be recommended.

The selection of a filter depends on the type of analysis that will be run on the sample later. For thermal carbon analysis, a quartz fiber filter is appropriate, since it withstands temperatures up to 1000 °C. It can also be extracted with organic solvents for further organic compounds speciation. Both analyses require pre-firing the filter, to clean it of organic impurities. However, due to the large specific surface area, a quartz filter is prone to positive sampling artifact, i.e. adsorption of organic gases during sample collection.

Teflon membrane filters have much smaller exposed surface area and are thought not to adsorb organic gases, but they are not thermally stable and not easy to use for extraction. They cannot be easily pre-cleaned before use, so they may contribute some organic impurities. Teflon-coated glass fiber filters (TIGF) are not stable enough in high temperatures to be used for carbon analyses, but they are an excellent choice for the collection of samples to be used for organic solvent extraction. They can be easily pre-cleaned by extraction with solvents, they are easy to work with (in contrast to quartz filters), are available in many different sizes and types (including filters with improved efficiency for sub-micron particles), and are inexpensive. The effectiveness of Teflon coating in reducing adsorption has not been studied; however, our data indicate that the adsorption is not significant for these types of filters.

Figure 1 shows the comparison of polycyclic aromatic hydrocarbons (PAH) concentrations in diluted (~30 times, using the DRI dilution tunnel) light duty diesel exhaust, collected using a XAD-coated annular denuder (Gundel et al., 1995) and a Teflon-coated glass fiber filter (TIGF, T60A20) backed by a PUF/XAD/PUF “sandwich” cartridge. The filter samples from the denuder and filter/PUF/XAD/PUF sampler are compared (B.Zielinska, unpublished results). The PAH quantified ranged from naphthalene (present entirely in the gas phase) to coronene (adsorbed on particles); see Table 1 for the explanation of mnemonics (methyl-, dimethyl-, and trimethyl-isomers are combined for clarity of presentation). Figure 1 shows a relatively good agreement between denuded and undenuded filter samples, with the denuded filter sample being usually higher than the undenuded sample. This indicates that volatilization during sample collection

(blow-off, negative artifact) is probably more important than filter adsorption for the sample collected on Teflon-coated glass fiber filters.

To account for positive artifact when samples are collected on quartz fiber filters, the second quartz filter is placed behind the first (i.e. QQ combination), or a second sampling port is added containing a Teflon filter followed by a quartz filter (i.e. Q and TQ combination) (McDow and Huntzicker, 1990; Turpin et al., 1994). Since the Teflon filter is thought not to adsorb vapor phase organics, it would trap particles and allow vapors to pass through to the back-up quartz filter. The Q filter alone in the other sampling port would receive both particle and vapor phase material. Thus, a measure of organic carbon (OC) just from particles is found by subtracting the OC present on the back-up Q from that on the single Q. However, it has to be emphasized that this method does not correct for volatilization artifact, which can be substantial in pristine areas with significant secondary aerosol fraction. Literature estimates of artifact contributions to OC mass measurements range from -80% for volatilization-induced bias to +50% for adsorption-induced bias (Turpin et al., 2000).

The other artifacts associated with filter sampling include chemical changes of some of the more reactive organic compounds during prolonged sampling (such as reactions with ozone or nitrogen dioxide in the presence of nitric acid) and contaminations due to the insufficient filter cleaning before sampling or a filter contact with contaminated sampling equipment.

However, despite these disadvantages, this method is capable of providing the most detailed information concerning the secondary organic aerosol, if it is combined with detailed chemical speciation.

1.2 Size Segregated Sampling

Impactors can be used to obtain size-segregated samples of organic aerosol, however due to the small sample sizes, their application to the detailed chemical speciation of organic aerosol is still limited. Particles collected in impactors are usually subjected to smaller pressure drops than filter-collected samples, resulting in lower losses due to volatilization. Particle bouncing may be a problem, especially at low humidity, since organic analysis excludes the use of grease.

A Micro-Orifice Uniform Deposit Impactor (MOUDI) has a sampling rate of 30 L/min. Samples can be collected on substrates such as aluminum foil, which does not adsorb organic gases, and can be analyzed for total carbon by the thermal-optical methods. The information concerning OC/EC split can be also obtained; however, since no optical correction for pyrolysis can be applied, the split is approximate only. This may be more important for ambient samples with higher fraction of secondary organic aerosol than for source samples, since secondary organics tend to be more polar, thus more prone to pyrolysis. The aluminum foil can be extracted and analyzed for selected organic compounds, but the generally low sample mass may preclude detailed organic speciation. However, in our experience, the low sample mass is in part compensated by the very low background of pre-cleaned aluminum foil. This allows the concentration of the extract to a very low final volume (~ 20 μ l), thus allowing for higher analytical sensitivity.

1.3 Denuder Sampling

The denuder strips the gas-phase species from the air stream by diffusion to an adsorbent surface (e.g. activated carbon, XAD resins, etc.) before collection of the particles on a filter. Since the removal of gas-phase organics disturbs the gas-particle equilibrium and drives the volatilization of the particulate material from the filter, an adsorbent bed (such as polyurethane foam, XAD resins, etc) should be used downstream of the filter to capture any particle-phase organics volatilized from the filter. The denuder technique is not really straightforward; the selection of

the correct denuder type, its dimensions, flow rate, etc., greatly influence the results and incorrect conclusions could be drawn if the user is not familiar with the denuder technique.

To obtain meaningful data from the denuder sampling, the collection efficiency of the denuder should be either 100% or be accurately known for the species to be measured under variety of ambient conditions. Denuder collection efficiency depends on the denuder surface area (+), the diffusivity (+) and vapor pressure (-) of the compound, the temperature (-) and flow rate (-) of the air stream, and the presence of competing species, including water vapor (Kamens and Coe, 1997; Lane et al., 1988). (The + and - indicates the effect of increasing each parameter on efficiency). It has been shown (R. Rasmussen, private communication) that the efficiency of activated charcoal denuders is greatly influenced by ambient humidity.

In order to increase the collection efficiency of the denuder, the PC-BOSS was developed by Eatough and co-workers (1999), which uses a virtual impactor upstream of the denuder that removes a majority of the gases and particles smaller than 0.1 μm from the aerosol flow. The disadvantage of this system is that the gas-particle distribution is changed even before the aerosol enters the denuder. In addition, particulate OC estimates have to be corrected for particle losses in the inlet of 46 to 48%.

In summary, although size-selective and denuder sampling methods are certainly very useful for investigating the property of organic aerosol, a filter sampling method is presently the main method for ambient PM sample collection, due to its simplicity, relatively low cost and a large sample size. To account for semi-volatile organic compounds (SVOC), the filter is often followed by a solid adsorbent, such as PUF plugs, XAD resins, or "sandwich" type PUF/XAD/PUF cartridges.

2. Analyses

A variety of methods are used to characterize organic carbon in atmospheric PM samples. The methods may be divided into "total" methods that characterize only certain properties of organic PM (such as organic carbon content, functional groups, isotope ratios, etc) and molecular-level methods that characterize individual organic compounds

2.1 "Total" Analyses

2.1.1 Thermal/Optical Carbon Analysis

Thermal/optical carbon analysis allows for measuring and separating total amount of organic and elemental carbon (OC/EC). The basis of this technique is that organic carbon is volatilized from a sample (collected on quartz filter) when heated without oxygen, whereas oxygen is required for elemental carbon combustion (Johnson et al., 1981; Chow et al., 1993). There are several methods and protocols for conducting these analyses, which can differ in their OC/EC split designation. It is important to realize that the definition of OC and EC is operational only and it is tied to the method of carbon measurement (TOT, TOR, NIOSH 5040, see Chow et al, 2001, for the method comparison) and do not necessarily correspond to a physical meaning of "organic" or "elemental" carbon. For obtaining the estimation of organic compound mass concentration, the OC concentration is generally multiplied by values ranging from 1.2 to approximately 1.8 to account for hydrogen, oxygen and other elements that constitute organic molecules. However, this factor itself is a source of uncertainty, since it depends on organic compound composition, which may be different in different locations. In remote locations, the higher contribution of secondary organic aerosol, which contains higher proportion of oxygenated (oxidized) compounds, would result in a higher average molecular weight per carbon weight ratio. Turpin et al. (2000) suggest that a ratio 1.9 – 2.3 is more accurate for aged aerosol, 2.2 – 2.6 for an aerosol heavily impacted by wood smoke and 3.2 for "water soluble" organic PM.

Although thermal/optical carbon analysis is a useful method in combination with other measurements, it provides very little insight into the types of sources of the organic compounds present.

2.1.2 Spectroscopic Methods

Fourier transform infrared (FTIR), Raman, nuclear magnetic resonance (NMR) and other spectroscopic methods provide functional group and bond information. FTIR spectra can be obtained directly from ZnSe impactor substrates, without extraction. Blando et al. (1998) used sequential rinsing of ZnSe impactor substrates with hexane (to remove non-polar organics), then acetone (to remove polar organic) and finally water (to remove inorganic salt). This method has been used to determine the polarity of various organic functional groups in the sample. The method does not provide quantitative information, or the information concerning individual compounds.

2.2 Molecular Level Methods

Organic compound speciation provides the most valuable information about organic aerosol composition, sources, and atmospheric transformation processes. Presently it is not possible to completely resolve all organic carbon mass into concentrations of specific organic compounds and no single analytical technique is capable of analyzing the entire range of organics. The molecular level methods usually require extraction of a sample with organic solvent(s), followed by analysis by gas chromatography/mass spectrometry (GC/MS), GC/FTIR/MS, GC with various detectors, HPLC/MS and other methods.

2.2.1 GC/MS, GC/FTIR/MS

The most widely used analysis method for complex mixtures of organic compounds is high-resolution capillary gas chromatography with mass spectrometric detection (GC/MS). Sequential extraction with solvents of increasing polarity and liquid chromatographic separation are frequently used prior to GC/MS analysis to simplify the complex organic mixtures. However, GC/MS methods have typically resolved only 10-15% of the organic mass into specific compounds (Turpin et al., 2000). This is because high-molecular organics (>C40) and highly polar compounds (especially multifunctional) do not elute through a GC column. Polar organic compounds require derivatization prior to analysis, to convert them into less polar and more volatile derivatives that will elute through a GC column. However, the derivatization techniques are compound-class specific and thus several different methods may be required for a comprehensive analysis of one ambient sample. The derivatization reagent by-products, the complexity of derivatization products, lack of standards, and limited mass spectral libraries makes these analyses difficult and time consuming.

The most widely used derivatization methods include silylation (replacement of active hydrogen atom in -COOH or -OH functional groups with trimethylsilyl group) and methylation (for example, with diazomethane for mono- and dicarboxylic acids). For ketoacids, dicarbonyls, and hydroxyacids, conversion of carbonyl groups to dibutoxy acetal (Kawamura et al., 1996) and two step derivatization technique with O-(2,3,4,5,6-pentafluorobenzyl) hydroxy amine (PFBHA), followed by silylation with BSTFA (Yu et al, 1998) have been used. This last method utilizes PFBHA reaction with carbonyl group to form oxime derivatives, thus preventing enol formation from carbonyls, since the enol could react with BSTFA and complicate data interpretation.

Since the derivatization methods are currently the main tool for polar compound analysis, research is needed to simplify and standardize the derivatization procedures. There is a need for better and more universal derivatization reagents and less laborious procedures. For example, on-line, inlet based trimethylsilyl derivatization procedure for GC analysis of mono- and dicarboxylic acids has been proposed (Docherty and Ziemann, 2001). This technique involves

the co-injection of analyte and BSTFA reagent, followed by a gas-phase derivatization reaction in the injection port of a GC/FID or GC/MS system. Although the technique was tested for a limited number of compounds (only mono- and dicarboxylic acids), this is certainly a step in a right direction.

The combined GC/FTIR/MS technique offers the advantage of additional information from the FTIR spectrum, complementary to mass spectrum information, and helpful in identification of individual components, especially isomers; often these compounds have very similar mass spectra, but unique IR spectra.

2.2.2 High-Performance Liquid Chromatography (HPLC)

HPLC coupled with a mass spectrometer or a photodiode array detector seems to be especially suitable for the analysis of polar organic compounds. Aqueous solutions can be injected into reverse-phase columns, and polar compounds do not need a derivatization step in order to elute from most of the LC columns. However, compared with GC and GC/MS, HPLC has seldom been used for the study of organic aerosol (Jacobsen et al., 2000). This is probably because LC columns offer less resolving power than GC columns and are usually designed for a narrower compound class. In addition, although several LC/MS systems are commercially available, they are not necessarily optimized for atmospheric research. From the two types of interfaces available between LC and MS, electrospray and particle beam, the particle beam seems to be more promising. Further development of separation methods and mass spectral libraries is also needed.

2.2.3 Novel Analytical Approaches

Several new and promising methods have recently been proposed for a molecular-level organic aerosol characterization. Neususs and co-workers (2000) used flash evaporation by Curie point pyrolysis coupled with GC/MS (CPP-GC/MS) for direct analysis of atmospheric semi-volatile organic compounds. The advantage of this method is that only a few micrograms of sample is needed (thus it could be used with size-segregated sampling) and no sample preparation is necessary. The disadvantage is that very polar compounds may either not elute from a GC column, or be destroyed during a flash evaporation process.

To compensate for this, the same authors (Neususs et al., 2000) proposed to use a complementary method, capillary electrophoresis (CE) for analysis of dicarboxylic and hydroxy dicarboxylic acids, as well as the common inorganic ions and methanesulfonate. In CE, ions are separated in a strong electric field, because of their different electrophoretic mobilities. The advantage of this method over ion chromatography and GC or HPLC is that inorganic and organic ions can be analyzed in a single run. Also, the separation efficiency is higher than in LC and the required sample amount is very low.

Thermal desorption particle beam mass spectrometry has been recently developed and used for identification of secondary organic aerosol products formed in an environmental chamber (Tobias and Ziemann, 2000). In this method, a number of particles were trapped on a cold stage and slowly heated, to separate compounds according to their volatility. This method has a great potential for organic compounds identification formed in controlled laboratory experiments, but it does not have sufficient resolving power to identify and quantify, compound by compound, organic complex mixtures of atmospheric aerosol.

3. *In situ* analysis techniques

3.1 Continuous OC/EC measurements

An automated carbon analyzer with 1 hour resolution time is now commercially available from Sunset Laboratory, Inc. It could be easily deployed in the field; it offers laser-based optical correction capabilities and comparability to NIOSH 5040 Method. However, since it uses a

quartz filter as a substrate, it does not resolve the problem of positive/negative filter artifacts. An automated, continuous carbon analyzer with OC/EC capabilities that does not use any filter as a substrate would be a solution to this problem.

3.2 Single Particle Mass Spectrometry

Single particle mass spectrometry is a promising technique for a real time characterization of individual particles. Although there are some differences between various instruments, the principle of operation is to fragment each particle into positive and/or negative ions using either a high-power laser or a heated surface and to measure the ions by a time-of-flight mass spectrometer (e.g. Thompson and Murphy, 1994; Johnston and Wexler, 1995; Silva and Prather, 1997). At present, quantitative determinations are difficult (or not possible) for this technique, and the instruments are generally more suitable for inorganic than organic species, but the future development of this technique could overcome these challenges.

References

- Blando, J.D., Porcja, R.J., Li, T.H., Bowman, D., Lioy, P.J., and Turpin, B.J. (1998). Secondary formation and the Smokey Mountain organic aerosol: An examination of aerosol polarity and functional group composition during SEAVS. *Environ. Sci. Technol.* 604-613.
- Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A. and Purcell, R.G. (1993). The DRI Thermal/Optical Reflectance Carbon Analysis System: Description, Evaluation and Applications in U.S. Air Quality Studies. *Atmos. Environ.*, **27A**, 1185-1201.
- Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., and Merrifield, T. (2001) Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci. Technol.*, **34**, 23-34.
- Docherty, K. S., and Ziemann, P. J. (2001): On-line, inlet-based trimethylsilyl derivatization for gas chromatography of mono- and dicarboxylic acids. *Journal of Chromatography A*, **921**, 265-275
- Eatough, D.J., Obeidi, F., Pang, Y., Ding, Y., Eatough, N.L., Wilson, W.E., (1999). Integrated and real-time diffusion denuder sampler for PM_{2.5}. *Atmos. Environ.*, **33**, 2835-2844
- Gundel, L.A., V.C. Lee, K.R.R. Mahanama, R.K. Stevens, and J.M. Daisey (1995). Direct Determination of the Phase Distributions of Semi-Volatile Polycyclic Aromatic Hydrocarbons Using Annular Denuders. *Atmos. Environ.*, **29**. 1719-1733.
- Jacobson, M.C., Hansson, H.C., Noon, K.J., and Charlson, R.J. (2000). Organic atmospheric aerosols: Review and state of the science. *Rev. Geophys.* **38**, 267-294.
- Johnson, R.L., J.J. Shah, R.A. Cary, and J.J. Huntzicker (1981). An automated thermal-optical method for the analysis of carbonaceous aerosol. In *Chemical Composition of Atmospheric Aerosols: Source/Air Quality Relationships*, E.S. Macias and P.K. Hopke, eds. American Chemical Society, Washington, DC.
- Johnston, M.V. and Wexler, A.S. (1995). MS of individual aerosol particles. *Analytical Chemistry* **67**, 721A-726A
- Kamens, R.M., Coe, D.L., (1997). A large gas-phase stripping device to investigate rates of PAH evaporation from airborne diesel soot particles. *Environ. Sci. Technol.*, **31**, 1830-1833.
- Kawamura, K., Kasukabe, H., and Barrie, L.A. (1996). Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in Arctic aerosols: One year of observations. *Atmos. Environ.* **30**, 1709.
- Lane, D.A., Johnson, N.D., Barton, S.C., Thomas G., H.S., Schroeder, W.H., (1988). Development and evaluation of a novel gas and particulate sampler for semivolatile chlorinated organic compounds in ambient air. *Environ. Sci. Technol.* **22**, 941-947.
- McDow, S.R. and Huntzicker, J.J. (1990). Vapor adsorption artifact in the sampling of organic aerosol: face velocity effects. *Atmos. Environ.* **24A**, 2563-2571.

