

**Final Proceedings**

**Workshop on**

**Combining Environmental Fate  
and Air Quality Modeling**

**Organized by the  
Reactivity Research Working Group's**

**Atmospheric Availability and Environmental Fate  
Subgroup**

**June 27-29, 2000  
Research Triangle Park, NC**

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Implementation Panel**

**American Chemistry Council - Ethylene Glycol Ethers Panel**

**American Chemistry Council - Propylene Glycol Ethers Panel**

**Chemical Specialty Manufacturers Association**

**Dunn-Edwards Corporation**

**National Paint and Coatings Association**

**Soap and Detergents Association**

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The organizing committee would like to recognize the tireless efforts and thoughtful leadership offered by Jonathan Kurland during the preparation and planning of this workshop. The committee is also grateful to the U.S. Environmental Protection Agency for providing the meeting facilities and audiovisual equipment used by workshop attendees.

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## EXECUTIVE SUMMARY

This paper contains the proceedings from a workshop on Combining Environmental Fate and Air Quality Modeling that was organized by the Reactivity Research Working Group's subgroup on Atmospheric Availability and Environmental Fate. The workshop brought together experts in multimedia and air quality disciplines to establish prospects and priorities for the integration of environmental fate and air quality models. The goal of the workshop was to produce a set of research recommendations that would help in the development of a model for evaluating the importance of multimedia processes on the ozone forming potential of volatile chemicals.

Forty experts from a variety of disciplines including multimedia modeling, air quality modeling, indoor air quality, and dispersion modeling participated in the workshop, which was held on June 27-29, 2000 at the EPA Administration Building in Research Triangle Park, NC (Appendix A). On the first day of the meeting, experts representing the above disciplines gave background presentations to introduce participants to important concepts in these fields (Appendix B). On the second day, participants were divided into three working groups and asked to consider the following:

- ?? Determine the importance of transport to and from water soil, sediment, and other media and of transformation in these media on the ozone forming potential of different VOC capable of contributing to tropospheric ozone and particulate matter (PM<sub>2.5</sub>).
- ?? Identify environmental fate processes that significantly influence the concentration of VOC in the atmosphere.
- ?? Investigate mechanisms to address the integration of fate and transportation into air quality models.
- ?? Propose priorities for the integration of environmental fate and air quality models.

These topics are further outlined and expanded in Appendix C.

Each working group contained experts from several disciplines. Participants reconvened on the third day of the meeting and a representative from each group presented their recommendations. The results from these presentations were used to establish future research priorities.

A staged research plan was developed to assess the importance of atmospheric availability on the ozone formation potential of VOCs.

1. Survey candidate chemicals using environmental fate models to determine the range of compounds whose ozone-forming potential is affected by partitioning.
2. Develop an initial screening box model that combines an air quality model and environmental fate (multimedia) model.

3. Use the screening model to compare the results of environmental fate models and the screening air quality/environmental fate model with regard to the fraction of various VOC oxidized in air.
4. Continue with the development of a grid model capable of being used for regulatory purposes, if environmental fate is found to have an appreciable effect on the ozone forming potential of important VOCs.

Somewhat lower priorities were later established by the Reactivity Research Working Group for the following research.

1. Consider the environmental fate of indoor emissions, indoor sinks and sources.
2. Consider the environmental fate of photochemical oxidation products and their impact on the estimation of the ozone-forming potential of VOCs (e.g., MIR values).

The workshop was successful in bringing together experts from a variety of disciplines to discuss the impact of multimedia processes on the ozone forming potential of VOCs. There was a useful exchange of information and ideas among workshop participants. The recommendations will help focus future research, leading to the development of a model that can evaluate the importance of multimedia processes on the formation of ozone by VOCs capable of contributing to tropospheric ozone.

## OVERVIEW

When volatile organic compounds (VOCs) are emitted into the atmosphere, they can undergo photochemical reactions that may contribute to the formation of ground-level ozone. It has been realized for a number of years that not all VOCs are equal in their effects on ground-level ozone formation. Some VOCs react so slowly they have almost no effect on ozone pollution episodes, others not only form ozone themselves but also enhance ozone formation from other VOCs, and others actually inhibit ozone formation. The impact of a VOC on formation of ozone or other measures of air quality is referred to as its atmospheric "reactivity". VOC regulations that take into account differences in VOC reactivity have the potential of being much more cost-effective than present policy. However, there are significant uncertainties as to how VOC reactivity should be quantified and determined, and there are major unresolved policy issues that affect what scientific research is most needed. In view of this, the EPA and other regulatory agencies joined with industry groups and interested researchers to form the Reactivity Research Working Group (RRWG) to coordinate policy-relevant research related to VOC reactivity. The Research Reactivity Working Group was organized in May 1998 and developed the following mission statement.

Our mission is to provide an improved scientific basis for reactivity-related regulatory policies. That will be accomplished by bringing together all parties actively interested in sponsoring, planning, performing or assessing policy-relevant scientific research on the reactivities of organic compounds emitted to ambient air, as related to the formation of ozone, PM<sub>2.5</sub>, and regional haze. This is for the purposes of coordinating such research and defining potential applications, while continuously involving key policy makers.

Soon after the release of its VOC Reactivity Science Assessment report, the RRWG established 9 subgroups to address the individual research topics and recommendations outlined by its members. Subgroup 3 on Atmospheric Availability and Environmental Fate was established to examine the impact of multimedia processes on the formation of tropospheric ozone. The subgroup recognized that VOC concentrations in the troposphere were affected by both the rate and extent of release from an emission source and by the rate of removal through a variety of competing processes. These factors were clearly important in assessing the effects of VOCs on ozone formation. However, the environmental fate and transport processes that described how a chemical partitioned among air, water, soil, and sediment were not incorporated into the air quality models used to predict tropospheric ozone impacts. Subgroup 3 proposed holding a workshop to discuss the importance of transport and transformations to and from water, soil, sediment, and other media on the ozone forming potential of VOCs. The workshop was conceived as an opportunity to assemble experts in the fields of multimedia modeling and urban air shed

modeling to consider the possibility of including multimedia processes in air quality models and propose new research on the topic.

The underlying hypothesis for the workshop was that atmospheric availability might be as important to the formation of tropospheric ozone as reactivity in the gaseous phase. This hypothesis resulted in workshop discussions concerning the overall impact of multimedia modeling predictions on atmospheric reactivity, the significance of environmental fate modeling on the formation of ozone, and the manner in which any changes in ozone formation are manifested.

