

CURRENT STATUS AND RESEARCH NEEDS RELATED TO BIOGENIC HYDROCARBONS

HEALTH AND ENVIRONMENTAL AFFAIRS
API PUBLICATION NUMBER 309
JUNE 1992

American Petroleum Institute
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Washington, D.C. 20005



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**HEALTH AND ENVIRONMENTAL AFFAIRS DEPARTMENT
API PUBLICATION NUMBER 309
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EXECUTIVE SUMMARY

The role of biogenic hydrocarbons emitted from vegetation continues to remain a troublesome uncertainty in developing effective control strategies to reduce photochemical oxidants. In order to address these uncertainties, the American Petroleum Institute has supported this work to review recent literature and current activities and to critique representative studies as a basis for developing a research plan for future investigations. In this report, an extensive compilation of recent studies related to emission measurements, emission patterns, emission inventories, ambient concentration measurements, and chemical modeling is presented. The compilation is based upon computerized literature searches in combination with a review of research studies currently underway in the U.S. and in Europe. Key papers from the literature were selected for detailed review with respect to both methods and results with an emphasis upon identifying those areas where further work is needed. The results from the compilation and review were then used to identify research needs and to specify research tasks required to improve our overall understanding of biogenic hydrocarbon emissions to a level sufficient for the development of effective ozone control strategies.

In the area of emission measurements and emission mechanisms there is a general lack of information. A systematic field and laboratory program is needed to obtain emission rate and environmental data describing emissions from the dominant U.S. species, including agricultural crops, in each region of the country. A comprehensive field survey of biogenic emissions would provide data for the development and testing of emission models capable of addressing the immense natural variability as well as the effects of seasonal changes, nutrient levels, and environmental stress upon emissions. Complementary laboratory chamber studies would provide the information needed to formulate an emission model in terms of fundamental vegetative dynamics and biochemistry. Both field and laboratory studies should be designed to measure isoprene, monoterpenes, and other hydrocarbons, including oxygenated species, in order to develop a complete emission fingerprint and to specify correctly the reactive mix of biogenic emissions.

Results from the emission measurements and modeling effort are needed for incorporation into regional emission inventory systems. In addition, further work is required to determine the accuracy of current land use data and biomass density estimates. This can be accomplished using a combination of ground-truth surveys and remotely sensed satellite data. Very recent work has demonstrated the feasibility of developing an emission inventory method based upon almost real-time satellite imagery. These approaches should provide the basis for the next generation of biogenic emission inventories.

The current U.S. emission inventory system addresses the effects of the forest canopy environment upon emissions through a simple canopy model. The accuracy of this model needs to be determined through field measurements of canopy radiation levels and leaf temperatures. Finally, any emission inventory system must be validated against ambient concentration measurements in a manner that tests the representativeness of the model at scales

ranging from the canopy scale to regional scales. Direct validation of the emission inventory must be a high priority in future research studies.

Ambient concentration measurements of biogenic hydrocarbons and their atmospheric oxidation products provide a benchmark for testing both emission inventory models as well as chemical kinetic models. These measurements should be extended to include a variety of ecosystems in different regions of the country during different times of the year. Methods must be developed to measure all of the important primary and secondary--oxygenated--species associated with oxidation of biogenic hydrocarbons. Relative burdens of biogenic and anthropogenic emissions should also be included in these measurements as a test of both biogenic and anthropogenic emission estimates.

While the initial stages of isoprene oxidation are relatively well understood, uncertainties exist concerning the actual ratio of products and the fate of these products in the atmosphere. The oxidation steps associated with terpene are more uncertain and the product mix, including the proportion of aerosol vs gas phase yields, is not known with any certainty. Further smog chamber studies are required to determine additional details of the oxidation mechanisms. Additional ambient measurements of both reactants and products--primary and secondary--are needed to obtain a complete understanding of the atmospheric fate.

There are a number of programs sponsored by various agencies currently in progress which address to some degree the issues raised in this review. The progress in these efforts must be monitored and the required research tasks must be modified accordingly. Careful consideration of the accuracy required in emission estimates and in chemical modeling is needed to guide further research. This analysis of accuracy requirements in conjunction with results from current studies must provide the basis for the details of the design of a comprehensive biogenic hydrocarbon research program.