- Neusüss, C., Pelzing, M., Plewka, A., and Herrmann, H. (2000): A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles: Methods and first results. *Journal of Geophysical Research*, **105**, 4513-4527
- Silva, P.J. and Prather, K.A. (1997). On-line characterization of individual particles from automobile emissions. *Environ. Sci. Technol.*, **31**, 3074-3080
- Thompson, D.S. and Murphy, D.M.(1994). Analyzing single aerosol particles in real time. *CHEMTECH*, **24**, 30-35
- Tobias,H.J. and Ziemann,P.J. (2000). Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids. *Environ. Sci. Technol.* **34**, 2105-2115.
- Turpin,B.J., Saxena,P., and Andrews,E. (2000). Measuring and simulating particulate organics in the atmosphere: Problems and prospects. *Atmos. Environ.* **34**, 2983-3013.
- Turpin,B.J., Hering, S.V., and Huntzicker,J.J. (1994). Investigation of organic aerosol sampling artifact in the Los Angeles Basin.. *Atmos. Environ.* **28**, 3061-3071.
- Yu, J., Flangan, R. C., Seinfeld, J. H. (1998): Identification of Products Containing -COOH, -OH, and -C=O in Atmospheric Oxidation of Hydrocarbons. *Environ. Sci. Technol.*, **32**, 2357-2371.

Table 1. PAH listed in Figure 1

Mnemonic	PAH
naphth	Naphthalene
mnaph	Methylnaphthalenes (2 isomers)
biphen	Biphenyl
dmenaph	Dimethylnaphthalene (6 isomers)
mebiph	Methylbiphenyls (3 isomers)
tmenaph	Trimethylnaphthalenes (12 isomers)
acnapy	Acenaphthylene
acnape	Acenaphthene
fluore	Fluorene
phenan	Phenanthrene
meflu	Methylfluorenes (3 isomers)
xanone	Xanthone
acquone	Acenaphthenequinone
mephen	Methylphenanthrene (5 isomers)
anrquone	Anthraquinone
dmephen	Dimethylphenanthrene (7 isomers)
anthra	Anthracene
fluora	Fluoranthene
pyrene	Pyrene
bntiop	Benzonaphthothiophene
mefl/py	MePyrene/MeFluoranthene (6 isomers)
bzcphe	Benzo(c)phenanthrene
baanth	Benz(a)anthracene
chrysn	Chrysene
bzantone	Benzanthrone
baa7_12	Benz(a)anthracene-7,12-dione
chry56m	5+6-methylchrysene
bbjkfl	Benzo(b+j+k)fluoranthene
bepyrn	BeP

peryle	Perylene
bapym	BaP
incdpy	Indeno[123-cd]pyrene
bghipe	Benzo(ghi)perylene
dbanth	Dibenz(ah+ac)anthracene
corone	Coronene

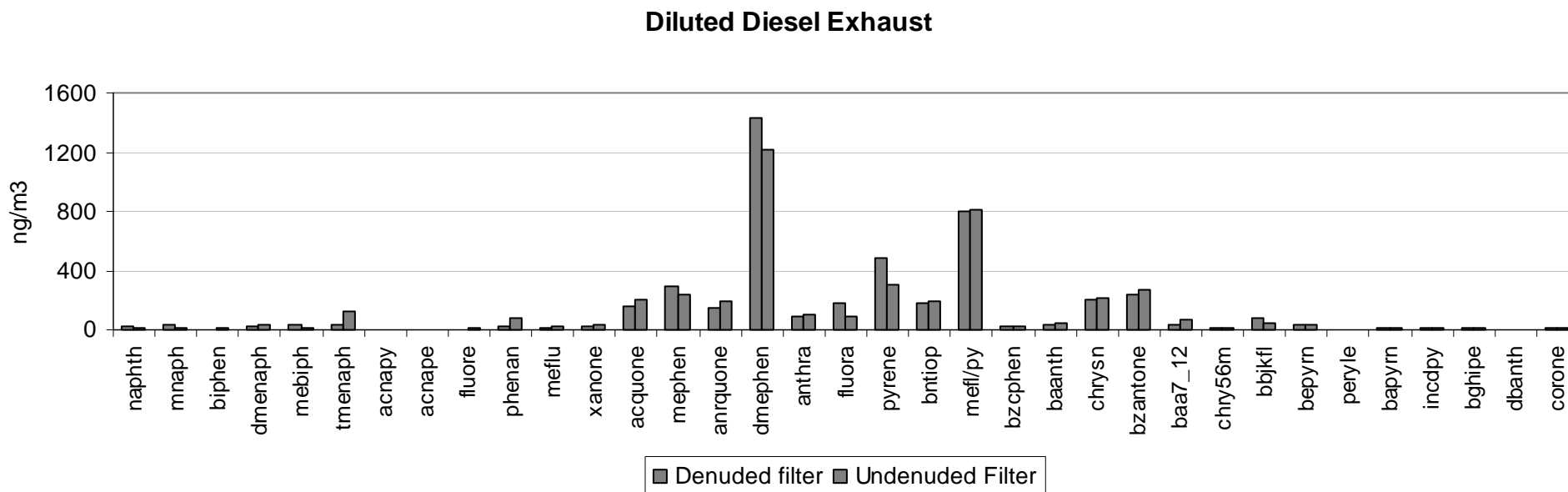


Figure 1. Comparison of PAH concentrations in diluted diesel exhaust collected on denuded and undenuded Teflon-coated glass fiber filters (see Table 1 for the explanation of mnemonics).

Manuscripts Recommended for Reading

Question 4

Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics Kawamura K, Sakaguchi F JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES 104 (D3): 3501-3509 FEB 20 1999

Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. Yu JZ, Griffin RJ, Cocker DR, Flagan RC, Seinfeld JH, Blanchard P GEOPHYSICAL RESEARCH LETTERS 26 (8): 1145-1148 APR 15 1999

Additional Foundation Paper

Source apportionment of airborne particulate matter using organic compounds as tracers Schauer JJ, Rogge WF, Hildemann LM, Mazurek MA, Cass GR ATMOSPHERIC ENVIRONMENT 30 (22): 3837-3855 NOV 1996

James Schauer, Ph.D., PE
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Civil and Environmental Engineering
Wisconsin State Laboratory of Hygiene

Question 5

What are the size, composition, and hygroscopic properties of secondary organic particles that are most likely to affect light extinction? Which end-products and formation mechanisms are likely to cause the largest and smallest effects on regional haze?

P Saxena et al, 1995, "Organics Alter Hygroscopic Behavior of Atmospheric Particles", JGR 100(D9):18,755-18,770.

A Virkkula et al, 1999, "Hygroscopic Properties of Aerosol Formed by Oxidation of Limonene, alpha-Pinene, and beta-Pinene", JGR 104(D3):3569-3579.

CN Cruz and SN Pandis, 2000, "Deliquescence and Hygroscopic Growth of Mixed Inorganic--Organic Atmospheric Aerosol", ES&T 34:4313-4319. Environmental Chemistry and Technology Program.

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Stanford University

Question 7

Jacobson, M.C., Hansson, H.C., Noon, K.J., and Charlson, R.J. (2000). Organic atmospheric aerosols: Review and state of the science. Rev. Geophys. 38, 267-294.

Turpin, B.J., Saxena, P., and Andrews, E. (2000). Measuring and simulating particulate organics in the atmosphere: Problems and prospects. *Atmos. Environ.* 34, 2983-3013.

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Workshop Guest Presenter Abstracts

Source Apportionment of PM_{2.5} and Carbon in Seattle using Chemical Mass Balance and Positive Matrix Factorization

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Three years of PM_{2.5} speciated data were collected and chemically analyzed using the IMPROVE protocol at the Beacon Hill site in Seattle. The data were analyzed by the Chemical Mass Balance Version 8 (CMB8) and Positive Matrix Factorization (PMF) source apportionment models. These models were both used to identify the major sources of PM_{2.5} mass, whereas only the PMF model was used to apportion the sources of organic and elemental carbon. The major sources of PM_{2.5} identified by the PMF model are vegetative burning and diesel vehicles. This is generally consistent with the CMB8 analysis which also identified motor vehicles (combined diesel and gasoline) and vegetative burning as major sources. Both models identified secondary sulfate and nitrate as contributing 20-30% of the PM_{2.5}. Using individual organic carbon (OC) and elemental carbon fractions (EC) in the PMF analysis allowed this model to allocate the PM_{2.5}, OC and EC to vegetative burning, diesel vehicles, gasoline vehicles, fuel oil and secondary sources associated with sulfates. A major difference in the results from the two models was the split between vegetative burning and motor vehicles. In the PMF analysis vegetative burning accounted for 35% of the mass, 57% of the OC and 47% of the EC. The CMB8 model attributed 17% of the PM_{2.5} mass to vegetative burning. Using CMB, motor vehicles accounted for the largest source of PM_{2.5} (44%). Using the PMF model, two motor vehicle source profiles were identified. One profile clearly corresponded to diesel vehicles (16% PM_{2.5}) and accounted for 36% of the total EC and 19% of the total OC in the aerosol. The second motor vehicle source profile was less dominated by EC and likely represents the gasoline and other non-diesel mobile sources. This motor vehicle source accounted for 6% of PM_{2.5}, 4.5% of the total OC, and 1% of the EC. The present study was undertaken to refine the results from previous analyses and to determine the usefulness of applying the PMF model to the Seattle ambient aerosol data. Results from the PMF model add insight to the source apportionment results. We found that using both models produces more robust results than using either model alone. *This work has been funded by the U S Environmental Protection Agency. It has been subjected to Agency review and approved for publication.*

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Secondary vs. Primary Particles

Outcomes of the *Secondary Organic Aerosols Workshop*, 2/4-5/02, Reno, NV., Desert Research Institute

Authors: Alex Laskin, Martin Iedema, James Cowin

Source apportionment of combustion and secondary aerosols is a difficult yet high priority task. We are measuring the quantitative oxygen to carbon ratios in hundreds of thousands of individual particles, using a customized version of computer-automated scanning-electron microscopy/energy-dispersed x-ray analysis. We get quantitative elemental analysis of each particle (down to 0.1 to 0.2 micron in size), for all elements (> B), including the light elements. Different combustion sources have different O/C ratios as averaged over all the particles. The carbonaceous aerosols on a particle-by-particle basis have O/C ratios from 0 to 50%. The O/C ratio measured by this single particle method in just the crabbiness particles, both in the average value, and in the distribution over O/C ratios provide a new method of apportioning combustion aerosols. We also see inorganic markers (S, Ca, N, K, V, Pb, etc) in the same individual carbonaceous particles, that should allow even better apportionment. The inorganic elemental markers can include those that would be otherwise masked by soil, etc. contributions, when only bulk analysis methods are available. Our small automated field collector permits time resolved (1 minute) or time-integrated measurements, and our high analysis rates (up to 50,000 particles per day) make for an effective and relatively inexpensive field tool.

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The Semi-volatile Nature of Secondary Organic Aerosols

Authors: Delbert J. Eatough, Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT

Recent research conducted by Brigham Young University has indicated the following about secondary organic aerosol:

Secondary organic aerosol is essentially all semi-volatile organic material.

Secondary organic aerosol is not retained on the heated filter of a TEOM monitor and hence is not detected by this sampling technique.

Essentially all of the organic material lost from the heated filter of a TEOM sampler is secondary organic aerosol. In addition, secondary ammonium nitrate is also lost.

Some secondary organic aerosol is also lost during sampling from single filter samplers such as the FRM PM_{2.5} sampler and equivalent techniques.

The amount of secondary organic aerosol lost from single filter samplers can vary from less than 1/3 during cold winter conditions to essentially all during warm summer aerosol collection.

Secondary organic aerosol can only be reliably collected using an appropriate denuder sampler.

Either a FRM PM_{2.5} sampler or the IMPROVE sampler can be easily modified to a denuder sampler with filters which can be analyzed by EPA and IMPROVE analytical procedures.

The research upon which these statements are based is briefly summarized in the following paragraphs.

Ammonium nitrate and semi-volatile organic compounds, SVOC, are significant components of fine particles in many urban atmospheres. These components however, are not properly identified with current EPA accepted methods such as the PM_{2.5} FRM or other single filter samplers due to a large loss of semi-volatile material, SVM, from the filter during sampling. Continuous PM_{2.5} mass measurements are attempted using methods such as the R&P TEOM monitor. This method however, heats the sample to remove particle-bound water which also results in evaporation of significant amounts of semi-volatile material.

Continuous RAMS (Eatough et al. 2001) and collocated TEOM monitor PM_{2.5} data have been obtained at the EMPACT and STAR sampling site in Salt lake City and Bountiful, Utah during a two-year period.

Results obtained for the continuous determination of total $PM_{2.5}$ mass with the RAMS have been validated by comparison with results obtained from collocated PC-BOSS (Lewtas et al. 2001, Modey et al. 2001) diffusion denuder integrated samples at the EPA EMPACT and STAR sampling sites in Salt Lake City and Bountiful, Utah during three intensive sampling periods (winter 1999-2000, summer 2000, and winter 2000-2001) (Long et al, 2002a,b). The continuous monitor results are illustrated in Figure 1. The difference between the RAMS and TEOM monitor measurements is due to both semi-volatile organic material and ammonium nitrate (SVM, semi-volatile material) which is not collected by the TEOM monitor. Comparison with single filter samplers (e.g. the FRM $PM_{2.5}$) indicates that the extent of collection of this SVM on a single Teflon or quartz filter is a function of temperature and relative humidity. In humid, winter conditions, an average of 20% of this SVM is lost from single filter samplers. In dry summer condition, essentially all of this SVM is lost from single filter samplers and the FRM $PM_{2.5}$ measurements agree with those obtained by a TEOM monitor (Long 2002b).

The $PM_{2.5}$ data illustrated in Figure 1, obtained using the above listed sampling methods were combined with other atmospheric data (Aethalometer EC and SO_2 , CO and NO_x gas phase data) indicative of emissions from various types of sources to estimate the probable sources of fine particulate material (Long et al. 2002a,b). During the 1-4 August period, the Salt Lake EMPACT site was heavily impacted by emissions from forest fires in the Wasatch Mountains to the east of the sampling site. During this time period, essentially all the $PM_{2.5}$ was from this source. The results of the 1-hour average apportionment calculations for this time period for the concentrations of primary $PM_{2.5}$ from wood smoke and the concentrations of 1-hour average EC measured with an Aethalometer are given in Figure 2. As expected, these two measurements have identical time patterns. In addition, the wood smoke $PM_{2.5}$ apportionment also matched exactly the TEOM monitor data, e.g. see Figure 1. Essentially all of the $PM_{2.5}$ measured by the TEOM monitor during this time period is nonvolatile primary wood smoke. In contrast, the semi-volatile material (SVM, the difference between the RAMS and TEOM monitor) has a different time pattern and is delayed in concentration peaks by 3 to 6 hours, Figure 2. For these samples, all of the SVM is secondary organic aerosol, the concentration of ammonium nitrate in these samples being small. The appearance of the SVM follows the formation of ozone, Figure 3. The SVM not measured by the TEOM monitor (or by the FRM $PM_{2.5}$ sampler) is the secondary organic aerosol formed from photochemical reactions from the organic and NO_x emissions from the forest fires (Long 2002 a,b).

The difference between the RAMS and TEOM monitor for the two winter sampling periods also shown in Figure 1 is also due to secondary aerosol. For these sampling periods both secondary organic aerosol and ammonium nitrate contribute to the SVM. The sources of the gas phase organic material and the NO_x which contribute to this secondary aerosol include emissions from wood smoke, mobile sources and oil refineries.

Evidence for day-time photochemical formation of semi-volatile secondary organic material is also seen in the diurnal pattern of $PM_{2.5}$ in the Pittsburgh urban area. The pattern of formation of sulfate, nonvolatile OM and SVOC at the NETL sampling site in Pittsburgh for a week in July 2001 is shown in Figure 4. Consideration of meteorological and back-trajectory data indicate that sulfate is a secondary aerosol formed during long range transport and the SVOC is secondary organic aerosol formed from local organic gas emissions (Modey 2002). As was the case for the Utah results, the semi-volatile secondary organic aerosol is not measured with either a TEOM monitor or the FRM $PM_{2.5}$ sampler during the summer. Some, but less than half, of this secondary organic aerosol is retained on a single filter sampler during the winter.

Finally, we have recently completed the evaluation of modification of the R&P Speciation monitor for the measurement of semi-volatile secondary organic material. One channel of the sampler was modified by the addition of a small BOSS denuder (Eatough 2001) followed by a filter pack with a quartz filter and a charcoal impregnated glass fiber filter, CIG. The positive quartz filter sampling artifact is eliminated with this sampler and total organic $PM_{2.5}$ material, including the secondary organic aerosol can be determined. A comparison of the results obtained using the PC-BOSS and the modified speciation sampler are shown in Figure 5 (Carter 2002). While, we have analyzed collected CIG samples by a TPV approach, researchers at both the University of Hawaii and Carnegie Mellon University have shown these filters can be analyzed using the EPA speciation analysis protocol.