## **BACKGROUND**

The objectives of the workshop were: 1) to produce research recommendations that would help in the development of a model which can evaluate the importance of multimedia processes on the ozone-forming potential of compounds; and 2) to establish prospects and research priorities for the integration of environmental fate and air quality models. The following questions served to guide many of the group discussions:

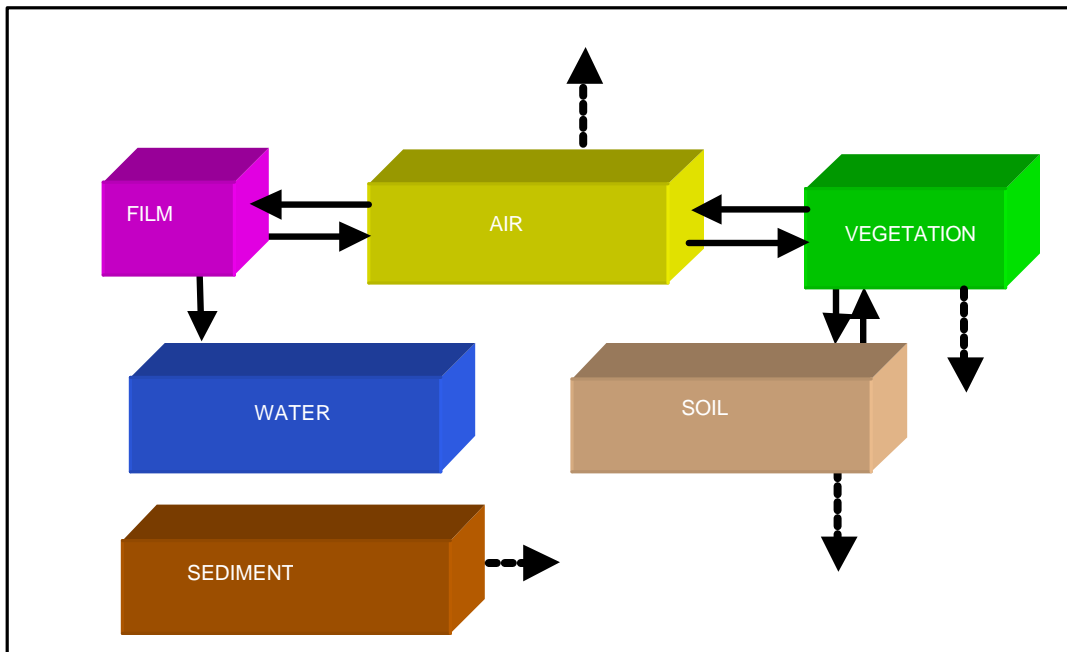
- ?? Do air quality and multimedia models need to be linked at a screening level for assessing the impact of different multimedia compartments?
- ?? Is it feasible to link Level IV, time-dependent multimedia models with photochemical box models?
- ?? Can a model integration scheme will provide a framework for directing needed research on compartmental chemistry and mass transfer rates?
- ?? Can a research paradigm be identified that provides a progressive, systematic approach for directing the development and evolution of an air quality model that incorporates all relevant multimedia processes?

Summaries of the talks that were presented at the start of the workshop to provide background information on each of the related fields follow.

### *Multimedia Urban Models (Miriam Diamond)*

The speaker has conducted numerous studies on the importance of multimedia partitioning in the urban environment. This work was highlighted to help workshop participants better understand the fate of compounds in the environment. She has conducted research on the importance of various surface films in the urban environment. Figure 1 depicts an urban multimedia model containing a film compartment that she has developed. Chemicals have only a short residence time in the films, but the films can be a means of sweeping compounds out of the air and into the water instead of depositing directly onto vegetation or in the soil.

Figure 1. Multimedia Urban Model



*Use of Fugacity-based Multimedia Models to Assess the Fate of Chemicals in the Environment (Charles Staples)*

This presentation on fugacity based multimedia models summarized how these models are set up and designed. An example showed how the mass balance for air includes transfers to and from soil and water, sources to the air, advection losses out of the model region, and transformation processes. To model a chemical, information is needed on the partition coefficients and degradation rates in multiple environmental media. The speaker also presented an example of the steady-state distribution of isobutanol, a chemical intermediate commonly used as a solvent. When emitted to air, 80% is found in the water, 14% in the soil, and 6% in the soil, thus for this chemical, the entire mass in not available for reactions in the atmosphere.

*Air Quality Models and Component Modules (Gail Tonneson)*

This presentation was a “background” talk on air quality modeling designed for a mixed audience of scientists and regulators in the fields of air quality modeling and multimedia modeling. The purpose of this talk was to provide sufficient background on scientific and data aspects of air quality modeling so that an interdisciplinary team of scientists could discuss approaches for integrated, multimedia modeling of low volatility compounds, including their fate and their possible contribution to air pollution. Key topics addressed include the following: types of air quality models, including dispersion models, simple box modes,



trajectory models, and gridded, regional scale air quality models; necessary inputs for air quality models, including meteorological fields, emissions inventories, and photochemical mechanisms; auxiliary models and preprocessors required for generating air quality model inputs; introduction to the photochemistry of gas phase and heterogeneous chemistry and aerosol formation; key uncertainties in model inputs and formulation; and approaches for model evaluation and validation.

While there are large uncertainties in model inputs and in the accuracy of models in forecasting future conditions, model predictions of concentrations of the hydroxyl radicals (OH) and ozone (O<sub>3</sub>) are relatively insensitive to these uncertainties and are useful for examining the fate of low volatility VOC. The aerosol formation mechanisms represented in regional scale air quality models are still somewhat primitive, particularly for the formation of secondary organic aerosols (SOA) from low volatility VOC. Improved SOA formation mechanisms is a key area requiring improvement for determining the fate and impacts of low volatility VOC. Relatively simple trajectory models, for example the OZIP/EKMA trajectory model, may be useful as a screening tool and a first step in linking multi-media models with photochemical air quality models.

*Environmental Fate of Indoor VOC Emissions: The Role of Indoor Chemistry (Jim Zhang)*

Another of the background presentations addressed the environmental fate of VOC's that are emitted in buildings, including houses, apartments, public buildings and commercial buildings. In addition to providing a list of some VOC's that might be emitted indoors, Dr. Zhang described alternate fates of those VOC's that might preclude emission to outdoor air. The particular emissions and typically higher concentration of indoor air pollutants demands some careful review of the reaction chemistry that might occur both in indoor air and on indoor surfaces. These reactions are constrained by shorter time frames, related to air exchange rates with outdoor air, than those of typical multimedia modeling. Still some of the surface chemistry and radical induced formation of particulates and semi-volatile condensation products give indication that indoor emissions may not simply migrate unchanged to the outdoor atmosphere.