1.0 LITERATURE COMPILATION

1.0 INTRODUCTION

The effects of biogenic hydrocarbon emissions upon the formation of atmospheric ozone were first considered as a serious air pollution issue in the late 1970's. A series of chemical modeling studies by Lurmann et al. (1984), among others, showed that during typical conditions biogenic emissions of volatile organic compounds (VOC) increased ambient ozone concentrations by only a small amount. Subsequent studies of biogenic emissions and chemistry were related to issues of organic acid formation (Placet et al., 1990) or to climate change and the global carbon cycle (Zimmerman et al., 1988). Recently, however, the continued non-attainment of the ozone standard in urban areas across the U.S. has prompted a second look at the importance of biogenic VOC's with regard to ozone formation and the effectiveness of current hydrocarbon control strategies (Chameides et al., 1988).

There is a growing body of literature now available covering measurements of biogenic emission rates, development of emission inventories, measurement of ambient biogenic VOC and product concentrations and modeling of ozone and biogenic VOC air chemistry. In addition, there are a number of extensive research programs now underway or in the planning stage which should yield important new information about biogenic VOC's in the atmosphere. It is very appropriate now to review the current literature as well as current activities and to identify areas of uncertainty and gaps in our understanding of biogenic VOC emissions and fate. A thorough review and evaluation will thus provide a basis to design additional research to complement or confirm ongoing work and to fill any gaps which may occur.

This chapter presents a compilation of previous literature and current studies dealing with the emissions and atmospheric chemistry of biogenic VOC's. In subsequent sections, a critical evaluation of the most comprehensive of these studies in each area is presented and the research needs and planning required to address the areas of major uncertainties in our current understanding is outlined. The overall objective of this work is to develop a clear description of the state of the science and to outline the steps needed to determine the role of biogenic VOC's in ozone formation and ozone control strategies.

In the remainder of this chapter, the methods used to compile this literature review are briefly outlined and an overview of the literature in each of several areas is presented. These areas include: biogenic emission measurements, ambient concentration measurements, chemical kinetics and modeling studies, and current studies. Complete references of the literature reviewed in each area are contained in the bibliography.

1.2 METHODS: LITERATURE SOURCES AND DATA BASES

This literature review was based upon a combination of computerized searches and compilation of known references. The primary data base used in the computer search was the Scientific and Technical Information Network International (STN). The chemical abstracts

section of this source was used. This section covers abstracts over the period 1960 to the present. This search was supplemented by reviewing recent pertinent journals and reports, using reference lists from current papers to expand the literature review, and incorporating other literature available to us.

1.3 OVERVIEW OF BIOGENIC EMISSION MEASUREMENTS

While emission rate measurements have been conducted using a variety of methods, most of the emission rate data have been obtained using either laboratory or field enclosures of seedlings or individual branches (see Tingey et al., 1979, 1980, 1981; Zimmerman, 1979a,b; Lamb et al., 1985; Winer et al., 1989; Juuti et al., 1990; and Bufler and Wegmann, 1991). A few studies have employed micrometeorological gradient methods (Lamb et al., 1985; Seila et al., 1982) or a tracer simulation flux approach (Lamb et al., 1986; Arnsts et al., 1982), but these efforts have mainly been aimed at validating branch enclosure results. The results from these studies generally demonstrate agreement between enclosure and non-enclosure methods within the bounds of experimental uncertainty. Most recently, Businger and Oncley (1990) have introduced an eddy conditional sampling approach which should be quite applicable for areal flux measurements of biogenic emissions from a vegetation canopy. The requirements for this kind of application have been outlined by Businger and Delaney (1990). In addition, Hills and Zimmerman (1990) have developed a novel continuous detection method for isoprene which has been used to measure rapid changes of isoprene emissions in a leaf cuvette by Guenther et al. (1990). These new developments should lead to improved emission measurements and a better understanding of the uncertainties involved in making emission rate and emission flux measurements.

1.3.1 Vegetation Species, Identified Compounds, and Emission Rates

The enclosure method of sampling is quite useful for surveying a large number of species and identifying the wide range of compounds emitted from vegetation. Compounds routinely identified with these measurements are isoprene and monoterpenes including alpha-pinene, beta-pinene, limonene, camphene, sabinene, myrcene, and Δ^3 -carene. Table 1.1 from a review by Singh and Zimmerman (1990) gives a long list of VOC's emitted from different species of vegetation. Emissions of isoprene and terpenes from specific forest species in the southeastern U.S. compiled in preparation for the Southeast Oxidant Study are listed in Table 1.2. These two lists demonstrate the complexity of natural VOC emissions. There are literally hundreds of compounds emitted from hundreds of species over a wide range of emission rates.

A large amount of information concerning specific compounds emitted from specific species was derived from extensive surveys by Zimmerman (1979a) in Tampa Bay, FL., by Winer et al. (1983) for vegetation in the Los Angeles basin, by Winer et al. (1989) for crops and other vegetation in the San Joaquin Valley, and by Lamb et al. (1985) for trees in Pennsylvania, Washington, and Georgia. Isidorov et al. (1985) reported a long list of compounds found in forested environments.