References

- Carter C., Long R.W., Eatough N.L., Eatough D.J., Olsen N., Wilson W.E. (2002) "Comparison of Speciation Samplers and PC-BOSS Results Obtained on the Wasatch Front During the Winter of 2001-2002," Proceedings AWMA 2002 Annual Meeting, in preparation.
- Eatough D.J., Eatough N.L., Obeidi F., Pang Y., Modey W., Long R.. (2001). "Continuous Determination of PM_{2.5} Mass, Including Semi-Volatile Species," *Aerosol Science and Technology*, 34:1-8.
- Lewtas J., Pang P., Booth D., Reimer S., Eatough D.J., Gundel L.A.. (2001). "Comparison of Sampling Methods for Semi-Volatile Organic Carbon Associated with PM_{2.5}," *Aerosol Science and Technology*, 34:9-22.
- Long R.W., Smith R., Smith S., Eatough N.L., Mangelson N.F., Eatough D.J., Pope C.A. III, Wilson W.E., (2002a) "Sources of Fine Particulate Organic Material Along the Wasatch Front." *Energy & Fuels*, in press.
- Long R.W., Eatough N.L., Mangelson N.F., Thompson W., Feit K., Smith S., Smith R., Eatough D.J.. (2002). "The Measurement of PM_{2.5}, Including Semi-Volatile Components, in the EMPACT Program: Results from the Salt Lake City Study and Implications for Public Awareness, Health Effects, and Control Strategies," *J. Urban Technol.*, submitted.
- Modey W.K., Pang Y., Eatough N.L., Eatough D.J. (2001) "Fine Particulate (PM_{2.5}) Composition in Atlanta, USA: Assessment of the Particle Concentrator-Brigham Young University Organic Sampling System, PC-BOSS, During the EPA Supersite Study," *Atmospheric Environment*, 51: 1302-1308.
- Modey W.K., Eatough D.J., Anderson R.R., Martello D.V., Satoshi T., Lucas L.J., Davidson C.I. (2002) "Diurnal Trends in Ambient Fine Particulate Material (PM_{2.5}) Composition: A 2001 Summer Study at Two Sampling Sites in Pittsburgh," Proceedings AWMA 2002 Annual Meeting, submitted.

Secondary Versus Primary Aerosols

Authors: Gary Casuccio, Traci Lersch, Steven Schlaegle

The characterization and apportionment of the carbonaceous component associated with PM_{2.5} is of great interest because it typically comprises a significant amount of the sample mass. Although much has been learned in recent years on elemental and organic carbon, there is still much to be learned. Electron microscopy methods (scanning electron microscopy, computer controlled scanning electron microscopy and transmission electron microscopy) can be used to provide detailed information (size, morphology and elemental composition) on individual particle characteristics that can be used to complement bulk analytical results. This presentation will provide a brief overview of the capabilities of the various electron microscopic techniques and how they are being used to assist in the characterization of carbonaceous particulate matter. The presentation will also discuss the potential to integrate Raman spectroscopy instrumentation with the scanning electron microscope to provide information on molecular structure.

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Hydration

Authors: Alex Laskin, Martin Iedema, James Cowin

Hygroscopicity of particles, and their ability to nucleate condensation, are strong functions of the particle composition, and will be strongly influenced by even very thin coatings of hygroscopic or hydrophobic compounds. And this changes with time as the particles age. We use an "environmental" scanning electron microscope, that is fully automated, to look at the hygroscopic nature of field-collected particles, from 0 to 100% relative humidity. It is differentially pumped, permitting a technique normally requiring vacuum conditions to operate at ambient water vapor pressures. The size of the particles is noted automatically as the relative humidity is raised. Then after re-evacuation, the same particles are analyzed elementally (>boron) by automated energy-dispersed x-ray analysis. Hundreds or thousands of particles can be studied per hour. The field collector for this is a small automated device that permits time resolved (1 minute) or time-integrated measurements. The particles are sealed and refrigerated... an archive for the humidity/elemental studies.

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Radiocarbon Measurements of SOA-Relevant Fractions for Source Attribution

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Radiocarbon (¹⁴C) measurements of atmospheric fine particulate matter (PM_{2.5}) provide a quantitative distinction between fossil-fuel-derived PM_{2.5} and biogenic sources of PM_{2.5} for source attribution. The ¹⁴C method has been applied to EPA-NIST projects over the last two decades, most recently in Nashville (SOS, 1999) and the Houston Area (TexAQ_S2000). These studies involved summertime PM_{2.5} which showed that natural biogenic sources are responsible for as much as 50% of the organic PM_{2.5} in these areas. Future intensive studies to model sources of secondary organic aerosol (SOA) through chemical measurements should include comparisons with ¹⁴C measurements of SOA-relevant organic fractions. We propose for consideration a multi-component isotopic and chemical study of the seasonal composition of primary and secondary organic aerosol. Seasonal comparisons are likely to be important to help distinguish natural sources of SOA from anthropogenic sources of primary as well as secondary aerosols. Emphasis would be on high-volume integrated sampling (>100 L min⁻¹) for tens-of-microgram quantities of particulate-organic carbon with robust procedures for artifact correction, as well as semi-volatile organic

carbon using, for example, the PC-BOSS system. The preparative chemistry would involve exhaustive extractions and methodologies including pressurized fluid extraction to isolate hydrophilic and hydrophobic compounds associated with SOA. Instrumental techniques such as GC-MS, Thermal Desorption-GC-MS, LC, LC-MS need to be developed to provide the means to identify as well as separate individual compounds via automated fraction collection to isolate SOA-relevant fractions for ^{14}C measurement.

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Measurement Methods

Authors: Alex Laskin, Martin Iedema, James Cowin

Source apportionment of combustion and secondary aerosols is a difficult yet high priority task. We are measuring the quantitative oxygen to carbon ratios in hundreds of thousands of individual particles, using a customized version of computer-automated scanning-electron microscopy/energy-dispersed x-ray analysis. We get quantitative elemental analysis of each particle (down to 0.1 to 0.2 micron in size), for all elements ($> \text{B}$), including the light elements. Different combustion sources have different O/C ratios as averaged over all the particles. The carbonaceous aerosols on a particle-by-particle basis have O/C ratios from 0 to 50%. The O/C ratio measured by this single particle method in just the crabbiness particles, both in the average value, and in the distribution over O/C ratios provide a new method of apportioning combustion aerosols. We also see inorganic markers (S, Ca, N, K, V, Pb, etc) in the same individual carbonaceous particles, that should allow even better apportionment. The inorganic elemental markers can include those that would be otherwise masked by soil, etc. contributions, when only bulk analysis methods are available. Our small automated field collector permits time resolved (1 minute) or time-integrated measurements, and our high analysis rates (up to 50,000 particles per day) make for an effective and relatively inexpensive field tool.

Multicapillary Collection Device for Speciated Analyses of Organic Aerosols and Vapors

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We are developing a multicapillary diffusion denuder that separates aerosols and organic vapors. Thermal desorption of the denuder and the aerosols with subsequent analysis by high-resolution gas chromatography will provide speciated organic analyses of both phases, information that will be useful in understanding secondary organic aerosol formation. The multicapillary diffusion denuder contains 289, ZB-1 (5 μm film thickness; Phenomenex, Torrance, CA) fused silica capillaries (0.254 m \times 0.53 mm ID,) in a 1.6 cm OD Silcosteel coated (Restek, Bellefonte, PA) stainless steel tube. The column sections are fused together with polyimide resin (HD Microsystems, Parlin, NJ). A glass fiber or quartz filter is positioned downstream of the diffusion denuder for collection of aerosols. The analytes are thermally extracted from the collection device and filters in specially designed thermal desorption units (CDS Analytical, Oxford, PA). The desorbed analytes are cryofocused in a cryogenically cooled, Gerstel inlet that is packed with fused silica wool. Analysis is by high-resolution gas chromatography with a Hewlett Packard 6890 gas chromatograph (Agilent, Wilmington, DE).

***Characterization of fine particle associated organic compounds:
Interlaboratory comparison and development of standard reference
materials***

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Organic chemicals adsorbed to fine particulate matter (PM) in the ambient air account for a major component of the mass and include source tracers as well as toxic compounds that may contribute to adverse human health effects. The US EPA has established a PM 2.5 research program including aerosol characterization studies at seven sites in the US and additional exposure and health studies at PM Research Centers. A working group of investigators from these and related research programs was established to advance the quality and comparability of data on the organic composition of aerosols. This group is conducting a series of interlaboratory trials using interim reference materials. The initial trial utilized particles sieved to less than 63 microns from a bulk portion of standard reference material (SRM) 1649a, Urban Dust, and an extract of these particles. The original SRM 1649, collected in Washington, DC and issued in 1982, has recently been recertified as 1649a (Wise et al. Polycyclic Aromatic Compounds 13:419-456, 2000). The second trial will utilize PM2.5 samples recently collected in Baltimore. A new bulk PM2.5 sample will be collected from the same site for a final expanded trial and development of a new SRM for contemporary PM2.5. Results from these trials will provide the basis for improved quality assurance measures and methods for characterizing the organic matter associated with PM. The target organic analytes vary among the participants and include: alkanes (including hopanes and cholestanes), alkenes, aromatic and polycyclic aromatic hydrocarbons (PAH), nitrated PAH, sterols, carbonyl compounds (e.g., ketones and aldehydes), acids (alkanoic and resin acids), phenols, methoxy phenols, and sugars. The participating laboratories are not constrained by a specific analytical method, however the analytical methods will be reported as well as detection and quantification limits. *This work has been funded by the U S Environmental Protection Agency. It has been subjected to Agency review and approved for publication.*

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Bibliography of Publications Related to Secondary Organic Aerosols

- Aalto,P.P., Hameri,K., Becker,E., Weber,R., Salm,J., Makela,J.M., Hoell,C., O'Dowd,C.D., Karlsson,H., Hansson,H.C., Vakeva,M., Koponen,I.K., Buzorius,G., Kulmala,M. (2001). Physical characterization of aerosol particles during nucleation events. *Tellus Series B-Chemical and Physical Meteorology*, **53**:344-58.
- Alcock,R.E. and Jones,K.C. (1999). New organic compounds in the environment. *Atmos. Environ.* **33**, 1645-1646.
- Allen,J.O., Dookeran,N.M., Taghizadeh,K., Lafleur,A.L., Smith,K.A., and Sarofim,A.F. (1997). Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environ. Sci. Technol.* **31**, 2064-2070.
- Allen,J.O., Durant,J.L., Dookeran,N.M., Taghizadeh,K., Plummer,E.F., Lafleur,A.L., Sarofim,A.F., and Smith,K.A. (1998). Measurement of C₂₄H₁₄ polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environ. Sci. Technol.* **32**, 1928-1932.
- Alves,C., Pio,C.A., and Duarte,A.C. (2000). Particulate size distributed organic compounds in a forest atmosphere. *Environ. Sci. Technol.* **34**, 4287-4293.
- Ambe,Y. and Mukai,H. (1997). Long term stability of benzo [a] pyrene in stored atmospheric particulate matter samples. *Chemosphere* **34**, 2023-2028.
- Andersson-Skold,Y. and Simpson,D. (2001). Secondary organic aerosol formation in northern Europe: A model study. *J.Geophys.Res.*, **106**:7357-74.
- Andrews,E. and Larson,S.M. (1993). Effect of surfactant layers on the size changes of aerosol particles as a function of relative humidity. *Environ. Sci. Technol.* **27**, 857-865.
- Ansari,A.S. and Pandis,S.N. (2000). Water absorption by secondary organic aerosol and its effect on inorganic aerosol behavior. *Environ. Sci. Technol.* **34**, 71-77.
- Asher,W.E., Pankow,J.F., Erdakos,G.B., and Seinfeld,J.H. (2002). Estimating the vapor pressures of multi-functional oxygen-containing organic compounds using group contribution methods. *Atmos. Environ.* **36**, 1483-1498.
- Atkinson,R., Aschmann,S.M., Carter,W.P.L., Winer,A.M., and Pitts,J.N. (1982). Alkyl nitrate formation from the NO_x-air photooxidations of C₂-C₈ N-alkanes. *J. Phys. Chem.* **86**, 4563-4569.
- Atkinson,R. and Carter,W.P.L. (1984). Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. *Chem. Rev.* **84**, 437-470.
- Atkinson,R., Aschmann,S.M., Carter,W.P.L., Winer,A.M., and Pitts,J.N. (1984). Formation of alkyl nitrates from the reaction of branched and cyclic alkyl peroxy-radicals with NO. *Int. J. Chem. Kinet.* **16**, 1085-1101.
- Atkinson,R. (1986). Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. *Chem. Rev.* **86**, 69.

- Atkinson,R., Aschmann,S.M., and Winer,A.M. (1987). Alkyl nitrate formation from the reaction of a series of branched RO₂ radicals with NO as a function of temperature and pressure. *J. Atmos. Chem.* **5**, 91-102.
- Azevedo,D.A., Moreira,L.S., and Soares de Siqueira,D. (1999). Composition of extractable organic matter in aerosols from urban areas of Rio de Janeiro city, Brazil. *Atmos. Environ.* **33**, 4987-5001.
- Barthelmie,R.J. and Pryor,S.C. (1997). Secondary organic aerosols: Formation potential and ambient data. *Sci. Total Environ.* **205**, 167.
- Bethel,H.L., Arey,J., and Atkinson,R. (2001). Products of the OH radical-initiated reaction of 3-hexene-2,5-dione. *Environ. Sci. Technol.* **35**, 4477-4480.
- Beving,D.E. and Ziemann,P.J. (2000). Effect of relative humidity on the chemical composition of secondary organic aerosol formed from reactions of 1-tetradecene and O₃. *Environ. Sci. Technol.* **34**, 2116-2125.
- Bidleman,T.F., Falconer,R.L., Harner,T. (1999). Particle/gas distribution of semivolatile organic compounds: Field and laboratory experiments with filtration samplers. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane,D.A., Ed. Gordon and Breach Science, Netherlands, pp. 39-71.
- Bigg,E.K. (2001). The aerosol in a boreal forest in spring. *Tellus Series B-Chemical and Physical Meteorology*, **53**:510-9.
- Blando,J.D., Porcja,R.J., Li,T.H., Bowman,D., Lioy,P.J., Turpin,B.J. (1998). Secondary formation and the Smoky Mountain organic aerosol: An examination of aerosol polarity and functional group composition during SEAVS. *Environ.Sci.Technol.*, **32**:604-13.
- Blando,J.D. and Turpin,B.J. (2000). Secondary organic aerosol formation in cloud and fog droplets: A literature evaluation of plausibility. *Atmos. Environ.* **34**, 1623-1632.
- Blando,J.D., Porcja,R.J., and Turpin,B.J. (2001). Issues in the quantitation of functional groups by FTIR spectroscopic analysis of impactor-collected aerosol samples. *Aerosol Sci. Technol.* **35**, 899-908.
- Bowman,F.M., Pilinis,C., and Seinfeld,J.H. (1995). Ozone and aerosol productivity of reactive organics. *Atmos. Environ.* **29**, 579-590.
- Bowman,F.M., Odum,J.R., Seinfeld,J.H., and Pandis,S.N. (1997). Mathematical model for gas-particle partitioning of secondary organic aerosols. *Atmos. Environ.* **31**, 3921-3932.
- Buhr,M.P., Parrish,D.D., Norton,R.B., Fehsenfeld,F.C., Sievers,R.E., and Roberts,J.M. (1990). Contributions of organic nitrates to the total reactive nitrogen budget at a rural eastern U.S. site. *J. Geophys. Res.* **95**, 9809-9816.
- Burtscher,H., Leonardi,A., Steiner,D., Baltensperger,U., and Weber,A. (1993). Aging of combustion particles in the atmosphere - results from a field study in Zurich. *Water Air and Soil Pollution* **68**, 137-147.
- Buzorius,G., Rannik,U., Nilsson,D., Kulmala,M. (2001). Vertical fluxes and micrometeorology during aerosol particle formation events. *Tellus Series B-Chemical and Physical Meteorology*, **53**:394-405.
- Caligiourou,A., Larsen,B.R., and Kotzias,D. (1999). Gas phase terpene oxidation products: A review. *Atmos. Environ.* **33**, 1423-1439.
- Caligiourou,A., Larsen,B.R., and Kotzias,D. (1999). Gas-phase terpene oxidation products: A review. *Atmos. Environ.* **33**, 1424-1439.
- Caricchia,A.M., Chiavarini,S., and Pezza,M. (1999). Polycyclic aromatic hydrocarbons in the urban particulate matter in the city of Naples. *Atmos. Environ.* **33**, 3731-3738.
- Castro,L.M., Pio,C.A., Harrison,R.M., and Smith,D.J.T. (1999). Carbonaceous aerosol in urban and rural European atmospheres: Estimation of secondary organic carbon concentrations. *Atmos. Environ.* **33**, 2771-2781.