The speaker concluded that indoor environments are often not passive boxes for VOC emissions. Also, indoor air chemistry is complex and not well appreciated at present. The surface to volume ratio in indoor environments is quite high so adsorption, absorption, and surface chemistry are more important indoors. Indoor environments also are more carefully controlled for temperature, light energy and humidity and may thus be more predictable regarding physical chemical characteristics. Finally, human activities can have a greater impact on air emissions indoors than on outdoor emissions; therefore, it may be an appropriate experimental environment for further study.

## *Modeling of Chemical Transport in the Atmosphere (Christian Seigneur)*

The processes that govern the transport of chemicals in the atmosphere were described in this presentation. Atmospheric transport processes include emissions, plume rise, advection and convection, turbulent dispersion, gas/particle partitioning, dry deposition and wet deposition. Trajectory (Lagrangian) models for chemical transport follow a parcel of air as it travels away from a source. Fixed-grid (Eulerian) models deal with emissions, chemistry and depositions within grid cell. Trajectory models are best suited for stack plumes, but are computationally expensive for multiple reactive plumes. Fixed grid models are best suited for areas with multiple sources and reactive species. Plume models can be imbedded into grids for better treatment of stack plumes. Partitioning of semi-volatile compounds between the gas phase and particle phase is a function of the thermodynamic properties of the compound, temperature, relative humidity and atmospheric particulate matter. Adsorption or absorption may occur, and they are modeled as functions of the supercooled liquid vapor pressure and the octanol/air partition coefficient respectively. Absorption of hydrophilic compounds on particles with an aqueous phase is governed by Henry's law.

Most air quality models assume one-way irreversible dry deposition by gravitational settling and turbulent transport against resistances such as aerodynamic resistance. For some compounds atmosphere/surface equilibrium is assumed (no net transfer). Wet deposition is removal by precipitation dissolved in water droplets. It is called rainout if it occurs in-cloud and washout if below-cloud. It is especially important if solubility in water is enhanced by chemical reactions in the aqueous phase, e.g., ammonium sulfate formation from ammonia in aqueous sulfuric acid. In air quality models dry and wet deposition of soluble organic compounds (aldehydes, alcohols, acids) is calculated, but deposition of organic compounds of low solubility is generally neglected.

## BREAKOUT GROUP REPORTS

### Group 1

#### *Rapporteurs:*

Don Fox	University of North Carolina
Brian Keen	Union Carbide Corporation

#### *Participants:*

Roger Atkinson	University of California, Riverside
Deborah Bennett	Lawrence Berkeley Laboratory
Frank Binkowski	U.S. Environmental Protection Agency
Manuel Cano	Equilon Enterprises LLC
Donald Dabdup	University of California, Irvine
Miriam Diamond	University of Toronto
David Guinnup	U.S. Environmental Protection Agency
Harvey Jeffries	University of North Carolina
Paul Makar	Environment Canada
Jim Neece	Texas Natural Resources Conservation Committee
Jay Olaguer	The Dow Chemical Company
Bill Stockwell	Desert Research Institute
Jim Zhang	Rutgers University

Group 1 concluded that the first priority for further research is a screening level assessment to estimate the effect of multimedia partitioning on the atmospheric availability of a wide range of chemicals. This is a relatively easy task that could be accomplished in conjunction with other projects. The following factors were deemed to be important considerations in the study design:

- ?? A variety of compounds covering a wide range of physical and chemical properties should be included in the screening assessment. The screening assessment should focus on primary emissions (i.e., compounds that are emitted directly to the environment) and secondary photooxidation products that can participate in ozone formation.
- ?? A Level III or greater multimedia model needs to be used in the screening assessment. A Level III model would provide a steady-state simulation that could cover a wide variety of environmental conditions.
- ?? Emissions to a variety of environmental compartments, notably air, water, and soil, should be included in the model simulations. Also, the assessment should consider a variety of different environmental conditions (e.g., amount of vegetation, different meteorological conditions, and different temperatures).

After completing a screening level assessment on a wide variety of compounds, researchers will need to evaluate the results and determine if multimedia partitioning affected the availability of a sufficient number of chemicals to merit a more detailed assessment. Criteria will need to be established for judging whether work should proceed to the next step. For instance, researchers will

need to assess whether the impacted chemicals are used in sufficient quantities to be of practical scientific concern and whether the chemicals are relevant to atmospheric reactivity.

Once a list of compounds has been identified for further investigation, researchers will need to develop a linked air quality/multimedia model for further in-depth analysis. The comprehensive model can be developed by either attaching an air quality model to a multimedia model or by incorporating a multimedia model into an existing air quality model. Once an approach has been decided upon, it will be important to establish compatibility requirements for the assembled model (e.g., the spatial and temporal scales will need to be explored along with the nature of the model linkage). The comprehensive model should be used to assess the fate of the target compounds that satisfied the experimental criteria developed following the screening assessment.

Model performance needs to be evaluated by calibrating and testing the results against actual ambient data. A data collection program should be designed that will facilitate model validation. This program would include the:

- ?? selection of a range of test chemicals;
- ?? selection of a range of test conditions and environmental characteristics;
- ?? identification and collection of existing data sets;
- ?? integration of data needs with existing data collection programs, such as the EPA Supersites Program;
- ?? use of multimedia sampling methods that could simultaneously examine chemicals in air, water, sediment, vegetation, soil and organic films.

The uncertainty, variability, and sensitivity of model results need to be calculated. This is an important step that will establish confidence in the results and promote the model as a useful predictive tool.

The following criteria were identified to aid in the test chemical selection process.

- ?? The compounds should have a wide range of physical and chemical properties that are relatively well known.
- ?? The source emissions of these compounds should be reasonably well known.
- ?? Analytical methods should be available to measure concentrations in a variety of environmental media (i.e., above the detection limit).
- ?? The compounds should be relatively abundant in the environment so that ambient concentrations can be accurately assessed.
- ?? The compounds should cover a range of partitioning behavior such that they are found in a range of environmental compartments.
- ?? The compounds need to be relevant to atmospheric reactivity and encompass important reaction mechanisms.

## **Group 2**

### *Rapporteurs:*

Eileen McCauley	California Air Resources Board
Dave Morgott	Eastman Kodak Company

### *Participants:*

Dan Baker	Equilon Enterprises LLC
John Chang	U.S. Environmental Protection Agency
Joyce Graff	Cosmetic Toiletry & Fragrance Association
Bill Johnson	U.S. Environmental Protection Agency
Richard Kamens	University of North Carolina
John Little	Virginia Polytechnic Institute
Tom McKone	University of California, Berkeley
Mehran Monabbati	SENES Consultants Limited
Dennis Peterson	ExxonMobil
Jon Pleim	National Oceanic & Atmospheric Administration/U.S. EPA
Christian Seigneur	Atmospheric Environmental Research
Gail Tonneson	University of California, Riverside

The discussions within group 2 were organized around two previously stated workshop objectives:

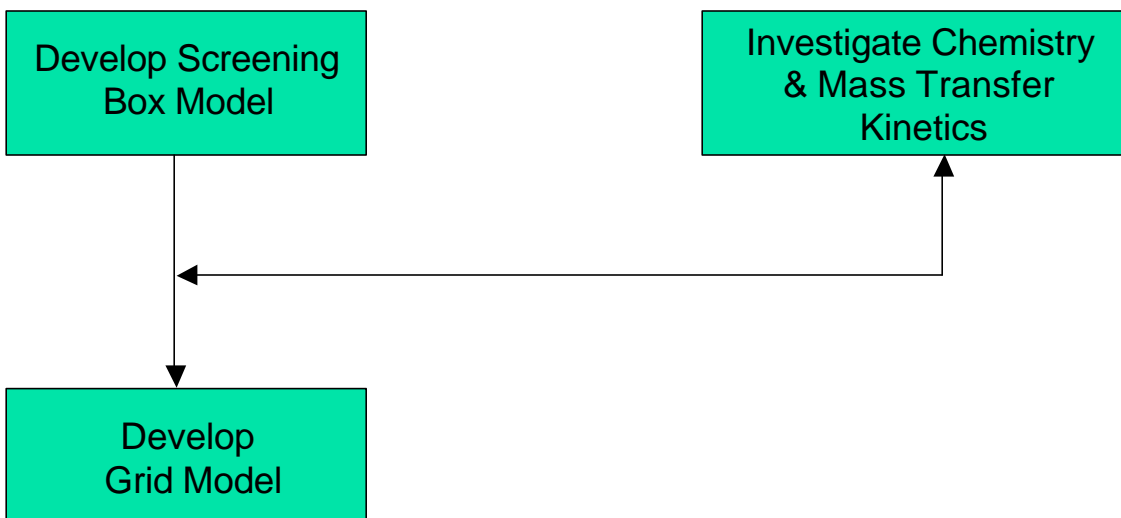
1. to produce research recommendations that will help in the development of a model which can evaluate the importance of multimedia processes on the ozone-forming potential of compounds, and
2. to establish prospects and research priorities for the integration of environmental fate and air quality models.

The group felt that it was currently feasible to combine a Level IV multimedia model with a photochemical box model to identify the impact of different multimedia compartments on ozone formation. This direct approach involving model construction before chemical evaluation was felt to be necessary in order to accurately assess the importance of different environmental processes within the context of an air-shed model. The group believed that the outlined model integration scheme provided a framework for directing other research on compartmental chemistry and mass transfer kinetics. The suggested research paradigm also provided a progressive, systematic approach for linking air quality and multimedia models at an initial screening level. This will aid in the development and evolution of a more sophisticated air quality model that could incorporate all relevant multimedia processes.

The initial combination of a Level IV multimedia model with a photochemical box model would provide the screening model to be used for the chemical assessment. The output from this model would help identify the chemical and kinetic research needed for modeling important physical and chemical processes. The group noted that inorganic nitrogen containing compounds and VOCs should both be studied using the screening model. If multimedia effects

were found to have a significant impact on ozone formation, researchers would then move to develop a more sophisticated grid model. The scheme outlined in Figure 2 summarizes the model development process.

Figure 2. Research algorithm



#### Phase I

- ?? Initial box model construction
- ?? Sensitivity analysis

#### Phase II

- ?? Add chemical complexity and kinetics
- ?? Expand to grid model

When constructing the box model, all multimedia compartments should be included. For example, indoor surfaces should be included as both an emissions source and sink if possible. The group suggested using a photochemical box model that can describe aerosol formation and partitioning. Finally, model sensitivity will need to be evaluated using chemicals with a range of vapor pressures, octanol/water partition coefficients, and chemical properties.

If multimedia partitioning is shown to have some effect on ozone formation, researchers will need more information on the chemistry and chemical reactions that occur in the different compartments. The group recommended the following steps for collecting this information:

- ?? Review all pertinent literature on the chemical reactions that apply to each compartment in the model (e.g., surface water, soil, vegetation, surface films, sediment, etc.).
- ?? Obtain reasonable estimates of the compartmental chemistry when data is unavailable (include nitrogen chemistry).

- ?? Improve estimates of mass transfer kinetics and emissions rates for chemicals and processes of interest.

Stage I of the suggested research plan would include model construction and a sensitivity analysis using range of chemical properties. The following goals were specifically identified for Stage I research:

- ?? Determine the most important compartments needing representation in the model.
- ?? Determine the chemical classes most affected by compartmental partitioning.
- ?? Determine the physical chemical properties that exert the most influence on the VOC that are sensitive to multimedia partitioning.
- ?? Determine the future data needs for grid model development.

### **Group 3**

#### *Rapporteurs:*

Doug Fratz	Chemical Specialties Manufacturers Association
Bob Hamilton	Amway Corporation

#### *Participants:*

Daewon Byun	National Oceanic & Atmospheric Administration/U.S. EPA
Bill Carter	University of California, Riverside
Nick Hazel	BP Amoco Europe
Ajith Kaduwala	California Air Resources Board
Dave McCready	Union Carbide Corporation
Stephen McDow	Drexel University
Randy Maddalena	Lawrence Berkeley Laboratory
Glenn Morrison	National Oceanic Atmospheric Administration
Ted Russell	Georgia Institute of Technology
Martin Scheringer	ETH Zurich
Charles Staples	Assessment Technologies

Group 3 independently examined the two main areas of impact for multimedia modeling: 1) the effect of alternate environmental fates on the VOC inventory used in atmospheric photochemical modeling and 2) the possible multimedia impacts on the photochemical process model. These were deemed to be the most important impacts of integrating multimedia events into air quality models. If multimedia modeling indicates that VOC emissions are partitioning into other compartments in the environment, the air emissions inventory would need to be correspondingly adjusted.