- Cecinato,A., Mabilia,R., and Marino,F. (2000). Relevant organic components in ambient particulate matter collected at Svalbard Islands (Norway). *Atmos. Environ.* **34**, 5061-5066.
- Chandramouli,B. and Kamens,R.M. (2001). The photochemical formation and gas-particle partitioning of oxidation products of decamethyl cyclopentasiloxane and decamethyl tetrasiloxane in the atmosphere. *Atmos.Environ.*, **35**:87-95.
- Chebbi,A. and Carlier,P. (1996). Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review. *Atmos. Environ.* **30**, 4233-4250.
- Chen,H.Y. and Preston,M.R. (1998). Azaarenes in the aerosol of an urban atmosphere. *Environ. Sci. Technol.* 577-583.
- Chen,X., Hulbert,D., and Shepson,P.B. (1998). Measurement of the organic nitrate yield from OH reaction with isoprene. *J. Geophys. Res.* **103**, 25563-25568.
- Chester,R., Bradshaw,G.F., Ottley,C.J., Harrison,R.M., Merrett,J.L., Preston,M.R., Rendell,A.R., Kane,M.M., and Jickells,T.D. (1993). The atmospheric distribution of trace metals, trace organics and nitrogen species over the North Sea. *Philos. Trans. R. Soc. London* **A343**, 543-556.
- Christoffersen,T.S., Hjorth,J., Horie,O., Jensen,N.R., Kotzias,D., Molander,L.L., Neeb,P., Ruppert,L., Winterhalter,R., Virkkula,A., Wirtz,K., and Larsen,B.R. (1998). cis-Pinic acid, a possible precursor for organic aerosol formation from ozonolysis of α -pinene. *Atmos. Environ.* **32**, 1657-1661.
- Chu,L.C. and Macias,E.S. (1981). Carbonaceous urban aerosol: Primary or secondary? In *Atmospheric Aerosol: Source/Air Quality Relationships*, Macias,E.S. and Hopke,P.K., Eds. American Chemical Society, Washington, DC, pp. 251-268.
- Chughtai,A.R., Williams,G.R., Atteya,M.M.O., Miller,N.J., and Smith,D.M. (1999). Carbonaceous particle hydration. *Atmos. Environ.* **33**, 2679-2687.
- Ciccioli,P., Cecinato,A., Brancaleoni,E.M., Bracchetti,A., and Frattoni,M. (1995). Polar volatile organic compounds (VOC) of natural origin as precursors of ozone. *Environmental Monitoring and Assessment* **31**, 211-218.
- Clegg,S.L., Seinfeld,J.H., Brimblecombe,P. (2001). Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds. *J.Aerosol Sci.*, **32**:713-38.
- Cocker,D.R., Flagan,R.C., Seinfeld,J.H. (2001). State-of-the-art chamber facility for studying atmospheric aerosol chemistry. *Environ.Sci.Technol.*, **35**:2594-601.
- Cocker,D.R., III, Whitlock,N.E., Flagan,R.C., Seinfeld,J.H. (2001). Hygroscopic properties of Pasadena, California aerosol. *Aerosol Sci.Technol.*, **35**:637-47.
- Cocker,D.R., III, Mader,B.T., Kalberer,M., Flagan,R.C., Seinfeld,J.H. (2001). The effect of water on gas-particle partitioning of secondary organic aerosol: II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems. *Atmos.Environ.*, **35**:6073-85.
- Cocker,D.R., III, Clegg,S.L., Flagan,R.C., Seinfeld,J.H. (2001). The effect of water on gas-particle partitioning of secondary organic aerosol. Part I: alpha-pinene/ozone system. *Atmos.Environ.*, **35**:6049-72.
- Cornell,S., Mace,K., Coeppicus,S., Duce,R., Huebert,B., Jickells,T., Zhuang,L.Z. (2001). Organic nitrogen in Hawaiian rain and aerosol. *J.Geophys.Res.*, **106**:7973-83.
- Corrigan,C.E. and Novakov,T. (1999). Cloud condensation nucleus activity of organic compounds: A laboratory study. *Atmos. Environ.* **33**, 2661-2668.
- Cotham,W.E. and Bidleman,T.F. (1992). Laboratory investigations of the partitioning of organochlorine compounds between the gas phase and atmospheric aerosols on glass fiber filters. *Environ. Sci. Technol.* **26**, 469-478.
- Cousins,I.T. and Mackay,D. (2001). Gas-particle partitioning of organic compounds and its interpretation using relative solubilities. *Environ. Sci. Technol.* **35**, 643-647.

- Cruz, C.N. and Pandis, S.N. (1997). A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei. *Atmos. Environ.* **31**, 2205-2214.
- Cruz, C.N. and Pandis, S.N. (1998). The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol. *J. Geophys. Res.* **103**, 13111-13124.
- Cruz, C.N. and Pandis, S.N. (2000). Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol. *Environ. Sci. Technol.* **34**, 4313-4319.
- Cui, W., Machir, J., Lewis, L., Eatough, D.J., and Eatough, N.L. (1997). Fine particulate organic material at Meadview during the Project MOHAVE Summer Intensive Study. *JAWMA* **47**, 357-369.
- Dabek-Zlotorzynska, E. and McGrath, M. (2000). Determination of low-molecular-weight carboxylic acids in the ambient air and vehicle emissions: A review. *Fresenius Z. Anal. Chem.* **367**, 507-518.
- de Joannon, M., Ragucci, R., Cavaliere, A., and Ciajolo, A. (2001). Identification of oxygenated compounds in combustion systems. *Chemosphere* **42**, 843-851.
- de Raat, W.K., Boers, J.P., Bakker, G.L., de Meijere, F.A., Hooimeijer, A., Lohman, P.H.M., and Mohn, G.R. (1995). Contribution of PAH and some of their nitrated derivatives to the mutagenicity of ambient airborne particles and coal fly ash. *Sci. Total Environ.* **153**, 7-28.
- Decesari, S., Facchini, M.C., Matta, E., Lettini, F., Mircea, M., Fuzzi, S., Tagliavini, E., and Putaud, J.P. (2001). Chemical features and seasonal variation of fine aerosol water-soluble organic compounds in the Po Valley, Italy. *Atmos. Environ.* **35**, 3691-3699.
- Dekermenjian, M., Allen, D.T., Atkinson, R., Arey, J. (1999). FTIR analysis of aerosol formed in the ozone oxidation of sesquiterpenes. *Aerosol Sci. Technol.*, **30**:349-63.
- Dekermenjian, M., Allen, D.T., Atkinson, R., Arey, J. (1999). FTIR analysis of aerosol formed in the photooxidation of naphthalene. *Aerosol Sci. Technol.*, **30**:273-9.
- Dick, W.D., Saxena, P., and McMurry, P.H. (2000). Estimation of water uptake by organic compounds in submicron aerosols measured during the Southeastern Aerosol and Visibility Study. *J. Geophys. Res.* **105**, 1471-1479.
- Didyk, B.M., Alvaro-Pezoa, L.A., Simoneit, B.R.T., Riveros, M.L., and Flores, A.A. (2000). Urban aerosol particles of Santiago, Chile: Organic content and molecular characterization. *Atmos. Environ.* **34**, 1167-1179.
- Dimashki, M., Harrad, S., and Harrison, R.M. (2000). Measurements of nitro-PAH in the atmospheres of two cities. *Atmos. Environ.* **34**, 2459-2469.
- Dobson, C.M., Ellison, G.B., Tuck, A.F., and Vaida, V. (2000). Atmospheric aerosols as prebiotic chemical reactors. *Proc. Natl. Acad. Sci. USA* **97**, 11864-11868.
- Docherty, K.S. and Ziemann, P.J. (2001). On-line, inlet-based trimethylsilyl derivatization for gas chromatography of mono- and dicarboxylic acids. *J. Chromatogr.* **921**, 265-275.
- Duncan, J.L., Schindler, L.R., and Roberts, J.T. (1998). A new sulfate-mediated reaction: Conversion of acetone to trimethylbenzene in the presence of liquid sulfuric acid. *Geophys. Res. Lett.* **25**, 631-634.
- Eatough, D.J., Wadsworth, A., Eatough, D.A., Crawford, J.W., Hansen, L.D., and Lewis, E.A. (1993). A multiple-system, multi-channel diffusion denuder sampler for the determination of fine-particulate organic material in the atmosphere. *Atmos. Environ.* **27A**, 1213-1219.
- Eatough, D.J. (1999). BOSS, the Brigham Young University Organic Sampling System: Determination of particulate carbonaceous material using diffusion denuder sampling technology. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane, D.A., Ed. Gordon and Breach Science, Amsterdam, pp. 233-285.
- Edney, E.O., Driscoll, D.J., Speer, R.E., Weathers, W.S., Kleindienst, T.E., Li, W., and Smith, D.F. (2000). Impact of aerosol liquid water on secondary organic aerosol yields of irradiated toluene/propylene/NO_x/(NH₄)₂SO₄/air mixtures. *Atmos. Environ.* **34**, 3907-3919.

- Elias, V.O., Simoneit, B.R.T., Pereira, A.S., Cabral, J.A., and Cardoso, J.N. (1999). Detection of high molecular weight organic tracers in vegetation smoke samples by high-temperature gas chromatography-mass spectrometry. *Environ. Sci. Technol.* **33**, 2369-2376.
- Ellis, E.C., Zeldin, M.D., Novakov, T. (1984) Determination of primary and secondary organic aerosols in Los Angeles. San Francisco, CA.
- Ellison, G.B., Tuck, A.F., and Vaida, V. (1999). Atmospheric processing of organic aerosols. *J. Geophys. Res.* **104**, 11633-11641.
- Fang, M., Zheng, M., Wang, F., To, K.L., Jaafar, A.B., and Tong, S.L. (1999). The solvent-extractable organic compounds in the Indonesia biomass burning aerosols - Characterization studies. *Atmos. Environ.* **33**, 783-795.
- Febo, A., Perrino, C., Allegrini, I. (1999). Selective gas and particle sampling: Diffusion denuders. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds*, Lane, D.A., Ed. Gordon and Breach Science, Netherlands, pp. 127-175.
- Feilberg, A., Kamens, R.M., Strommen, M.R., Nielsen, T. (1999). Modeling the formation, decay, and partitioning of semivolatile nitro-polycyclic aromatic hydrocarbons (nitronaphthalenes) in the atmosphere. *Atmos. Environ.*, **33**:1231-43.
- Feilberg, A., Kamens, R.M., Strommen, M.R., Nielsen, T. (1999). Photochemistry and partitioning of semivolatile nitro-PAH in the atmosphere. *Polycyclic Aromatic Compounds*, **14**:151-60.
- Feilberg, A. and Nielsen, T. (2000). Effect of aerosol chemical composition on the photodegradation of nitro-polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **34**, 789-797.
- Feilberg, A., Poulsen, M.W.B., Nielsen, T., and Skov, H. (2000). Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. *Atmos. Environ.* **35**, 353-366.
- Fister, T., Strossman, G., Willett, K., Odom, R., and Linton, R. (1995). *In situ* analysis of organic monolayers and their reactivity on single micrometer-sized particles by time-of-flight secondary ion mass spectrometry. *Int. J. Mass Spec. Ion Processes* .
- Fitz, D.R. (1990). Reduction of the positive organic artifact on quartz filters. *Aerosol Sci. Technol.* **12**, 142-148.
- Foreman, W.T. and Bidleman, T.F. (1990). Semivolatile organic compounds in the ambient air of Denver, Colorado. *Atmos. Environ.* **24A**, 2405-2416.
- Forstner, H.J.L., Flagan, R.C., and Seinfeld, J.H. (1997). Molecular speciation of secondary organic aerosol for photooxidation of the higher alkenes: 1-octene and 1-decene. *Atmos. Environ.* **31**, 1953-1964.
- Forstner, H.J.L., Seinfeld, J.H., and Flagan, R.C. (1997). Secondary organic aerosol formation from the photooxidation of aromatic hydrocarbons. Molecular composition. *Environ. Sci. Technol.* **31**, 1345-1358.
- Fraser, M.P., Grosjean, D., Grosjean, E., Rasmussen, R.A., and Cass, G.R. (1996). Air quality model evaluation data for organics: 1. Bulk chemical composition and gas/particle distribution factors. *Environ. Sci. Technol.* **30**, 1731-1743.
- Fraser, M.P., Cass, G.R., and Simoneit, B.R.T. (1998). Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. *Environ. Sci. Technol.* **32**, 2051-2060.
- Fraser, M.P., Cass, G.R., and Simoneit, B.R.T. (1999). Particulate organic compounds emitted from motor vehicle exhaust and in the urban atmosphere. *Atmos. Environ.* **33**, 2715-2724.
- Fraser, M.P., Kleeman, M.J., Schauer, J.J., and Cass, G.R. (2000). Modeling the atmospheric concentrations of individual gas-phase and particle-phase organic compounds. *Environ. Sci. Technol.* **34**, 1302-1312.

- Gao, S., Hegg, D.A., Frick, G., Caffrey, P.F., Pasternack, L., Cantrell, C., Sullivan, W., Ambrusko, J., Albrecht, T., Kirchstetter, T.W. (2001). Experimental and modeling studies of secondary organic aerosol formation and some applications to the marine boundary layer. *J. Geophys. Res.*, **106**:27619-34.
- Gelencsér, A., Barcza, T., Kiss, G., Molnár, Á., Hlavay, J., and Mészáros, E. (1998). Distribution of n-alkanes and PAHs in atmospheric aerosols. *Atmospheric Research* **46**, 223-231.
- Gelencsér, A., Sallai, M., Krivácsy, Z., Kiss, G., and Mészáros, E. (2000). Voltammetric evidence for the presence of humic-like substances in fog water. *Atmospheric Research* **54**, 157-165.
- Geron, C., Rasmussen, R.A., Arnts, R.R., and Guenther, A. (2000). A review and synthesis of monoterpene speciation from forests in the United States. *Atmos. Environ.* **34**, 1761-1781.
- Gery, M.W., Fox, D.L., Jeffries, H.E., Stockburger, L., and Weathers, W.S. (1985). A continuous stirred tank reactor investigation of the gas-phase reaction of hydroxyl radicals and toluene. *Int. J. Chem. Kinet.* **17**, 931-955.
- Gery, M.W., Fox, D.L., Kamens, R.M., and Stockburger, L. (1987). Investigation of hydroxyl radical reactions with o-xylene and m-xylene in continuous stirred tank reactor. *Environ. Sci. Technol.* **21**, 339-348.
- Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N.R., Hjorth, J., Kotzias, D., and Larsen, B.R. (2000). Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone. *Environ. Sci. Technol.* **34**, 1001-1010.
- Glasius, M., Wessel, S., Christensen, C.S., Jacobsen, J.K., Jorgensen, H.E., Klitgaard, K.C., Petersen, L., Rasmussen, J.K., Hansen, T.S., Lohse, C., Boaretto, E., and Heinemeier, J. (2000). Sources of formic acid studied by carbon isotopic analysis and air mass characterization. *Atmos. Environ.* **34**, 2471-2479.
- Gogou, A.I., Apostolaki, M., and Stephanou, E.G. (1998). Determination of organic molecular markers in marine aerosols and sediments: One-step flash chromatography compound class fractionation and capillary gas chromatographic analysis. *J. Chromatogr.* **799**, 215-231.
- Goss, K.U. (1993). Adsorption of organic vapors on ice and quartz sand at temperatures below 0 °C. *Environ. Sci. Technol.* **27**, 2826-2830.
- Goss, K.U. and Eisenreich, S.J. (1997). Sorption of volatile organic compounds to particles from a combustion source at different temperatures and relative humidities. *Atmos. Environ.* **31**, 2827-2834.
- Goss, K.U. and Schwarzenbach, R.P. (1998). Gas/solid and gas/liquid partitioning of organic compounds: Critical evaluation of the interpretation of equilibrium constants. *Environ. Sci. Technol.* **32**, 2025-2032.
- Goss, K.U. and Schwarzenbach, R.P. (1999). Empirical prediction of heats of vaporization and heats of adsorption of organic compounds. *Environ. Sci. Technol.* **33**, 3390-3393.
- Goss, K.U. and Schwarzenbach, R.P. (1999). Quantification of the effect of humidity on the gas/mineral oxide and gas/salt adsorption of organic compounds. *Environ. Sci. Technol.* **33**, 4073-4078.
- Goss, K.U. and Schwarzenbach, R.P. (2001). Linear free energy relationships used to evaluate equilibrium partitioning of organic compounds. *Environ. Sci. Technol.* **35**, 1-9.
- Granby, K., Christensen, C.S., and Lohse, C. (1997). Urban and semi-rural observations of carboxylic acids and carbonyls. *Atmos. Environ.* **31**, 1403-1416.
- Greenberg, A. (1999). Chemical and health consequences of particle/vapor partitioning of polycyclic aromatic hydrocarbons (PAH) and their derivatives. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds*, Vol. 2, Lane, D.A., Ed. Gordon and Breach Science, Netherlands, pp. 1-11.
- Griffin, R.J., Cocker, D.R., III, and Seinfeld, J.H. (1999). Incremental aerosol reactivity: Application to aromatic and biogenic hydrocarbons. *Environ. Sci. Technol.* **33**, 2403-2408.