The group agreed that the ultimate fate of these partitioned materials must be monitored. If partitioning is time dependent as expected by the multimedia model, which assumes extended equilibrium time frames, the re-emission of volatile organics or of reaction products must be considered. The temporary storage of reactive species may result in net neutral or negative impact on ozone formation. This is especially important if peak ozone concentrations in air are considered the basis for regulatory limits.

Likewise, the multimedia modeling could have a variety of effects on the photochemistry process. If multimedia processes selectively remove VOC species, the photochemistry of the local atmosphere may be significantly altered. Therefore, the input parameters for to the air quality model would need to be modified to reflect changing equilibria resulting from differing available species concentrations.

The group also discussed several important ancillary issues. These included topics such as model fit and the effects of multimedia processes on air shed model uncertainty and predictive ability. Another issue concerned the differences in time scale between air quality models, which dynamically look at ozone limit



exceedence events that can be 1-3 days in length, and multimedia models which are very large static box models in a state of equilibrium. Other important considerations included:

- ?? Local impacts ? what are the rates of equilibration and points of emissions?
- ?? Regional ozone levels ? do multimedia models help to better understand regional transport or background of ozone levels?
- ?? Regulatory policy ? should multimedia models be important in the development of a regulatory policy even though there may not be a significant impact on ozone formation?

In order to address these issues, a tiered approach was used to develop research recommendations. The following topics were examined independently in conjunction with the test plan design.

Emissions inventory issues:

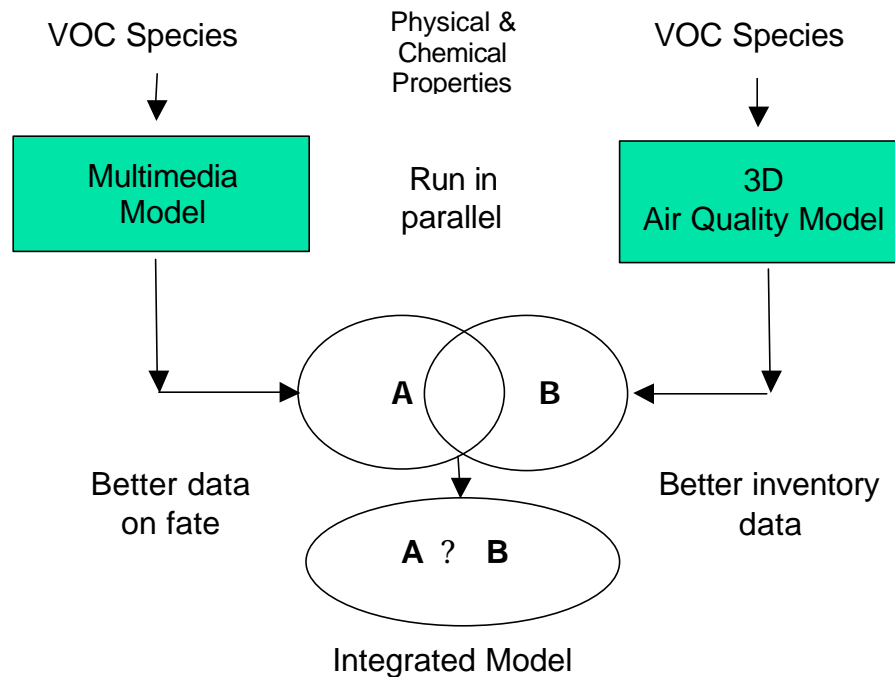
- ?? Emissions profile ? what are the impacts of having VOCs emitted in different multimedia compartments?
- ?? Environmental fate ? what, if any, are the alternate fates for these compounds? If the compounds are simply re-emitted to the air, is there any net effect? Clearly, if the compounds are removed (e.g. by biodegradation), there will be an impact on photochemical reactions.

Photochemical modeling issues:

- ?? Direct deposition ? if multimedia modeling demonstrated deposition to surfaces, then we could determine if this is important for certain VOCs.
- ?? Aerosol formation ? this issue includes condensation and adsorption onto existing aerosols. Are aerosols accounted for in local ozone production?
- ?? Heterogeneous reactions ? multimedia considerations may involve media surfaces or certain reactions that can have a positive or negative impact on heterogeneous reactions.

The plan depicted in Figure 3 was developed for the identification of compounds to be used in a screening level model. Because of the expenditures needed for the integration of multimedia and air quality models, the discussion focused on a screening process that used existing multimedia and air quality models. The group noted that it would be important to concentrate on VOC species that were important in the regulatory process.

Figure 3. VOC Chemical Evaluation Diagram



A = Multimedia partitioning significant for VOC emissions

B = Air quality modeling ~~demonstrates~~ shows deposition is significant relative to ~~for~~ ozone formation

VOC species that are substantially affected by multimedia compartmentalization would be included in circle A. VOC species ~~that are highly active in where deposition could affect photochemical reactivity models~~ the amount of ozone they produce would be included in circle B. The intersection of the two circles would form the VOC category from which candidates should be selected for further study since they would have maximum multi-media impact on ozone formation in each model.

The group indicated that a focus on episodic emissions could help to determine whether multimedia processes had an impact on the formation of ozone. One area of particular interest was indoor (household) multimedia fates. These may be important because households provide a lot of opportunity for partitioning and could lead to longer VOC retention times. Some examples of alternative fates included:

- ?? Down-the-drain events where compounds get mixed into waste water leaving the home.
- ?? Solid waste adsorption where VOCs are deposited on particles before clean-up and disposal in the garbage.
- ?? The consumption of compounds by combustion.
- ?? Temperature control and the large variety of surface types that could be important for low vapor pressure chemicals.

- ?? Biological degradation by insects, fungi, or bacteria.
- ?? Transformation processes that can convert a chemical to a more complex material that is not emitted or to a VOC with a different ozone forming potential.

Another important episodic event that may be impacted significantly by multimedia partitioning is emissions from industrial processes. These are usually in confined areas that may or may not involve some type of VOC control. These types of scenarios would need to be studied on a case-by-case basis. Additional processes may also need to be considered. For example, paint solvents trapped in and under the film coating may function as a sink process. Mixing two ingredients with disparate volatilities could reduce the overall vapor pressure and retard the evaporation of the more volatile ingredient. As with industrial process emissions, reactive transformations are a special case and would need to be studied individually. The group also addressed several general effects that could impact the emissions inventory. They included: washout via rain, fog, and clouds, and entrainment or reemission of a chemical following a spill on an absorbent surface. The effects of washout would be expected to be minimal on locally generated ozone, but could have an impact on downwind areas.

A brief overview was given of a Canadian Modeling Center urban case study that showed how a simple multimedia model could be used in screening level assessment. The objective was to demonstrate the types of information that could be gained to see how multimedia might impact photochemistry models. The study looked at how other media impacted the amount of chemical available in the atmosphere for reactions which lead to ozone formation.

Multimedia events could affect photochemical modeling in three different areas:

1. Direct deposition
  - ?? removal by biological and chemical degradation
  - ?? removal by advection or fluid flow following deposition on a stream or lake
2. Aerosol Formation
  - ?? removal by advection may take compound out of local box but may place it downwind for reaction.
  - ?? removal by deposition
3. Heterogeneous Chemistry

The following list of research recommendations was ultimately developed and submitted for consideration by the group:

- 1) Multimedia screening analysis
  - ?? hypothetical mapping of:
    - ~~??~~ boundary conditions
    - ~~??~~ physiochemical properties
    - ~~??~~ sensitivity
  - ?? photochemical model screen

- ?? maximization of the deposition factor
- 2) Determination of the relative loss to alternative fates
- 3) Test the sensitivity to multimedia landscape variation (Emphasis on urban)
- 4) Screen for sensitivity to the aerosol formation factor
- 5) Prioritize indoor air emissions
- 6) Rain/fog/cloud disposition effects screen (with Level IV model)
- 7) Study of possible sink effects
- 8) Harmonization of different model types
  - ?? validity
  - ?? uncertainty
  - ?? utility

## **DISCUSSION AND COMMENTS**

Tom McKone suggested using a Monte Carlo approach for selecting chemical properties for test runs rather than making test runs on a number of compounds. He noted that by using this approach, one could define the range of desired physical/chemical properties.

Eileen McCauley added that the workgroup is interested in ozone formation. If the compounds do not have an impact on ozone concentration, then they are not of interest to the RRWG.

Tom McKone noted that in the initial model there would be no spatial resolution since only a single grid cell would be used.

Miriam Diamond suggested that we need to test a wide range of environmental conditions in the model runs.

Eileen McCauley agreed and noted that we would certainly expect different results from Toronto and Los Angeles.

Sue Lewis asked if people are considered sinks. Tom McKone responded that people could be considered sinks. For example, dry cleaning workers are sinks for perchloroethylene and farm workers are sinks for certain pesticides.

Bill Carter indicated noted that one point that was not brought up is the potential mechanisms for absorption onto surfaces. Also, when the temperature goes up, ozone formation increases. Brian Keen noted that all surfaces are not created equal.

Dave Guinnup added that we need to be careful when adjusting emissions inventories for ozone forming potential. It needs to be done in such a way that we know that the adjustments have been made.

Doug Fratz said there are a number of compartments we need to look into, including water, indoor air, and outdoor air. There could be permanent sinks that we need to evaluate. Transport could impact air quality models because it could take VOCs out of the region. A question that the group could not answer is of the surface amounts in an urban air shed during a nonattainment episode, what percent of surfaces are suspended versus stationary?

Don Fox asked for comment on how photochemical models look at partitioning between gas and particle phase.

Gary Whitten said one type of methodology not discussed would be parameterization of nitrous acid. You could use this with multimedia grid model to assess validity.

Robert Wendoll noted that one of the issues that came up repeatedly in Group 1 was the need to better account for secondary products of primary emissions. These products may have very different physical and chemical properties that make them more or less susceptible to multimedia partitioning.

Brian Keen stated that we need to investigate biogenic emissions during screening. We need to understand the fate of these emissions, as well as how some of these compounds impact the removal of other compounds.

Robert Hamilton indicated that indoor air provides a relatively good controlled environment that can be used to investigate the impact of multimedia processes.

## **CONSENSUS SUMMARY**

The underlying hypothesis for the workshop was that atmospheric availability might be as important to the formation of tropospheric ozone as reactivity in the gaseous phase. This hypothesis resulted in workshop discussions concerning the overall impact of multimedia modeling predictions on atmospheric reactivity, the significance of environmental fate modeling on the formation of ozone, and the manner in which any changes in ozone formation are manifested.

To address the first question an environmental fate process model must be constructed. This model consists of a coupled set of environmental compartments that exchange mass as shown in Figure 1. If compounds at equilibrium are entirely in the air compartment, then there is no multimedia impact on the air quality model. It is very important to obtain as much information as possible regarding chemistry and rate studies for input to the models. This begins by reviewing all pertinent literature on the chemical reactions that apply to each compartment in the model (surface water, soil, vegetation, surface films, sediment, etc.). If data are unavailable, reasonable estimates of compartmental chemistry (including nitrogen chemistry) must be obtained. It is important to

improve estimates of mass transfer and emissions rates for chemicals and processes of interest.

Multimedia modeling has been used mainly in the study of persistent organic pollutants (POPs). Recently it has been extended to shorter times and smaller areas, including urban areas and to include such compartments as urban films. Films can be important as a means of sweeping compounds out of the air into water instead of depositing directly onto vegetation or in the soil.

The second question relating to the hypothesis is what is the impact or significance of environmental fate in the formation of ozone. Multimedia processes may play a role in two places - in the emissions inventory and in the photochemical modeling. It is important that the emissions inventory provide the best possible information as to the actual emissions to the atmosphere. For some compounds, multimedia processes may result in a decreased fraction of emissions actually present in the air. There must be losses between the compartments for there to be a multimedia impact on the air quality model. Multimedia processes may also need to be considered in photochemical models. Partitioning of intermediate chemical species into other media including aerosols and transformation in the particle phase into compounds which are then remitted are only two of many possible processes which may have an effect on ozone formation. It is also important in the photochemical model to identify any products of oxidation that are important in the formation of ozone. If these secondary products disappear or are not available for reaction, then the model runs are inaccurate.

The workshop members suggested that investigation of the importance of multimedia processes on ozone formation begins with the development of an initial screening box model. In the development of the initial screening box model it is important to include all multimedia compartments. In addition, the indoor environment must be included as an emissions source and sink. The photochemical box model that is selected for use must describe aerosol formation and partitioning. Finally, model sensitivity must be analyzed using chemicals with a range of vapor pressures, octanol/water partition coefficients, and chemical properties. After performing a sensitivity analysis, chemistry and mass transfer rates are added to the model. If environmental fate is found to be important, the process continues with the development of a grid model.

Finally, it is important to identify where to get the best fit between the two kinds of model. This is because multimedia and air quality models work with different grid sizes and use different timeframes. For example, local impacts usually have a small grid and short time frame and are further from correct equilibrium approximations than regional scale impacts.