- Griffin,R.J., Cocker,D.R., III, Seinfeld,J.H., and Dabdub,D. (1999). Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons. *Geophys. Res. Lett.* **26**, 2721.
- Griffin,R.J., Cocker,D.R., Flagan,R.C., Seinfeld,J.H. (1999). Organic aerosol formation from the oxidation of biogenic hydrocarbons. *J.Geophys.Res.*, **104**:3555-67.
- Grosjean,D. and Friedlander,S.K. (1975). Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere. *JAPCA* **25**, 1038-1044.
- Grosjean,D., Cauwenberghe,K.V., Schmid,J.P., Kelley,P.E., and Pitts,J.N., Jr. (1978). Identification of C₃-C₁₀ aliphatic dicarboxylic acids in airborne particulate matter. *Environ. Sci. Technol.* **12**, 313-317.
- Grosjean,D. and Friedlander,S.K. (1979). Formation of organic aerosols from cyclic olefins and diolefins. In *Character and Origins of Smog Aerosols*, Hidy,G.M., Mueller,P.K., Grosjean,D., Appel,B.R., Wesolowski,J.J., Eds. Wiley, New York, pp. 435-473.
- Grosjean,D. (1984). Photooxidation of 1-heptene. *Sci. Total Environ.* **37**, 195-211.
- Grosjean,D. and Seinfeld,J.H. (1989). Parameterization of the formation potential of secondary organic aerosols. *Atmos. Environ.* **23**, 1733-1747.
- Grosjean,D. (1992). *In-situ* organic aerosol formation during a smog episode: Estimated production and chemical functionality. *Atmos. Environ.* **26A**, 953-963.
- Grosjean,D., Williams,E.L., II, and Grosjean,E. (1993). Ambient levels of peroxy-n-butyl nitrates at a southern California mountain forest smog receptor location. *Environ. Sci. Technol.* **27**, 326.
- Grosjean,D., Grosjean,E., and Williams,E.L., II (1993). Atmospheric chemistry of unsaturated alcohols. *Environ. Sci. Technol.* **27**, 2478-2485.
- Grosjean,D., Williams,E.L., II, Grosjean,E., and Novakov,T. (1994). Evolved gas analysis of secondary organic aerosols. *Aerosol Sci. Technol.* **21**, 306-324.
- Grosjean,D. (1998). Reactions of o-cresol and nitrocresol with NO_x in sunlight and with ozone-nitrogen dioxide mixtures in the dark. *Environ. Sci. Technol.* **19**, 968-974.
- Gundel,L.A., Daisey,J.M., de Carvalho,L.R.F., Kado,N.Y., and Schuetzle,D. (1993). Polar organic matter in airborne particles: Chemical characterization and mutagenic activity. *Environ. Sci. Technol.* **27**, 2112-2119.
- Gundel,L.A. and Lane,D.A. (1998). Direct determination of semi-volatile organic compounds with sorbent-coated diffusion denuders. *J. Aerosol Sci.* **29**, s341-s342.
- Gundel,L.A. and Lane,D.A. (1999). Sorbent-coated diffusion denuders for direct measurement of gas/particle partitioning by semi-volatile organic compounds. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane,D.A., Ed. Gordon and Breach Science, Amsterdam, pp. 287-332.
- Gustafson,K.E. and Dickhut,R.M. (1997). Particle/gas concentrations and distributions of PAHs in the atmosphere of southern Chesapeake Bay. *Environ. Sci. Technol.* **31**, 140-147.
- Haagen-Smit,A.J. (1952). Chemistry and physiology of Los Angeles Smog. *Ind. Eng. Chem.* **44**, 1342-1346.
- Haefliger,O.P., Bucheli,T.D., and Zenobi,R. (2000). Laser mass spectrometric analysis of organic atmospheric aerosols 1. Characterization of emission sources. *Environ. Sci. Technol.* **34**, 2178-2183.
- Haefliger,O.P., Bucheli,T.D., and Zenobi,R. (2000). Laser mass spectrometric analysis of organic atmospheric aerosols 2. Elucidation of urban air pollution processes. *Environ. Sci. Technol.* **34**, 2184-2189.
- Hall,P.A., Watson,A.F.R., Garner,G.V., Hall,K., Smith,S., Waterman,D., and Horsfield,B. (1999). An investigation of micro-scale sealed vessel thermal extraction-gas chromatography-mass spectrometry

- (MSSV-GC-MS) and micro-scale sealed vessel pyrolysis-gas chromatography-mass spectrometry applied to a standard reference material of an urban dust/organics. *Sci. Total Environ.* **235**, 269-276.
- Hallquist, M., Wängberg, I., Ljungström, E., Barnes, I., and Becker, K.H. (1999). Aerosol and product yields from NO₃ radical-initiated oxidation of selected monoterpenes. *Environ. Sci. Technol.* **33**, 553-559.
- Hameri, K., Rood, M.J., and Hansson, H.C. (1992). Hygroscopic properties of a NaCl aerosol coated with organic compounds. *J. Aerosol Sci.* **23**, S437-S440.
- Hameri, K., Vakeva, M., Aalto, P.P., Kulmala, M., Swietlicki, E., Zhou, J., Seidl, W., Becker, E., O'Dowd, C.D. (2001). Hygroscopic and CCN properties of aerosol particles in boreal forests. *Tellus Series B-Chemical and Physical Meteorology*, **53**:359-79.
- Hansson, H.C., Wiedensohler, A., Rood, M.J., and Covert, D.S. (1990). Experimental determination of the hygroscopic properties of organically coated aerosol particles. *J. Aerosol Sci.* **21**, S241-S244.
- Harner, T. and Bidleman, T.F. (1998). Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air. *Environ. Sci. Technol.* **32**, 1494-1502.
- Hasson, A.S., Orzechowska, G., and Paulson, S. (2001). Production of stabilized Criegee intermediates and peroxides in the gas phase ozonolysis of alkenes 1. Ethene, *trans*-2-butene, and 2,3-dimethyl-2butene. *J. Geophys. Res.* **106**, 34131-34142.
- Hasson, A.S., Ho, A.W., Kuwata, K.T., and Paulson, S. (2001). Production of stabilized Criegee intermediates and peroxides in the gas phase ozonolysis of alkenes 2. Asymmetric and biogenic alkenes. *J. Geophys. Res.* **106**, 34143-34154.
- Hatakeyama, S., Ohno, M., Takagi, H., and Akimoto, H. (1987). Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air. *Environ. Sci. Technol.* **12**, 52-57.
- Hatakeyama, S., Tanonaka, T., Weng, J., Bandow, H., Takagi, H., and Akimoto, H. (1998). Ozone-cyclohexene reaction in air: Quantitative analysis of particulate products and the reaction mechanism. *Environ. Sci. Technol.* **19**, 935-941.
- Havers, N., Burba, P., Lambert, J., and Klockow, D. (1998). Spectroscopic characterization of humic-like substances in airborne particulate matter. *Atmos. Chemis* **29**, 45-54.
- Heederik, D., Douwes, J., Wouters, I., and Doekes, G. (2000). Organic dusts: Beyond endotoxin. *Inhal. Toxicol.* **12**, 27-33.
- Heisler, S.L. and Friedlander, S.K. (1977). Gas-to-particle conversion in photochemical smog: Aerosol growth laws and mechanisms for organics. *Atmos. Environ.* **11**, 157-168.
- Hemming, B.L. and Seinfeld, J.H. (2001). On the hygroscopic behavior of atmospheric organic aerosols. *Industrial & Engineering Chemistry Research*, **40**:4162-71.
- Hildemann, L.M., Markowski, G.R., Jones, M.C., and Cass, G.R. (1991). Submicrometer aerosol mass distributions of emissions from boilers, fireplaces, automobiles, diesel trucks, and meat-cooking operations. *Aerosol Sci. Technol.* **14**, 138-152.
- Hildemann, L.M., Markowski, G.R., and Cass, G.R. (1991). Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* **25**, 744-759.
- Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1991). Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography. *Environ. Sci. Technol.* **25**, 1311-1325.
- Hildemann, L.M., Cass, G.R., Mazurek, M.A., and Simoneit, B.R.T. (1993). Mathematical modeling of urban organic aerosol: Properties measured by high-resolution gas chromatography. *Environ. Sci. Technol.* **27**, 2045-2055.
- Hildemann, L.M., Rogge, W.F., Cass, G.R., Mazurek, M.A., and Simoneit, B.R.T. (1996). Contribution of primary aerosol emissions from vegetation-derived sources to fine particle concentrations in Los Angeles. *J. Geophys. Res.* **101**, 19541-19549.

- Hitzenberger, R., Berner, A., Giebl, H., Kromp, R., Larson, S.M., Rouc, A., Koch, A., Marischka, S., and Puxbaum, H. (1999). Contribution of carbonaceous material to cloud condensation nuclei concentrations in European background (Mt. Sonnblick) and urban (Vienna) aerosols. *Atmos. Environ.* **33**, 2647-2659.
- Hoffmann, T., Odum, J.R., Bowman, F.A., Collins, D., Klockow, D., Flagan, R.C., and Seinfeld, J.H. (1997). Formation of organic aerosols from the oxidation of biogenic hydrocarbons. *J. Atmos. Chem.* **26**, 189-222.
- Hoffmann, T., Bandur, R., Marggraf, U., and Linscheid, M. (1998). Molecular composition of organic aerosols formed in the α -pinene/O₃ reaction: Implications for new particle formation processes. *J. Geophys. Res.* **103**, 25569-25578.
- Holes, A., Eusebi, A., Grosjean, D., and Allen, D.T. (1997). FTIR analysis of aerosol formed in the photooxidation of 1,3,5-trimethylbenzene. *Aerosol Sci. Technol.* **26**, 516-526.
- Hoppel, W., Fitzgerald, J., Frick, G., Caffrey, P., Pasternack, L., Hegg, D., Gao, S., Leitch, R., Shantz, N., Cantrell, C., Albrecht, T., Ambrusko, J., Sullivan, W. (2001). Particle formation and growth from ozonolysis of α -pinene. *J. Geophys. Res.*, **106**:27603-18.
- Huntzicker, J.J. and Turpin, B.J. (1991). Secondary organic aerosol in the Los Angeles Basin. California Air Resources Board, by Oregon Graduate Institute of Science and Technology, Beaverton, OR.
- Hurley, M.D., Sokolov, O., Wallington, T.J., Takesawa, H., Karasawa, M., Klotz, B., Barnes, I., and Becker, K.H. (2001). Organic aerosol formation during the atmospheric degradation of toluene. *Environ. Sci. Technol.* **35**, 1358-1366.
- Ishii, S., Hisamatsu, Y., Inazu, K., Kadoi, M., and Aika, K.I. (2000). Ambient measurement of nitrotriphenylenes and possibility of nitrotriphenylene formation by atmospheric reaction. *Environ. Sci. Technol.* **34**, 1893-1899.
- Izumi, K. and Fukuyama, T. (1990). Photochemical aerosol formation from aromatic hydrocarbons in the presence NO_x. *Atmos. Environ.* **24A**, 1433-1441.
- Jacobson, M.C., Hansson, H.C., Noone, K.J., and Charlson, R.J. (2000). Organic atmospheric aerosols: Review and state of the science. *Rev. Geophys.* **38**, 267-294.
- Jacobson, M.Z. (1999). Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption. *J. Geophys. Res.* **104**, 3527-3542.
- Jang, M. and McDow, S.R. (1997). Products of benz[a]anthracene photodegradation in the presence of known organic constituents of atmospheric aerosols. *Environ. Sci. Technol.* **31**, 1046-1053.
- Jang, M., Kamens, R.M., Leach, K.B., and Strommen, M.R. (1997). A thermodynamic approach using group contribution methods to model the partitioning of semivolatile organic compounds on atmospheric particulate matter. *Environ. Sci. Technol.* **31**, 2805-2811.
- Jang, M. and Kamens, R.M. (1998). A thermodynamic approach for modeling partitioning of semivolatile organic compounds on atmospheric particulate matter: Humidity effects. *Environ. Sci. Technol.* **32**, 1237-1243.
- Jang, M. and Kamens, R.M. (1999). Newly characterized products and composition of secondary aerosols from the reaction of α -pinene with ozone. *Atmos. Environ.* **33**, 459-474.
- Jang, M. and Kamens, R.M. (1999). A predictive model for adsorptive gas partitioning of SOCs on fine atmospheric inorganic dust particles. *Environ. Sci. Technol.* **33**, 1825-1831.
- Jang, M. and Kamens, R.M. (2001). Characterization of secondary aerosol from the photooxidation of toluene in the presence of NO_x and 1-propene. *Environ. Sci. Technol.* **35**, 3626-3639.
- Jang, M. and Kamens, R.M. (2001). Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environ. Sci. Technol.* **35**, 4758-4766.

- Jang, M.S. and Kamens, R.M. (2001). Characterization of secondary aerosol from the photooxidation of toluene in the presence of NO_x and 1-propene. *Environ. Sci. Technol.*, **35**:3626-39.
- Jang, M.S. and Kamens, R.M. (2001). Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. *Environ. Sci. Technol.*, **35**:4758-66.
- Janson, R., Rosman, K., Karlsson, A., Hansson, H.C. (2001). Biogenic emissions and gaseous precursors to forest aerosols. *Tellus Series B-Chemical and Physical Meteorology*, **53**:423-40.
- Jaoui, M. and Kamens, R.M. (2001). Mass balance of gaseous and particulate products analysis from alpha-pinene/NO_x/air in the presence of natural sunlight. *J. Geophys. Res.*, **106**:12541-58.
- Jenkin, M.E., Shallcross, D.E., and Harvey, J.N. (2000). Development and application of a possible mechanism for the generation of cis-pinic acid from the ozonolysis of a- and b- pinene. *Atmos. Environ.* **34**, 2837-2850.
- Jenkins, B.M., Jones, A.D., Turn, S.Q., and Williams, R.B. (1996). Particle concentrations, gas-particle partitioning and species intercorrelations for polycyclic aromatic hydrocarbons (PAH) emitted during biomass burning. *Atmos. Environ.* **30**, 3825-3836.
- Jensen, T., Fredenslund, A., and Rasmussen, P. (1981). Pure-component vapor pressures using UNIFAC group contribution. *Industrial and Engineering Chemistry, Fundamentals* **20**, 239-246.
- Jeon, S.J., Meuzelaar, H.L.C., Sheya, S.A.N., Lighty, J.S., Jarman, W.M., Kasteler, C., Sarofim, A.F., and Simoneit, B.R.T. (2001). Exploratory studies of PM₁₀ receptor and source profiling by GC/MS and principal component analysis of temporally and spatially resolved ambient samples. *JAWMA* **51**, 766-784.
- Jiang, W., Singleton, D.L., Hedley, M., McLaren, R., Dann, T., and Wang, D. (1997). Comparison of organic compound compositions in the emissions inventory and ambient data for the Lower Fraser Valley. *JAWMA* **47**, 851-860.
- Jinhui, X. and Lee, F.S.C. (2001). Analysis of nitrated polynuclear aromatic hydrocarbons. *Chemosphere* **42**, 245-250.
- Johnson, B.J., Betterton, E.A., and Craig, D. (1996). Henry's law coefficients of formic and acetic acids. *Atmos. Chemis* **24**, 113-119.
- Juuti, S. and Hoekstra, E.J. (1998). New directions: The origins and occurrence of trichloroacetic acid. *Atmos. Environ.* **32**, 3059-3060.
- Kalberer, M., Yu, J., Cocker, D.R., Flagan, R.C., and Seinfeld, J.H. (2000). Aerosol formation in the cyclohexene-ozone system. *Environ. Sci. Technol.* **34**, 4894-4901.
- Kamens, R.M., Jeffries, H.E., Gery, M.W., Wiener, R.W., Sexton, K.G., and Sexton, G.B. (1981). The impact of a -pinene on urban smog formation: An outdoor smog chamber study. *Atmos. Environ.* **15**, 969-981.
- Kamens, R.M., Gery, M.W., Jeffries, H.E., Jackson, M., and Cole, E.I. (1982). Ozone-isoprene reactions: product formation and aerosol potential. *Int. J. Chem. Kinet.* **14**, 955-975.
- Kamens, R.M., Guo, Z., Fulcher, J.N., Bell, D.A. (1986) The influence of temperature on the daytime PAH decay on atmospheric soot particles. *79th Annual Meeting of the Air Pollution Control Association*, Minneapolis, MN.
- Kamens, R.M., Guo, Z., Fulcher, J.N., and Bell, D.A. (1988). Influence of humidity, sunlight and temperature on the daytime decay of polyaromatic hydrocarbons on atmospheric soot particles. *Environ. Sci. Technol.* **22**, 103-108.
- Kamens, R.M., Karam, H., Guo, J., Perry, J.M., and Stockburger, L. (1989). The behavior of oxygenated polycyclic aromatic hydrocarbons on atmospheric soot particles. *Environ. Sci. Technol.* **23**, 801-806.

- Kamens,R.M., Guo,J., Guo,Z., and McDow,S.R. (1990). Polynuclear aromatic hydrocarbon degradation by heterogeneous reactions with N₂O₅ on atmospheric particles. *Atmos. Environ.* **24A**, 1161.
- Kamens,R.M., Odum,J.R., and Fan,Z.H. (1995). Some observations on times to equilibrium for semivolatile polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **29**, 43-50.
- Kamens,R.M., Jang,M., Chien,C.J., Leach,K. (1999). Aerosol formation from the reaction of alpha-pinene and ozone using a gas-phase kinetics aerosol partitioning model. *Environ.Sci.Technol.*, **33**:1430-8.
- Kamens,R.M., Fan,Z., Jang,M., Odum,J.R., Hu,J., Coe,D., Zhang,J., Chen,S., Leach,K. (1999). The use of denuders for semivolatile characterization studies in outdoor chambers. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane,D.A., Ed. Gordon & Breach Science, Amsterdam, pp. 333-368.
- Kamens,R.M. and Jaoui,M. (2001). Modeling aerosol formation from alpha-pinene plus NO_x in the presence of natural sunlight using gas-phase kinetics and gas-particle partitioning theory. *Environ. Sci. Technol.* **35**, 1394-1405.
- Kanakidou,M., Tsigaridis,K., Dentener,F.J., and Crutzen,P.J. (2000). Human-activity-enhanced formation of organic aerosols by biogenic hydrocarbon oxidation. *J. Geophys. Res.* **105**, 9243-4254.
- Kaupp,H. and Umlauf,G. (1992). Atmospheric gas-particle partitioning of organic compounds: Comparison of sampling methods. *Atmos. Environ.* **26A**, 2259-2267.
- Kavouras,I.G., Mihalopoulos,N., and Stephanou,E.G. (1999). Formation and gas/particle partitioning of monoterpenes photo-oxidation products over forests. *Geophys. Res. Lett.* **26**, 55-58.
- Kavouras,I.G., Mihalopoulos,N., and Stephanou,E.G. (1999). Secondary organic aerosol formation vs primary organic aerosol emission: In situ evidence for the chemical coupling between monoterpene acidic photooxidation products and new particle formation over forests. *Environ. Sci. Technol.* **33**, 1028-1037.
- Kavouras,I.G., Lawrence,J.E., Koutrakis,P., Stephanou,E.G., and Oyola,P. (1999). Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago, Chile: Source reconciliation and evaluation of sampling artifacts. *Atmos. Environ.* **33**, 4977-4986.
- Kawamura,K. and Kaplan,I.R. (1987). Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. *Environ. Sci. Technol.* **21**, 105-110.
- Kawamura,K. and Ikushima,K. (1993). Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere. *Environ. Sci. Technol.* **27**, 2227-2235.
- Kawamura,K., Kasukabe,H., and Barrie,L.A. (1996). Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in Arctic aerosols: One year of observations. *Atmos. Environ.* **30**, 1709.
- Kawamura,K. and Sakaguchi,F. (1999). Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics. *J. Geophys. Res.* **104**, 3501-3509.
- Kendall,M., Hamilton,R.S., Watt,J., and Williams,I.D. (2001). Characterization of selected speciated organic compounds associated with particulate matter in London. *Atmos. Environ.* **35**, 2483-2495.
- Kerminen,V. (1999). Roles of SO₂ and secondary organics in the growth of nanometer particles in the lower atmosphere. *J. Aerosol Sci.* **30**, 1069-1078.
- Kerminen,V.M., Ojanen,C., Pakkanen,T., Hillamo,R., Aurela,M., and Merilainen,J. (2000). Low-molecular-weight dicarboxylic acids in an urban and rural atmosphere. *J. Aerosol Sci.* **31**, 349-362.
- Kerminen,V.M. (2001). Relative roles of secondary sulfate and organics in atmospheric cloud condensation nuclei production. *J.Geophys.Res.*, **106**:17321-33.
- Kesselmeier,J., Bode,K., Gerlach,C., and Jork,E.M. (1998). Exchange of atmospheric formic and acetic acids with trees and crop plants under controlled chamber and purified air conditions. *Atmos. Environ.* **32**, 1765-1776.