The following four questions were chosen to direct the first stage of research into combining environmental fate and air quality models:

- ?? What are the most important compartments needing representation in the model?
- ?? Which chemical classes are most affected by compartmental partitioning?
- ?? What physical/chemical properties are important in assessing which VOCs are most affected by multimedia processes?
- ?? What are the future data needs for grid model development?

A staged research plan was developed to assess the importance of atmospheric availability on the ozone formation potential of VOCs.

1. Survey candidate chemicals with environmental fate models to see the range of compounds whose ozone-forming potential is possibly affected. The focus is on correcting emissions inventories. If there is no multimedia effect in terms of the emissions inventory, there is no need to combine the multimedia with the air quality models. Which chemical classes are most affected by compartmental partitioning? What physical/chemical properties are important in assessing which VOCs are most affected by multimedia processes?
2. Model development begins with the development of an initial screening box model that combines an air quality model and environmental fate (multimedia) model. In the development of the model it is important to include all multimedia compartments. The photochemical box model that is selected for use must describe aerosol formation and partitioning. What physical/chemical properties are important in assessing which VOCs are most affected by multimedia processes? Sensitivity analysis will provide a framework for directing needed research on compartmental chemistry and mass transfer rates.
3. Use the screening model to compare the results of environmental fate models and the screening air quality/environmental fate model with regard to the fraction of various VOC oxidized in air. What are the most important compartments needing representation in the model? Which chemical classes are most affected by compartmental partitioning? If compounds are in equilibrium between the various compartments, then there is no multimedia impact on the air quality model. There must be losses between the compartments for there to be a multimedia impact on the air quality model. Finally, model sensitivity must be analyzed using chemicals with a range of vapor pressures, octanol/water partition coefficients, and chemical properties.
4. If environmental fate is found to be important, the process continues with the development of a grid model capable of use for regulatory purposes. The suggested research paradigm provides a progressive, systematic approach for directing the development and evolution of an air quality model that incorporates all relevant multimedia processes. What are the future data needs for grid model development? Finally, it is important to identify where to get the best fit between the two kinds of model. This is because multimedia

and air quality models work with different grid sizes and use different time frames there is a natural clashing between the models. For example, local impacts usually have a small grid and short time frame and are further from correct equilibrium approximations than regional scale impacts.

Somewhat lower priorities were later established by the RRWG for the following research.

1. Consideration of the environmental fate of indoor emissions, indoor sinks and sources. These may be unimportant relative to other sources, but they are important to regulating products, particularly consumer products and household paint, that are used extensively indoors.
2. Consideration of the environmental fate of products of photochemical oxidation and its impact on estimations of the ozone-forming potential of VOC (e.g., MIR values). If these secondary products are transported to other compartments before they react in air are then consumed, then the model predictions are inaccurate.



**APPENDIX A**  
**Workshop Program**

## **Workshop on Combining Environmental Fate and Air Quality Modeling**

Sponsored by the  
**Reactivity Research Working Group**  
**Subgroup 3 on Atmospheric Availability and Environmental Fate**

The Reactivity Research Working Group (RRWG) was organized in May 1998 to bring together people from the EPA Offices of Research and Development and Air Quality Planning and Standards, industry, and the scientific community. The mission of the RRWG is to "...provide an improved scientific basis for reactivity-related regulatory policies". This will be accomplished by bringing together all parties actively interested in sponsoring, planning, performing or assessing policy-relevant scientific research on the reactivities of organic compounds emitted to ambient air, as related to the formation of ozone, PM<sub>2.5</sub>, and regional haze. The RRWG seeks to coordinate such research and define potential applications, while continuously involving key policymakers." The RRWG is affiliated with NARSTO.

### **Background**

Preliminary work indicates that multimedia processes may have an affect on the ozone forming ability of some volatile organic compounds (VOCs). The RRWG selected this topic as worthy of investigation. A working group has been formed to develop research priorities. At an initial meeting, the group defined their goal as helping to determine the importance of transport and transformations to and from water, soil, sediment, and other media on the ozone forming potential of different VOCs capable of contributing to tropospheric ozone.

### **Purpose of the Workshop**

To bring together experts in the fields of both air quality modeling and multimedia modeling to establish prospects and priorities for integration of environmental fate and air quality models. The goal is to produce research recommendations that will help in the development of a model which can evaluate the importance of multimedia processes on the ozone-forming potential of compounds.

### **Workshop Description**

The initial half-day session will present background material to introduce participants to the basics of the subjects outside their fields of expertise. The next day participants will be divided into three small working groups. Each group will contain experts from several disciplines and will develop a multimedia process diagram and, based on the relative importance of the processes, a list of research priorities. On the last day participants will meet together to combine the individual lists of research needs into a single list which will be presented to the RRWG that afternoon. The background talks, summaries of the

breakout group presentations, highlights of the consensus report and a polished summary of the workshop will be published on the NARSTO web site.

## **Duration**

Two-day meeting of scientific experts and ½ day open session with the RRWG

Date: June 27-29. Participants are invited to attend the RRWG meeting on June 29-30.

Place: EPA Administration Building, Research Triangle Park, NC

Organization: RRWG Subgroup 3 with assistance from CMA

Participants: Approximately 30 invited experts on environmental fate and air quality modeling from research institutions, industry and regulatory agencies. Due to the unusual format of the meeting and the need for a balanced, small number of participants, the RRWG subgroup 3 will set up a science committee that will invite participants using a peer referral process.

Some members of the task group will serve as rapporteurs at the breakout sessions and record keepers. The meetings are open to observers.

## **Supporting Organizations:**

- ?? ACC Solvents Council
- ?? ACC Long-range Research Initiative, Atmospheric Chemistry Technical Implementation Panel
- ?? ACC Ethylene Glycol Ethers Panel
- ?? ACC Propylene Glycol Ethers Panel
- ?? Chemical Specialties Manufacturers Association
- ?? Dunn-Edwards Corporation
- ?? National Paint and Coatings Association

## **Final Schedule**

### **June 27**

1:00-1:15 Introduction - Brian Keen, Union Carbide Corp.

#### **Background Presentations**

1:15 - 1:45 Multimedia Models - Miriam Diamond, Univ. of Toronto

1:45 - 2:15 Use of Fugacity-based Multi-media Models to Assess the Fate of Chemicals in the Environment - Charles Staples, Assessment Technologies

2:15 - 2:45 Air Quality Models and Component Modules - Gail Tonneson, Univ. of California, Riverside

2:45 - 3:15 Break

- 3:15 - 3:45 Air Quality Models and Component Modules - Gail Tonneson, Univ. of California, Riverside
- 3:45 - 4:15 Environmental Fate of Indoor VOC Emissions: The Role of Indoor Chemistry - Jim Zhang, Rutgers Univ.
- 4:15 - 4:45 Modeling of Chemical Transport in the Atmosphere - Christian Seigneur, Atmospheric & Environmental Research
- 6:00 - 7:00 Social Hour - Doubletree Guest Suites 2515 Meridian Parkway

**June 28**

- 8:30 - 10:00 Discussion of background information and proposed key questions
- 10:00 - 10:15 Break
- 10:15 - 12:30 Breakout groups to create a diagram of processes involved in multimedia and air quality models.
- 12:30 - 1:30 Lunch
- 1:30 - 4:30 Continuation of the breakout groups. Estimate the relative importance of the processes included in the process diagram and select the most important research needs.

Evening Record the results of the breakout groups.

**June 29**

- 8:30 - 10:00 Sharing results of the break-out groups
- 10:00 - 10:15 Break
- 10:15 - 11:45 Preparation of a consensus report
- 11:45 - 1:00 Lunch
- 1:00 Report to RRWG and discussion

**APPENDIX B**

**Workshop Presentations**

Titles and speakers:

**1. Multimedia Models**

Miriam Diamond, University of Toronto

**2. Use of Fugacity-based Multi-media Models to Assess the Fate of Chemicals in the Environment**

Charles Staples, Assessment Technologies

**3. Air Quality Models and Component Modules**

Gail Tonnesen, University of California, Riverside

**4. Environmental Fate of Indoor VOC Emissions: The Role of Indoor Chemistry**

Junfeng (Jim) Zhang, Environmental and Occupational Health Sciences Institute, Rutgers University

**5. Modeling of Chemical Transport in the Atmosphere**

Christian Seigneur, Atmospheric & Environmental Research

**APPENDIX C**  
**Key Topics List**

## Key Topics - for the background speakers and breakout groups

- ?? Identify the state of the science of environmental fate modeling and on incorporation of environmental fate (partitioning) into air quality models (emission and fate).
  - ?? Introduction - Why we are here. The problem is the per cent reaction in air.
  - ?? What media exchange VOC with the atmosphere and how do they do it? [1st talk]
  - ?? How do environmental fate models treat dispersion of VOC into the atmosphere and adsorption and absorption into other media from the atmosphere? [Second talk]
  - ?? What are the inputs and outputs of air quality models? How do air quality models treat dispersion of VOC into the atmosphere and adsorption and absorption into other media from the atmosphere? [Combined Talks]
  - ?? What are the peculiarities of indoor air models and the lessons from it for air quality modeling? [Condensed talk]
  - ?? How do dense plume and area source dispersion models treat dispersion of VOC into the atmosphere and adsorption and absorption into other media from the atmosphere? [Condensed talk]

Questions on dispersion modeling to be answered by a talk

How do your models treat:

- ?? removal of VOC by photochemical oxidation
- ?? changes in temperature during the day, the mixing height
- ?? wind
- ?? vertical mixing
- ?? transport to and from surface water and soil
- ?? removal by wet and dry deposition [rain and aerosols]
- ?? emissions [source of data, form in the model]
- ?? time [dynamic or equilibrium model]
- ?? flexibility [“hard wired” parameters or adjustable?]
- ?? chemical speciation [individual or “lumped” properties]
  
- ?? Determine the importance of transport and transformations to and from water, soil, sediment, and other media on the ozone forming potential of different VOCs capable of contributing to tropospheric ozone (and PM<sub>2.5</sub>). [Breakout groups]



?? Identify environmental fate processes that influence the concentration of VOC in the atmosphere. [As opposed to VOC concentrations in media due to contamination from the atmosphere.]

?? Consider influences on emissions from the surface and on removal from the atmosphere.

?? Is removal reversible (“sinks”) or irreversible due to reaction

?? Consider the fate of oxidation products.

?? Establish prospects and priorities for integration of environmental fate and air quality models. Investigate mechanisms to address the integration of fate and transportation into air quality issues. [Entire Group]

?? Are we limited by data or by modeling constraints?

?? Identify basic physical and chemical needs/considerations

?? What is the best means of integration?

? ? Revised air quality model - what are required of it?

example - speciated chemicals and their physico-chemical properties

? ? Revised environmental fate model

example - scenario-dependent ozone formation (reactivity)

? ? Adjustment factor on air quality model inputs from environmental fate models

example - down-the-drain factors and LVP exemption

? ? Other

?? Evaluate how likely the above will change the way reactivity should be addressed.

?? Do alternative fates of oxidation products require revision of the MIR scale.

?? Formulate questions and topics to be addressed in a state-of-the-science paper.

## **Deliverables**

### **Background Talks**

The initial half day session will present background material to introduce participants to the basics of the subjects of their general area of expertise. They should be electronic form for distribution before the meeting to participants and for later posting with the rest of the conference proceedings. Don Fox said he could bring a computer and projector so that PowerPoint presentations could be made.

The presentations should be general, for an audience of scientists from outside the field. Academics have such talks already prepared for departmental seminars.

### **Discussion Group**

The group will meet together part of the next morning to discuss the background material and the key questions posed by the organizers.

I suggest a question-and-answer period with the presenters as a panel. Bill Johnson will be the note-taker (audio recording) as at the RRWG meeting. An edited transcript will be part of the record. The leader of the discussion will assist in getting the key items articulated.

### **Breakout group reports**

Participants will be divided into three working groups. Each group will contain experts from several disciplines. They will examine the multimedia process diagram, tracing the possible compartments and interchanges, and, based on the relative importance of the processes, develop a list of research priorities to reflect the impact of environmental fate on air quality modeling..

We should have reports from each breakout group. This could be done having the rapporteur, assisted an associate from within this subgroup, keep a list of bulleted items. This is needed anyway to present to the group as a whole for consideration. For the following discussion they would need to be at least on flip charts. The rapporteur and associate could transcribe and clean up the reports for publication in the proceedings.

### **Consensus Document**

On the last morning participants will meet to achieve consensus on

?? the state of the science of environmental fate modeling and on incorporation of environmental fate (partitioning) into air quality models (emission and fate).

?? the importance of transport and transformations to and from water, soil, sediment, and other media on the ozone forming potential of different VOCs capable of contributing to tropospheric ozone (and PM<sub>2.5</sub>).

The group should prepare a single list of research recommendations which will help in the development of a model which can evaluate the importance of multimedia processes on the ozone-forming potential of compounds and present it to the RRWG that afternoon.

A technical writer or one of the participants could be hired to prepare a report suitable for publication.