- Ketola, R.A., Mansikka, T., Ojala, M., Kotiaho, T., and Kostianinen, R. (1997). Analysis of volatile organic sulfur compounds in air by membrane inlet mass spectrometry. *Anal. Chem.* **69**, 4536-4539.
- Khwaja, H.A. (1995). Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site. *Atmos. Environ.* **29**, 127-140.
- Kirchstetter, T.W., Corrigan, C.E., and Novakov, T. (2001). Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters. *Atmos. Environ.* **35**, 1663-1671.
- Kitto, A.M., Pirbazari, M., Badriyha, B.N., Ravindran, V., Tyner, R., and Synolakis, C.E. (1997). Emissions of volatile and semi-volatile organic compounds and particulate matter from hot asphalts. *Environmental Technology* **18**, 121-138.
- Kleeman, M.J. and Cass, G.R. (1999). Effect of emissions control strategies on the size and composition distribution of urban particulate air pollution. *Environ. Sci. Technol.* **33**, 177-189.
- Kleeman, M.J., Schauer, J.J., and Cass, G.R. (1999). Size and composition distribution of fine particulate matter emitted from wood burning, meat charbroiling, and cigarettes. *Environ. Sci. Technol.* **33**, 3516-3523.
- Kleindienst, T.E., Smith, D.F., Li, W., Edney, E.O., Driscoll, D.J., Speer, R.E., and Weathers, W.S. (1999). Secondary organic aerosol formation from the oxidation of aromatic hydrocarbons in the presence of dry submicron ammonium sulfate aerosol. *Atmos. Environ.* **33**, 3669-3682.
- Koch, S., Winterhalter, R., Uherek, E., Koloff, A., Neeb, P., and Moortgat, G.K. (2000). Formation of new particles in the gas-phase ozonolysis of monoterpenes. *Atmos. Environ.* **34**, 4031-4042.
- Koch, S., Winterhalter, R., and Moortgat, G.K. (2001). Reply to: Comment on "Formation of new particles in the gas-phase ozonolysis of monoterpenes" by Koch et al. [*Atmos. Environ.* 34 (2000) 4031-4042]. *Atmos. Environ.* **35**, 4525-4526.
- Kotzick, R. and Niessner, R. (1999). The effects of aging processes on critical supersaturation ratios of ultrafine carbon aerosols. *Atmos. Environ.* **33**, 2669-2677.
- Krieger, M.S. and Hites, R.A. (1992). Diffusion denuder for the collection of semivolatile organic compounds. *Environ. Sci. Technol.* **26**, 1551-1555.
- Kubatova, A., Vermeylen, R., Claeys, M., Cafmeyer, J., Maenhaut, W., Roberts, G., and Artaxo, P. (2000). Carbonaceous aerosol characterization in the Amazon Basin, Brazil: Novel dicarboxylic acids and related compounds. *Atmos. Environ.* **34**, 5037-5051.
- Kulmala, M., Hameri, K., Aalto, P.P., Makela, J.M., Pirjola, L., Nilsson, E.D., Buzorius, G., Rannik, U., Dal Maso, M., Seidl, W., Hoffman, T., Janson, R., Hansson, H.C., Viisanen, Y., Laaksonen, A., and O'Dowd, C.D. (2001). Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus Series B-Chemical and Physical Meteorology* **53**, 324-343.
- Kunit, M. and Puxbaum, H. (1996). Enzymatic determination of the cellulose content of atmospheric aerosols. *Atmos. Environ.* **30**, 1233-1236.
- Lane, D.A., Johnson, N.D., Burton, S.C., Thomas, G.H.S., and Schroeder, W.H. (1988). Development and evaluation of a novel gas and particle sampler for semivolatile chlorinated organic compounds in ambient air. *Environ. Sci. Technol.* **22**, 941-947.
- Lane, D.A., Johnson, N.D., Hanley, M.J., Schroeder, W.H., and Ord, D.T. (1992). Gas and particle phase concentrations of a-HcH, b-HcH, and HCB in Ontario air. *Environ. Sci. Technol.* **26**, 126-133.
- Lane, D.A. and Johnson, N.D. (1999). Gas/particle partition measurements with the gas and particle (GAP) sampler. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane, D.A., Ed. Gordon and Breach Science, Netherlands, pp. 177-200.
- Latimer, H.K., Kamens, R.M., Chandra, G. (1998). The atmospheric partitioning of decamethylcyclopentasiloxane (D5) and 1-hydroxynonamethylcyclopentasiloxane (D4TOH) on different types of atmospheric particles. *Chemosphere*, **36**:2401-14.

- Lazaridis, M. (1999). Gas-particle partitioning of organic compounds in the atmosphere. *J. Aerosol Sci.* **30**, 1165-1170.
- Leach, K.B., Kamens, R.M., Strommen, M.R., Jang, M. (1999). Partitioning of semivolatile organic compounds in the presence of a secondary organic aerosol in a controlled atmosphere. *J. Atmos. Chem.*, **33**:241-64.
- Lee, W.M.G. and Tsay, L.Y. (1994). The partitioning model of polycyclic aromatic hydrocarbon between gaseous and particulate (PM₁₀) phases in urban atmosphere with high humidity. *Sci. Total Environ.* **145**, 163-172.
- Leone, J.A., Flagan, R.C., Grosjean, D., and Seinfeld, J.H. (1985). An outdoor smog chamber and modeling study of toluene-NO_x photooxidation. *Int. J. Chem. Kinet.* **17**, 177-216.
- Lewis, R.G. and Coutant, R.W. (1999). Determination of phase-distributed polycyclic aromatic hydrocarbons in air by grease-coated denuders. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds*, Vol. 2, Lane, D.A., Ed. Gordon and Breach Science, Netherlands, pp. 201-231.
- Li, C.K. and Kamens, R.M. (1993). The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. *Atmos. Environ.* **27A**, 523-532.
- Liang, C. and Pankow, J.F. (1996). Gas/particle partitioning of organic compounds to environmental tobacco smoke: Partition coefficient measurements by desorption and comparison to urban particulate material. *Environ. Sci. Technol.* **30**, 2800-2805.
- Liang, C., Pankow, J.F., Odum, J.R., and Seinfeld, J.H. (1997). Gas/particle partitioning of semivolatile organic compounds to model inorganic, organic, and ambient smog aerosols. *Environ. Sci. Technol.* **31**, 3086-3092.
- Ligocki, M.P. and Pankow, J.F. (1989). Measurements of the gas/particle distributions of atmospheric organic compounds. *Environ. Sci. Technol.* **23**, 75-83.
- Limbeck, A. and Puxbaum, H. (1999). Organic acids in continental background aerosols. *Atmos. Environ.* **33**, 1847-1852.
- Limbeck, A., Puxbaum, H., Otter, L., and Scholes, M.C. (2001). Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA). *Atmos. Environ.* **35**, 1853-1862.
- Lohmann, R., Harner, T., Thomas, G.O., and Jones, K.C. (2000). A comparative study of the gas-particle partitioning of PCDD/Fs, PCBs, and PAHs. *Environ. Sci. Technol.* **34**, 4943-4951.
- Mader, B.T. and Pankow, J.F. (2000). Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters 1. Partitioning of polychlorinated dibenzodioxins, polychlorinated dibenzofurans and polycyclic aromatic hydrocarbons to teflon membrane filters. *Atmos. Environ.* **34**, 4879-4887.
- Mader, B.T. and Pankow, J.F. (2001). Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters 2. Partitioning of polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and polycyclic aromatic hydrocarbons to quartz fiber filters. *Atmos. Environ.* **35**, 1217-1223.
- Mader, B.T. and Pankow, J.F. (2001). Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters 3. An analysis of gas adsorption artifacts in measurements of atmospheric SOC and organic carbon (OC) when using teflon membrane filters and quartz fiber filters. *Environ. Sci. Technol.* **35**, 3422-3432.
- Makar, P.A. (2001). The estimation of organic gas vapour pressure. *Atmos. Environ.* **35**, 961-974.
- Makela, J.M., Yli-Koivisto, S., Hiltunen, V., Seidl, W., Swietlicki, E., Teinila, K., Sillanpaa, M., Koponen, I.K., Paatero, J., Rosman, K., Hameri, K. (2001). Chemical composition of aerosol during particle formation events in boreal forest. *Tellus Series B-Chemical and Physical Meteorology*, **53**:380-93.

- Malm, W.C. and Gebhart, K.A. (1993) Source apportionment of organic and light absorbing carbon using receptor modeling techniques. *86th Annual Meeting of the Air & Waste Management Association*, Denver, CO.
- Malm, W.C. and Gebhart, K.A. (1996). Source apportionment of organic and light-absorbing carbon using receptor modeling techniques. *Atmos. Environ.* **30**, 843-856.
- Malm, W.C. and Day, D.E. (2001). Estimates of aerosol species scattering characteristics as a function of relative humidity. *Atmos. Environ.* **35**, 2845-2860.
- Manchester, J.B., Schauer, J.J., and Cass, G.R. (2001). The distribution of particle-phase organic compounds in the atmosphere and source contributions to atmospheric particulate matter concentrations during the Southern California Children's Health Study. Report No. CARB 98-320. by University of Wisconsin-Madison.
- Marti, J.J., Weber, R.J., McMurry, P.H., Eisele, F., Tanner, D.J., and Jefferson, A. (1997). New particle formation at a remote continental site: Assessing the contributions of SO₂ and organic precursors. *J. Geophys. Res.* **102**, 6331-6340.
- Masel, R.I. (1996). *Principles of Adsorption and Reaction on Solid Surfaces*. Wiley, New York.
- Mayol-Bracero, O.L., Rosario, O., Corrigan, C.E., Morales, R., Torres, I., and Perez, V. (2001). Chemical characterization of submicron organic aerosols in the tropical trade winds of the Caribbean using gas chromatography/mass spectrometry. *Atmos. Environ.* **35**, 1735-1745.
- Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1991). Biological input to visibility-reducing aerosol particles in the remote arid southwestern United States. *Environ. Sci. Technol.* **25**, 684-694.
- Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simoneit, B.R.T., Rogge, W.F. (1993). Methods of analysis for complex organic aerosol mixtures from urban emission sources of particulate carbon. In *Sampling and Analysis of Airborne Pollutants*, Winegar, E.D. and Keith, L.H., Eds. Lewis Publishers, Boca Raton, FL, pp. 177-190.
- Mazurek, M.A., Masonjones, M.C., Masonjones, H.D., Salmon, L.G., Cass, G.R., Hallock, K.A., and Leach, M. (1997). Visibility-reducing organic aerosols in the vicinity of Grand Canyon National Park: Properties observed by high resolution gas chromatography. *J. Geophys. Res.* **102**, 3779-3794.
- McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., and Watson, J.G. (2000). Fine particle and gaseous emission rates from residential wood combustion. *Environ. Sci. Technol.* **34**, 2080-2091.
- McDow, S.R. and Huntzicker, J.J. (1990). Vapor adsorption artifact in the sampling of organic aerosol: Face velocity effects. *Atmos. Environ.* **24A**, 2563-2571.
- McDow, S.R. and Huntzicker, J.J. (1993). Vapor adsorption artifact in the sampling of organic aerosol. In *Sampling and Analysis of Airborne Pollutants*, Winegar, E.D. and Keith, L.H., Eds. Lewis Publishers, Boca Raton, FL, pp. 191-208.
- McDow, S.R., Sun, Q.R., Vartiainen, M., Hong, Y.S., Yao, Y.L., Fister, T., Yao, R.Q., and Kamens, R.M. (1994). Effect of composition and state of organic components on polycyclic aromatic hydrocarbon decay in atmospheric aerosols. *Environ. Sci. Technol.* **28**, 2147-2153.
- McDow, S.R., Vartiainen, M., Sun, Q., Hong, Y., Yao, Y., and Kamens, R.M. (1995). Combustion aerosol water content and its effect on polycyclic aromatic hydrocarbon reactivity. *Atmos. Environ.* **29**, 791-798.
- McDow, S.R. (1999). Sampling artifact errors in gas/particle partitioning measurements. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane, D.A., Ed. Gordon and Breach Science, Netherlands, pp. 105-126.
- McMurry, P.H. and Grosjean, D. (1985). Photochemical formation of organic aerosols: Growth laws and mechanisms. *Atmos. Environ.* **19**, 1445-1451.

- Meng,Z., Seinfeld,J.H., Saxena,P., and Kim,Y.P. (1997). Gas/aerosol distribution of formic and acetic acids. *Aerosol Sci. Technol.* **23**, 561-578.
- Mikhailov,E.F., Vlasenko,S.S., Krämer,L., and Niessner,R. (2001). Interaction of soot aerosol particles with water droplets: Influence of surface hydrophilicity. *J. Aerosol Sci.* **32**, 697-711.
- Muzyka,V., Veimer,S., and Shmidt,N. (1998). Particle-bound benzene from diesel engine exhaust. *Scan. J. Work Environ. Health* **24**, 481.
- Mylonas,D.T., Allen,D.T., Ehrman,S.H., and Pratsinis,S.E. (1991). The sources and size distributions of organonitrates in Los Angeles aerosol. *Atmos. Environ.* **25A**, 2855-2861.
- Neususs,C., Pelzing,M., Plewka,A., and Herrmann,H. (2000). A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles: Methods and first results. *J. Geophys. Res.* **105**, 4513-4527.
- Nielsen,T., Platz,J., Granby,K., Hansen,A.B., Skov,H., and Egeløv,A.H. (1998). Particulate organic nitrates: Sampling and night/day variation. *Atmos. Environ.* **32**, 2601-2608.
- Noda,J. and Ljungstrom,E. (2002). Aerosol formation in connection with NO₃ oxidation of unsaturated alcohols. *Atmos. Environ.* **36**, 521-525.
- Nolte,C.G., Fraser,M.P., and Cass,G.R. (1999). Gas phase C₂-C₁₀ organic acids concentrations in the Los Angeles atmosphere. *Environ. Sci. Technol.* **33**, 540-545.
- Nolte,C.G., Schauer,J.J., Cass,G.R., and Simoneit,B.R.T. (1999). Highly polar organic compounds present in meat smoke. *Environ. Sci. Technol.* **33**, 3313-3316.
- Novakov,T. and Corrigan,C.E. (1996). Cloud condensation nucleus activity of the organic component of biomass smoke. *Geophys. Res. Lett.* **23**, 2141-2144.
- Novakov,T., Corrigan,C.E., Penner,J.E., Chuang,C.C., Rosario,O., and Bracero,O.L.M. (1997). Organic aerosols in the Caribbean trade winds: A natural source? *J. Geophys. Res.* **102**, 21307-21314.
- O'Brien,R.J., Crabtree,J.H., Holmes,J.R., Hoggan,M.C., and Bockian,A.H. (1975). Formation of photochemical aerosol from hydrocarbons. Atmospheric analysis. *Environ. Sci. Technol.* **9**, 577-582.
- Odum,J.R., Hoffman,T., Bowman,F.A., Collins,D., Flagan,R.C., and Seinfeld,J.H. (1996). Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.* **30**, 2580-2585.
- Odum,J.R., Jungkamp,T.P.W., Griffin,R.J., Forstner,H.J.L., Flagan,R.C., and Seinfeld,J.H. (1997). Aromatics, reformulated gasoline, and atmospheric organic aerosol formation. *Environ. Sci. Technol.* **31**, 1890-1897.
- Odum,J.R., Jungkamp,T.P.W., Griffin,R.J., Flagan,R.C., and Seinfeld,J.H. (1997). The atmospheric aerosol-forming potential of whole gasoline vapor. *Science* **276**, 96-99.
- Oh,S. and Andino,J.M. (2000). Effects of ammonium sulfate aerosols on the gas-phase reactions of the hydroxyl radical with organic compounds. *Atmos. Environ.* **34**, 2901-2908.
- Oros,D.R. and Simoneit,B.R.T. (2000). Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel* **79**, 515-536.
- Palen,E.J., Allen,D.T., Pandis,S.N., Paulson,S.E., Seinfeld,J.H., and Flagan,R.C. (1993). Fourier transform infrared analysis of aerosol formed in the photooxidation of 1-octene. *Atmos. Environ.* **27A**, 1471-1477.
- Palmer,H.B. and Cullis,C.F. (1965). The formation of carbon from gases. In *Chemistry and Physics of Carbon*, Walker,P.L., Ed. Marcel Dekker, New York, pp. 265-325.
- Pandis,S.N., Paulson,S.E., Seinfeld,J.H., and Flagan,R.C. (1991). Aerosol formation in the photooxidation of isoprene and b-pinene. *Atmos. Environ.* **25**, 997-1008.
- Pandis,S.N., Harley,R.A., Cass,G.R., and Seinfeld,J.H. (1992). Secondary organic aerosol formation and transport. *Atmos. Environ.* **26A**, 2269-2282.

- Pandis, S.N., Paulson, S.E., Baltensperger, U., Seinfeld, J.H., Flagan, R.C., Palen, E.J., Allen, D.T. (1992). Aerosol production during the photooxidation and natural hydrocarbons. In *Precipitation Scavenging and Atmosphere-Surface Exchange. Vol. 3 - The Summers Volume: Applications and Appraisals*, Schwartz, S.E. and Slinn, W.G.N., Eds. Hemisphere Publishing Corp., Washington, DC, pp. 1641-1652.
- Pandis, S.N., Wexler, A.S., and Seinfeld, J.H. (1993). Secondary organic aerosol formation and transport - II. Predicting the ambient secondary organic aerosol size distribution. *Atmos. Environ.* **27A**, 2403-2416.
- Pankow, J.F. (1987). Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.* **21**, 2275-2283.
- Pankow, J.F. (1988). The calculated effects of non-exchangeable material on the gas-particle distributions of organic compounds. *Atmos. Environ.* **22**, 1405-1409.
- Pankow, J.F. and Bidleman, T.F. (1991). Effects of temperature, TSP and percent non-exchangeable material in determining the gas-particle partitioning of organic compounds. *Atmos. Environ.* **25A**, 2241-2249.
- Pankow, J.F. (1991). Common y-intercept and single compound regressions of gas-particle partitioning data vs. $1/T$. *Atmos. Environ.* **25A**, 2229-2239.
- Pankow, J.F. and Bidleman, T.F. (1992). Interdependence of the slopes and intercepts from log-log correlations of measured gas-particle partitioning and vapor pressure: I. Theory and analysis of available data. *Atmos. Environ.* **26A**, 1071-1080.
- Pankow, J.F. (1992). Application of common y-intercept regression parameters for $\log K_p$ vs $1/T$ for predicting gas-particle partitioning in the urban environment. *Atmos. Environ.* **26A**, 2489-2498.
- Pankow, J.F. (1993). A simple box model for the annual cycle of partitioning of semi-volatile organic compounds between the atmosphere and the Earth's surface. *Atmos. Environ.* **27A**, 1139-1152.
- Pankow, J.F., Storey, J.M.E., and Yamasaki, H. (1993). Effects of relative humidity on gas/particle partitioning of semivolatile organic compounds to urban particulate matter. *Environ. Sci. Technol.* **27**, 2220-2226.
- Pankow, J.F. (1994). An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.* **28**, 185-188.
- Pankow, J.F. (1994). An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.* **28**, 189-194.
- Pankow, J.F. (1999). Fundamentals and mechanisms of gas/particle partitioning in the atmosphere. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane, D.A., Ed. Gordon and Breach Science, Netherlands, pp. 25-37.
- Pankow, J.F., Seinfeld, J.H., Asher, W.E., Erdakos, G.B. (2001). Modeling the formation of secondary organic aerosol. 1. Application of theoretical principles to measurements obtained in the alpha-pinene/, beta-pinene/, sabinene/, Delta(3)-carene/, and cyclohexene/ozone systems. *Environ.Sci.Technol.*, **35**:1164-72.
- Paulson, S.E., Pandis, S.N., Baltensperger, U., Seinfeld, J.H., Flagan, R.C., Palen, E.J., Allen, D.A., Schaffner, C., Giger, W., and Portmann, A. (1990). Characterization of photochemical aerosols from biogenic hydrocarbons. *J. Aerosol Sci.* **21**, S245-S248.
- Peng, C. and Chan, C.K. (2001). The water cycles of water-soluble organic salts of atmospheric importance. *Atmos. Environ.* **35**, 1193-1202.
- Peters, J. and Seifert, B. (1998). Losses of benzo (a) pyrene under the conditions of hi-volume sampling. *Atmos. Environ.* **14**, 117.

- Pio,C., Alves,C., and Duarte,A. (2000). Organic components of aerosols in a forested area of central Greece. *Atmos. Environ.* **35**, 389-401.
- Pio,C.A., Alves,C.A., and Duarte,A.C. (2001). Identification, abundance and origin of atmospheric organic particulate matter in a Portuguese rural area. *Atmos. Environ.* **35**, 1365-1375.
- Pirjola,L. and Kulmala,M. (2001). Development of particle size and composition distributions with a novel aerosol dynamics model. *Tellus Series B-Chemical and Physical Meteorology*, **53**:491-509.
- Pistikopoulos,P., Masclet,P., and Mouvier,G. (1990). A receptor model adapted to reactive species: Polycyclic aromatic hydrocarbons - Evaluation of source contributions in an open urban site I. Particle compounds. *Atmos. Environ.* **24A**, 1189-1197.
- Pitts,J.N. and Grosjean,D. (1978). Detailed characterization of gaseous and size-resolved particulate pollutants at a South Coast Air Basin smog receptor site: Levels and models of formation of sulfalte, nitrate and organic particulates and their implications for control strategies. Report No. ARB-5-384. by California Air Resources Board, Sacramento, CA.
- Pitts,J.N., Jr., van Cauwenberghe,K., Grosjean,D., Schmid,J.P., Fitz,D.R., Besler,W.R., Jr., Knudson,G.B., and Hynds,P.M. (1978). Atmospheric reactions of polycyclic aromatic hydrocarbons: Facile formation of mutagenic derivatives. *Science* **202**, 515-519.
- Pudykiewicz,J.A. (1999). Atmospheric transport models and gas/particle partitioning. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane,D.A., Ed. Gordon and Breach Science, Netherlands, pp. 13-23.
- Pun,B.K., Seigneur,C., Grosjean,D., and Saxena,P. (1999). Gas-phase formation of water-soluble organic compounds in the atmosphere: A retrosynthetic analysis. *J. Atmos. Chem.* **35**, 199-223.
- Rasmussen,T.A. and Went,F.W. (1965). Volatile organic material of plant origin in the atmosphere. *Proc. Natl. Acad. Sci. USA* **53**, 215-220.
- Reilly,P.T.A., Gieray,R.A., Whitten,W.B., and Ramsey,J.M. (1998). Real-time characterization of the organic composition and size of individual diesel engine smoke particles. *Environ. Sci. Technol.* **32**, 2672-2679.
- Reiss,R., Ryan,P.B., Tibbetts,S.J., and Koutrakis,P. (1995). Measurement of organic acids, aldehydes, and ketones in residential environments and their relation to ozone. *JAWMA* **45**, 811-822.
- Richard,T., Hildemann,L., Jang,M., Jaoui,M., Kamens,R., Lee,S., Malm,W.C., Pandis,S., Pankow,J., Schauer,J., Watson,J.G., and Zielinska,B. (2002). Secondary Organic Aerosols Research Strategy to Apportion Biogenic/Anthropogenic Sources... An Outcome of the First Secondary Organic Aerosols Workshop, February 4-5, 2002, Desert Research Institute, Reno, Nevada. by Fort Lewis College, Durango, CO.
- Roberts,J.M. (1990). The atmospheric chemistry of organic nitrates. *Atmos. Environ.* **24A**, 243-287.
- Roby,R.J. and Harrington,J.A. (1981). Organic nitrites in aged exhaust from alcohol-fueled vehicles. *JAPCA* **31**, 995-996.
- Rocha,T.A.P., Horvath,H., Oliveira,J.A.B.P., and Duarte,A.C. (1999). Trends in alkanes and PAHs in airborne particulate matter from Oporto and Vienna: Identification and comparison. *Sci. Total Environ.* **236**, 231-236.
- Roe,S.M. and Fields,P.G. (1994) Assessing the significance of secondary organic aerosol contributions to regional particulate inventories. *U.S. EPA/A&WMA Specialty Conference - The Emissions Inventory: Applications and Improvement*, Raleigh, NC.
- Rogge,W.F., Mazurek,M.A., Hildemann,L.M., Cass,G.R., and Simoneit,B.R.T. (1993). Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation. *Atmos. Environ.* **27A**, 1309-1330.

- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1997). Sources of fine organic aerosol 7. Hot asphalt roofing tar pot fumes. *Environ. Sci. Technol.* **31**, 2726-2730.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1997). Sources of fine organic aerosol 8. Boilers burning No. 2 distillate fuel oil. *Environ. Sci. Technol.* **31**, 2731-2737.
- Rohrl, A. and Lammel, G. (2002). Determination of malic acid and other C4 dicarboxylic acids in atmospheric aerosol samples. *Chemosphere* **46**, 1195-1199.
- Röhrl, A. and Lammel, G. (2001). Low-molecular weight dicarboxylic acids and glyoxylic acid: Seasonal and air mass characteristics. *Environ. Sci. Technol.* **35**, 95-101.
- Ruiz, J., Bilbao, R., and Murillo, M. (1998). Adsorption of different VOC onto soil minerals from gas phase: Influence of mineral, type of VOC, and air humidity. *Environ. Sci. Technol.* **32**, 1079-1084.
- Sakugawa, H. and Kaplan, I.R. (1995). Stable carbon isotope measurements of atmospheric organic acids in Los Angeles, California. *Geophys. Res. Lett.* **22**, 1509-1512.
- Satsumabayashi, H., Kurita, H., Yokouchi, Y., and Ueda, H. (1990). Photochemical formation of particulate dicarboxylic acids under long-range transport in central Japan. *Atmos. Environ.* **24A**, 1443-1450.
- Saxena, P., Hildemann, L.M., McMurry, P.H., and Seinfeld, J.H. (1995). Organics alter hygroscopic behavior of atmospheric particles. *J. Geophys. Res.* **100**, 18755-18770.
- Saxena, P. and Hildemann, L.M. (1996). Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds. *Atmos. Chemis* **24**, 57-109.
- Saxena, P. and Hildemann, L.M. (1997). Water absorption by organics: Survey of laboratory evidence and evaluation of UNIFAC for estimating water activity. *Environ. Sci. Technol.* **31**, 3318-3324.
- Schauer, J.J., Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., and Simoneit, B.R.T. (1996). Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* **30**, 3837-3855.
- Schauer, J.J., Fraser, M.P., Cass, G.R., and Simoneit, B.R.T. (1998). Use of organic compounds as tracers for source contributions to atmospheric fine particle concentrations: Analysis of a severe photochemical smog episode. *J. Aerosol Sci.* **29**, S225-S226.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., and Simoneit, B.R.T. (1999). Measurement of emissions from air pollution sources. C₁ through C₂₉ organic compounds from meat charbroiling. *Environ. Sci. Technol.* **33**, 1566-1577.
- Schauer, J.J. and Cass, G.R. (2000). Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environ. Sci. Technol.* **34**, 1821-1832.
- Schell, B., Ackermann, I.J., Hass, H., Binkowski, F.S., Ebel, A. (2001). Modeling the formation of secondary organic aerosol within a comprehensive air quality model system. *J. Geophys. Res.*, **106**:28275-93.
- Schuetzle, D., Cronn, D., Crittenden, A.L., and Charlson, R.J. (1975). Molecular composition of secondary aerosol and its possible origin. *Environ. Sci. Technol.* **9**, 838-845.
- Seinfeld, J.H., Erdakos, G.B., Asher, W.E., Pankow, J.F. (2001). Modeling the formation of secondary organic aerosol (SOA). 2. The predicted effects of relative humidity on aerosol formation in the alpha-pinene-, beta-pinene-, sabinene-, Delta(3)-carene-, and cyclohexene-ozone systems (vol 35, pg 1806, 2001). *Environ.Sci.Technol.*, **35**:3272.
- Seinfeld, J.H., Erdakos, G.B., Asher, W.E., Pankow, J.F. (2001). Modeling the formation of secondary organic aerosol (SOA). 2. The predicted effects of relative humidity on aerosol formation in the alpha-pinene-, beta-pinene-, sabinene-, Delta(3)-Carene-, and cyclohexene-ozone systems. *Environ.Sci.Technol.*, **35**:1806-17.
- Sheehan, P.E. and Bowman, F.M. (2001). Estimated effects of temperature on secondary organic aerosol concentrations. *Environ. Sci. Technol.* **35**, 2129-2135.

- Sheffield,A.E., Currie,L.A., Klouda,G.A., and Donahue,D.J. (1990). Accelerator mass spectrometric determination of carbon-14 in the low-polarity organic fraction of atmospheric particles. *Anal. Chem.* **62**, 2098-2102.
- Sheffield,A.E., Gordon,G.E., Currie,L.A., and Reiderer,G.E. (1994). Organic elemental and isotopic tracers of air pollution sources in Albuquerque, NM. *Atmos. Environ.* **28**, 1371-1384.
- Shulman,M.L., Charlson,R.J., and Davis,E.J. (1997). The effects of atmospheric organics on aqueous droplet evaporation. *J. Aerosol Sci.* **25**, 737-752.
- Siegl,W.O., Hammerle,R.H., Herrmann,H.M., Wenclawiak,B.W., and Luers-Jongen,B. (1999). Organic emissions profile for a light-duty diesel vehicle. *Atmos. Environ.* **33**, 797-806.
- Simoneit,B.R.T. (1985). Application of molecular marker analysis to vehicular exhaust for source reconciliations. *Int. J. Environ. & Chem.* **22**, 203-233.
- Simoneit,B.R.T. (1986). Characterization of organic constituents in aerosols in relation to their origin and transport: A review. *Int. J. Environ. Anal. Chem.* **23**, 207-237.
- Simoneit,B.R.T., Cardoso,J.N., Robinson,N.F., and Brazil,R.J. (1990). An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. *Chemosphere* **21**, 1285-1301.
- Simoneit,B.R.T., Sheng,G., Chen,X., Fu,J., Zhang,J., and Xu,Y. (1991). Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmos. Environ.* **25A**, 2111-2129.
- Simoneit,B.R.T. (1999). A review of biomarker compounds as source indicators and tracers for air pollution. *Environ. Sci. Pollut. Res.* **6**, 159-169.
- Sofuoglu,A., Odabasi,M., Tasdemir,Y., Khalili,N.R., and Holsen,T.M. (2001). Temperature dependence of gas-phase polycyclic aromatic hydrocarbon and organochlorine pesticide concentrations in Chicago air. *Atmos. Environ.* **35**, 6503-6510.
- Souza,S.R., Vasconcellos,P.C., and Carvalho,L.R.F. (1999). Low molecular weight carboxylic acids in an urban atmosphere: Winter measurements in Sao Paulo City, Brazil. *Atmos. Environ.* **33**, 2563-2574.
- Spanke,J., Rannik,U., Forkel,R., Nigge,W., Hoffmann,T. (2001). Emission fluxes and atmospheric degradation of monoterpenes above a boreal forest: field measurements and modelling. *Tellus Series B-Chemical and Physical Meteorology*, **53**:406-22.
- Stemmler,K. and von Gunten,U. (2000). OH radical-initiated oxidation of organic compounds in atmospheric water phases. Part 1: Reactions of peroxy radicals derived from 2-butoxyethanol in water. *Atmos. Environ.* **34**, 4241-4252.
- Stemmler,K. and von Gunten,U. (2000). OH radical-initiated oxidation of organic compounds in atmospheric water phases. Part 2: Reactions of peroxy radicals with transition metals. *Atmos. Environ.* **34**, 4253-4264.
- Stephanou,E.G. (1992). Biogenic and anthropogenic organic compounds in eolian particles in the east Mediterranean region - I. Occurrence and origin. *Atmos. Environ.* **26A**, 2821-2830.
- Stephanou,E.G. and Stratigakis,N. (1993). Oxocarboxylic and α,ν -dicarboxylic acids: Photooxidation products of biogenic unsaturated fatty acids present in urban aerosols. *Environ. Sci. Technol.* **27**, 1403-1407.
- Stephanou,E.G., Kavouras,I., and Mihalopoulos,N. (2001). Comment on "Formation of new particles in the gas-phase ozonolysis of monoterpenes" by Koch et al. [*Atmos. Environ.* 34 (2000) 4031-4042]. *Atmos. Environ.* **35**, 4523-4524.
- Stern,J.E., Flagan,R.C., Grosjean,D., and Seinfeld,J.H. (1987). Aerosol formation and growth in atmospheric aromatic hydrocarbon photooxidation. *Environ. Sci. Technol.* **21**, 1224-1231.

- Storey, J.M.E. and Pankow, J.F. (1992). Gas-particle partitioning of semi-volatile organic compounds to model atmospheric particulate materials - I. Sorption to graphite, sodium chloride, alumina, and silica particles under low humidity conditions. *Atmos. Environ.* **26A**, 435-443.
- Strader, R., Pandis, S.N., and Lurmann, F.W. (1998). Evaluation of secondary organic aerosol formation in winter. Prepared for California Air Resources Board, Sacramento, CA, by Carnegie Mellon University, Pittsburgh, PA.
- Strader, R., Lurmann, F.W., and Pandis, S.N. (1999). Evaluation of secondary organic aerosol formation in winter. *Atmos. Environ.* **33**, 4849-4863.
- Strommen, M.R. and Kamens, R.M. (1997). Development and application of a dual-impedance radial diffusion model to simulate the partitioning of semivolatile organic compounds in combustion aerosols. *Environ. Sci. Technol.* **31**, 2983-2990.
- Stroud, C.A., Roberts, J.M., Williams, J., Goldan, P.D., Kuster, W.C., Ryerson, T.B., Sueper, D., Parrish, D.D., Trainer, M., Fehsenfeld, F.C., Flocke, F., Schauffler, S.M., Stroud, V.R.F., Atlas, E. (2001). Alkyl nitrate measurements during STERAO 1996 and NARE 1997: Intercomparison and survey of results. *J. Geophys. Res.*, **106**:23043-53.
- Tang, H., Lewis, E.A., Eatough, D.J., Burton, R.M., and Farber, R.J. (1994). Determination of the particle size distribution and chemical composition of semi-volatile organic compounds in atmospheric fine particles with a diffusion denuder system. *Atmos. Environ.* **28**, 939-947.
- Tao, Y. and McMurry, P.H. (1989). Vapor pressures and surface free energies of C₁₄-C₁₈ monocarboxylic acids and C₅ and C₆ dicarboxylic acids. *Environ. Sci. Technol.* **23**, 1519-1523.
- Thomas, E.R., Frost, G.J., Rudich, Y. (2001). Reactive uptake of ozone by proxies for organic aerosols: Surface-bound and gas-phase products. *J. Geophys. Res.*, **106**:3045-56.
- Tobias, H.J. and Ziemann, P.J. (2000). Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids. *Environ. Sci. Technol.* **34**, 2105-2115.
- Tobias, H.J., Docherty, K.S., Beving, D.E., Ziemann, P.J. (2000) Effect of relative humidity on the chemical composition of secondary organic aerosol formed from the reactions of 1-tetradecene and ozone. *Environ. Sci. Technol.*, [In Press].
- Tran, N.K., Steinberg, S.M., and Johnson, B.J. (2000). Volatile aromatic hydrocarbons and dicarboxylic acid concentrations in air at an urban site in the southwestern U.S. *Atmos. Environ.* **34**, 1845-1852.
- Turpin, B.J., Cary, R.A., and Huntzicker, J.J. (1990). An *in-situ*, time-resolved analyzer for aerosol organic and elemental carbon. *Aerosol Sci. Technol.* **12**, 161-171.
- Turpin, B.J. and Huntzicker, J.J. (1991). Secondary formation of organic aerosol in the Los Angeles Basin: A descriptive analysis of organic and elemental carbon concentrations. *Atmos. Environ.* **25A**, 207-215.
- Turpin, B.J., Liu, S.P., Podolske, K.S., Gomes, M.S.P., Eisenreich, S.J., and McMurry, P.H. (1993). Design and evaluation of a novel diffusion separator for measuring gas/particle distributions of semivolatile organic compounds. *Environ. Sci. Technol.* **27**, 2441-2449.
- Turpin, B.J., Huntzicker, J.J., and Hering, S.V. (1994). Investigation of organic aerosol sampling artifacts in the Los Angeles Basin. *Atmos. Environ.* **28**, 3061-3071.
- Turpin, B.J. and Huntzicker, J.J. (1995). Identification of secondary organic aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS. *Atmos. Environ.* **29**, 3527-3544.
- Turpin, B.J., Saxena, P., Allen, G.A., Koutrakis, P., McMurry, P.H., and Hildemann, L.M. (1997). Characterization of the southwestern desert aerosol, Meadview, AZ. *JAWMA* **47**, 344-356.

- Turpin, B.J., Liu, S.P., McMurry, P.H., Eisenreich, S.J. (1999). Definitive measurement of semivolatile PAHs with a diffusion separator: Design and investigation of sampling artifacts in filter-adsorbent samplers. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane, D.A., Ed. Gordon & Breach Science, Amsterdam, pp. 369-392.
- Turpin, B.J., Saxena, P., and Andrews, E. (2000). Measuring and simulating particulate organics in the atmosphere: Problems and prospects. *Atmos. Environ.* **34**, 2983-3013.
- Umlauf, G. (1999). Measuring gas/particle fractions of trace organic compounds in ambient air. Evaluation of electrostatic precipitation, impaction and conventional filtration for separating particles. In *Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Vol. 2*, Lane, D.A., Ed. Gordon and Breach Science, Netherlands, pp. 73-103.
- van Vaeck, L. and van Cauwenberghe, K. (1984). Conversion of polycyclic aromatic hydrocarbons on diesel particulate matter upon exposure to ppm levels of ozone. *Atmos. Environ.* **18**, 323-328.
- Veltkamp, P.R., Hansen, K.J., Barkley, R.M., and Sievers, R.E. (1996). Principal component analysis of summertime organic aerosols at Niwot Ridge, Colorado. *J. Geophys. Res.* **101**, 19495-19504.
- Virkkula, A., van Dingenen, R., Raes, F., and Hjorth, J. (1999). Hygroscopic properties of aerosol formed by oxidation of limonene, α -pinene, and β -pinene. *J. Geophys. Res.* **104**, 3569-3580.
- Waggoner, A.P., Weiss, R.E., and Larson, T.V. (1983). *In situ*, rapid response measurement of $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ in urban Houston: A comparison with rural Virginia. *Atmos. Environ.* **17**, 1723-1731.
- Wang, S.C., Flagan, R.C., and Seinfeld, J.H. (1992). Aerosol formation and growth in atmospheric organic/ NO_x systems II. Aerosol dynamics. *Atmos. Environ.* **26A**, 421-434.
- Wang, S.C., Paulson, S.E., Grosjean, D., Flagan, R.C., and Seinfeld, J.H. (1992). Aerosol formation and growth in atmospheric organic/ NO_x systems - I. Outdoor smog chamber studies of C_7 and C_8 hydrocarbons. *Atmos. Environ.* **26A**, 403-420.
- Wania, F., Haugen, J.E., Lei, Y.D., and Mackay, D. (1998). Temperature dependence of atmospheric concentrations of semivolatile organic compounds. *Environ. Sci. Technol.* **32**, 1013-1021.
- Watson, J.G., Fujita, E.M., Chow, J.C., Zielinska, B., Richards, L.W., Neff, W.D., and Dietrich, D. (1998). Northern Front Range Air Quality Study. Final report. Prepared for Colorado State University, Fort Collins, CO, by Desert Research Institute, Reno, NV.
- Watts, R.R., Wallingford, K.M., Williams, R.W., House, D.E., and Lewtas, J. (1998). Airborne exposures to PAH and $\text{PM}_{2.5}$ particles for road paving workers applying conventional asphalt and crumb rubber modified asphalt. *J. Expo. Anal. Environ. Epidemiol.* **8**, 213-229.
- Weingartner, E., Burtscher, H., and Baltensperger, U. (1997). Hygroscopic properties of carbon and diesel soot particles. *Atmos. Environ.* **31**, 2311-2328.
- Welke, B., Ettlinger, K., and Riederer, M. (1998). Sorption of volatile organic chemicals in plant surfaces. *Environ. Sci. Technol.* **32**, 1099-1104.
- Went F. (1960). Blue hazes in the atmosphere. *Nature*, **187**:641-3.
- Went, F.W. (1960). Organic matter in the atmosphere, and its possible relation to petroleum formation. *Proc. Natl. Acad. Sci. USA* **46**, 212-221.
- Went, F.W., Slemmons, D.E., and Mozingo, H.N. (1967). The organic nature of atmospheric condensation nuclei. *Proc. Natl. Acad. Sci. USA* **58**, 69-74.
- Williams, P.M., Robertson, K.J., Soutar, A., and Griffin, S.M. (1992). Isotopic signatures (C^{14} , C^{13} , N^{15}) as tracers of sources and cycling of soluble and particulate organic matter in the Santa Monica Basin, California. *Progress in Oceanography* **30**, 253-290.

- Williams,R.W., Watts,R.R., Stevens,R.K., Stone,C.L., and Lewtas,J. (1999). Evaluation of a personal air sampler for twenty-four hour collection of fine particles and semivolatile organics. *J. Expo. Anal. Environ. Epidemiol.* **9**, 158.
- Winiwarter,W., Puxbaum,H., Fuzzi,S., Facchini,M.C., Orsi,G., Beltz,N., Enderle,K., and Jaeschke,W. (1988). Organic acid gas and liquid-phase measurements in Po Valley: Fall-winter conditions in the presence of fog. *Tellus* **40B**, 348-357.
- Winterhalter,R., Neeb,P., Grossmann,D., Koloff,A., Horie,O., and Moortgat,G. (1999). Products and mechanism of the gas phase reaction of ozone with beta-pinene. *J. Atmos. Chem.* **35**, 165-197.
- Xiong,J.Q., Zhong,M., Fang,C., Chen,L.C., and Lippmann,M. (1998). Influence of organic films on the hygroscopicity of ultrafine sulfuric acid aerosol. *Environ. Sci. Technol.* **32**, 3536-3541.
- Yassaa,N., Meklati,B.Y., Cecinato,A., and Marino,F. (2001). Particulate n-alkanes, n-alkanoic acids and polycyclic aromatic hydrocarbons in the atmosphere in Algiers City area. *Atmos. Environ.* **35**, 1843-1851.
- Yu,J.Z., Flagan,R.C., Seinfeld,J.H. (1998). Identification of products containing -COOH, -OH, and -C=O in atmospheric oxidation of hydrocarbons. *Environ.Sci.Technol.*, **32**:2357-70.
- Yu,J.Z., Cocker,D.R., Griffin,R.J., Flagan,R.C., and Seinfeld,J.H. (1999). Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products. *J. Atmos. Chem.* **34**, 207-258.
- Yu,J.Z., Griffin,R.J., Cocker,D.R., Flagan,R.C., Seinfeld,J.H., Blanchard,P. (1999). Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. *Geophys.Res.Lett.*, **26**:1145-8.
- Yu,S. (2000). Role of organic acids (formic, acetic, pyruvic and oxalic) in the formation of cloud condensation nuclei (CCN): A review. *Atmospheric Research* **53**, 185-217.
- Zappoli,S., Andracchio,A., Fuzzi,S., Facchini,M.C., Gelencsér,A., Kiss,G., Krivácsy,Z., Molnár,A., Mészáros,E., Hansson,H.C., Rosman,K., and Zebühr,Y. (1999). Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. *Atmos. Environ.* **33**, 2733-2743.
- Zervas,E., Montagne,X., and Lahaye,J. (1999). Collection and analysis of organic acids in exhaust gas comparison of different methods. *Atmos. Environ.* **33**, 4953-4962.
- Zervas,E. and Tazerout,M. (2000). Organic acids emissions from natural-gas-fed engines. *Atmos. Environ.* **34**, 3921-3929.
- Zhang,X.Q., McMurry,P.H., Hering,S.V., and Casuccio,G.S. (1993). Mixing characteristics and water content of submicron aerosol measured in Los Angeles and at the Grand Canyon. *Atmos. Environ.* **27A**, 1593-1607.
- Zheng,M., Fang,M., Wang,F., and To,K.L. (2000). Characterization of the solvent extractable organic compounds in PM_{2.5} aerosols in Hong Kong. *Atmos. Environ.* **34**, 2691-2702.
- Zwirner-Baier,I. and Neumann,H.G. (1999). Polycyclic nitroarenes (nitro-PAHs) as biomarkers of exposure to diesel exhaust. *Mutat. Res. -Genet. Toxicol. Environ. Mutag.* **441**, 135-144.

ⁱ Went, F.W, Organic Matter in the Atmosphere, and its possible Relation to Petroleum Formation, Proc National Academy of Sciences, Botany, 212-221, 1959.

ⁱⁱ Guenther, A.B.; Monson, R.K.; Fall, R.; Isoprene and Monoterpene Emission Variability: Observation with Eucalyptus and Emission rate Algorithm Development, J. Geophys. Res., 96, 10799-10808, 1991

ⁱⁱⁱ Griffin, R. J.; Cocker, D. R., III; Flagan, R. C.; Seinfeld, J. H. Organic Aerosol Formation from the Oxidation of Biogenic Hydrocarbons. *J. Geophys. Res.*, 104, 3555-3567. 1999

-
- ^{iv} Andersson-Sköld Y. and Simpson D., Secondary Organic Aerosol Formation in Northern Europe: a Model Study, *J. Geophys. Res.*, 106, 7357-7374, 2001
- ^v Helmig D., L.; Klinger, L.F.; Greenberg, J.; Zimmermann, P.; Emissions and Identification of Individual Organic Compounds From Vegetation in Three Ecosystems in the U.S., 207 ACS Meeting Am. Chem. Soc., San Diego, California, 13-18, March 1994.
- ^{vi} Yu, J.; Griffin, R.J.; Cooker III, D.R.; Flagan, R.C.; Seinfeld, J.H.; Observations of Gaseous and Particulate Products of MonoTerpene Oxidation in Forested Atmospheres, *J. Geophys. Res. Let.*, 26, 1145-1148, 1999
- ^{vii} Hannele, H.; Laurila, T.; Rinne, L.; Puhto, K.; The Ambient Concentration of Biogenic Hydrocarbons at a Northern European, Boreal Site, *Atmos. Environ.*, 4971-4982, 2000.
- ^{viii} Ehhalt, D.H. Gas phase chemistry of the troposphere, pp. 21-109, in R. Zellner (edit.), *Global Aspects of Atmospheric Chemistry*, Steinkopff-Verlag, Darmstadt, and Springer-Verlag, New York, 1999.
- ^{ix} Kurtenbach, R.; K.J. Brockmann, J.; J. Lorzer; A. Niedojadlo; K. H. Becker [VOV-Measurements in Urban Air of the City of Wuppertal, in TFS-LT3 annual Report (German), K.H. Becker editor, 1998.
- ^x Fujita, E.M.; Z. Lu; L. Sheetz; G. Harshfeld; B. Zilinska Determination of Mobile Source Emissions Fraction Using Ambient Field Measurements, Report to the Coordinating Research Council (CRC), 215 Perimeter Center Parkway, Atlanta, GA, 1997.
- ^{xi} Ciccioli, R.; E. Brancaleoni; M. Frattoni The Reactive Hydrocarbons in the Atmosphere at Urban and Regional Scales, in *Reactive Hydrocarbons in the Atmosphere*, C.N. Hewitt(editor) Academic Press, San Diego, 1999.
- ^{xii} Goldan, P.D., Kuster, W.C.; Fehsenfeld, F.C.; Montzka, S.A.; Hydrocarbon Measurements in the Southeast United States: the Rural Oxidants in the Southern Environment (ROSE) Program 1990, *J. Geophys. Res.*, 100, 259454-25963, 1995.
- ^{xiii} Sagebiel, J.C.; Zielinska, B.; Rierson, W.P.; Gertler, A.W.: Real-World Emissions and Calculated Reactivities of Organic Species from Motor Vehicles, *Atmos. Environ.*, 30, 2287-2296, 1996.
- ^{xiv} Jang, M.; Kamens, R.M.; Characterization of Secondary Aerosol from the Photooxidation of Toluene in the Presence of NO_x and 1-Propene, *Environ. Sci. Technol.*, 35, 3625-3639, 2001
- ^{xv} Prager, M. J.; Stephens, E. R.; Scott, W. E.; Aerosol Formation for Gaseous Air Pollutants, *Ind. Eng. Chem.* 52, 521-524, 1960
- ^{xvi} Izumi, K.; Fukuyama, T.; Photochemical Aerosol Formation From Aromatic Hydrocarbons in the Presence of NO_x, *Atmos. Environ.* 24, 1433-1441, 1990
- ^{xvii} Hatakeyama, S.; Izumi, K.; Fukuyama, T.; Akimoto, H.; Reactions of ozone with α -pinene and β -pinene in air: yield of gaseous and particulate products. *J. Geophys. Res.* 20, 13013-13024, 1989.
- ^{xviii} Yu, J., Flagan R. C.; Seinfeld, J.; Identification of products Containing -COOH, -OH, -C=O in Atmospheric Oxidation of Hydrocarbons, *Environ. Sci. and Technol.*, 32, 2357-2370, 1998.
- ^{xix} Jang, M., and R. M. Kamens, Newly characterized products and composition of secondary aerosols from reaction of α -pinene with ozone, *Atmos. Environ.*, 33, 459-474, 1999.
- ^{xx} Odum, J. R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R. C.; Seinfeld, J. H. Gas/Particle Partitioning and Secondary Organic Aerosol Yields, *Environ. Sci. Technol.*, 30, 2580-2585, 1996.
- ^{xxi} Glasius, M., Lahaniati, M.; Caligiou, A.; Di Bella, D.; Jensen, N. R.; Hjorth, J.; Duane M. J.; Kotzias, D.; Larsen B. R.; Carboxylic Acids in Secondary Aerosols from Oxidation of Cyclic Monoterpenes by Ozone, *Environ. Sci. and Technol.* 34, 1001-1010, 2000.
- ^{xxii} Hull, L. A. Terpene Ozonolysis Products. In *Atmospheric Biogenic Hydrocarbons*; Bufalini, J. J.; Arnst, R. R., Eds.; Ann Arbor Science: Ann Arbor, MI, 1981; Vol. 2, 161-186, 1981
- ^{xxiii} Griffin, R. J.; Cocker, D. R., III; Flagan, R. C.; Seinfeld, J. H. Organic Aerosol Formation from the Oxidation of Biogenic Hydrocarbons. *J. Geophys. Res.*, 104, 3555-3567, 1999
- ^{xxiv} Pankow, J. F. An absorption model of gas/particle partitioning of organic compounds in the atmosphere *Atmos. Environ.* 28, 185-188, 1994.
- ^{xxv} Schauer, J.J.; Rogge, W.F.; Hildemann, L.M.; Mazurek, M.; Cass, G.R.: Source Apportionment of Airborne Particulate Matter Using organic Compounds as Tracers, *Atmos. Environ.*, 30, 3837-3855, 1996.
- ^{xxvi} Kamens, R. M., and Jaoui, M., Modeling aerosol formation from α -pinene + NO_x in the presence of natural sunlight using gas phase kinetics and gas-particle partitioning theory, *Environ. Sci. Technol.* 35, 1394-1405, 2001.

^{xxvii} Jang, M., Kamens; R.M, Atmospheric Secondary Aerosol Formation by Heterogeneous Reactions of Aldehydes in the Presence of a Sulfuric Acid Aerosol Catalyst *Environ. Sci. Technol.*, 35, 4758-4766, 2001.