Table 1.1. Organics in Volatile Emissions of Arboreous Plants

Compound	Plant species [#]	Compound	Plant species [#]
Propylene	8,9	Chloroform	16
Burylene	1-12,15,16	Dimethyl sulphide	15
Isoprene	(1-4)** ,5-17	Santene	8,11
Hydrocarbon C ₅ H ₁₀	1,2,5-9,13-15	Cyclofenchene	8-10,15
2-Methylbutane	1-8,12	Bornilene	8-17
2,3-Deimethyl butadiene	8,13,14	Tricyclene	7,8*,9-10
Hydrocarbon C ₈ H ₁₂	8,9	α -Thujene	9,10,13-17
Hydrocarbon C ₉ H ₁₀	1,6,11,16	α -Pinene	3,(7,8,11,12,14)*
Methanol	15		(9,10,13,15,17)** ,16
Ethanol	3-5,10,12-15	δ -Fenchene	9,10,12
3-Hexene-1-ol	1,2,5*,7,8	ϵ -Fenchene	9,12
Propanal	6	α -Fenchene	7-17
Isobutanal	16	β -Fenchene	7-10,12
Crotonal	17	Camphene	3,(7,9,10,12)* ,*(8,11)**
Isobutenal	1-4,9,7		13-17
Acetone	1-17	Sabinene	12,13,15,17,(14,16)*
Butanone-2	8,13-15	β -Pinene	3,7-11,15
Methyl vinyl ketone	2,4	Myrcene	7-13,14*,15-17
Pentanone-2	6,8,15	3-Carene	7*,8-10,12-15,16*,17
Pentanone-3	5,7-10,15,16	α -Phellandrene	3,8-11
Furan	6	β -Phellandrene	8-11,14
2-Methyl furan	1-5,12,13	α -Terpinene	8-10,17
3-Methyl furan	1-5,12,13	β -Terpinene	3,8-10,13-15
Ethyl furan	1,2,4,8	γ -Terpinene	9,13-15,17
Vinyl furan	1,2,4,8	Limonene	3,7-17
Ethyl acetate	9	Terpinolene	9-17
3-Hexene-1-ol acetate	1,4-8	1,8-Cineol	3,8,14
Methyl (α -methyl) butyrate	14**	Fenchone	16*
Methyl (α -methyl) capronolate	14	Thujone	16**
Methyl chloride	14-16	Camphor	8
		p-Cymene	7-17
		Menthane	14

#1. Bay-leaved willow; 2. Aspen; 3. Balsam poplar; 4. European oak; 5. European birch; 6. Sorb; 7. European larch; 8. European fir; 9. Scots pine; 10. Siberian pine; 11. Silver fir; 12. Common juniper; 13. Zeravshan juniper; 14. Pencil cedar; 15. Evergreen cypress; 16. Northern white cedar; 17. Chinese arbor vitae (one asterisk refers to an important VOC component and two asterisks refer to the dominant VOC component).

Source: Isidorov et al. (1985)

Table 1.2 (Source: Southern Oxidants Study)

Forest tree species of the southeastern United States and the published rates of emission of isoprene and terpenes for those that have been studied. Most rates of emission are expressed as micrograms of carbon emitted per gram dry weight of leaf tissue per hour (see Units). Thus isoprene emission in $\mu\text{g/h}$ means μg of carbon, not isoprene (for isoprene and terpenes, carbon accounts for about 88% of the molecular weight).

Species	Isoprene emission	Terpene emission	Units	Sample size	Reference	Comments
<i>Abies fraseri</i> (Fraser fir)	-	+			Rasmussen, 1972	
<i>Acer rubrum</i> (red maple)	0.0	3.5	A	9	Zimmermann, 1979	day, a
	0.0	2.4	A	9	Zimmermann, 1979	night, b
	0	2.1	A	1	Lamb et al., 1984	day, 24.4°C, c
<i>Betula allegheniensis</i> (yellow birch)	+	-		3	Evans et al., 1982	
<i>Betula nigra</i> (river birch)						
<i>Carpinus caroliniana</i> (American hornbeam)						
<i>Carya aquatica</i> (water hickory)	-	-0.4	A	4	Zimmermann, 1979	day, a
	-	-0.3	A	4	Zimmermann, 1979	night, b
<i>Carya cordiformis</i> (swamp hickory)	0.0	-0.4	A	4	Zimmermann, 1979	day, a
	0.0	-0.2	A	4	Zimmermann, 1979	night, b
<i>Carya glabra</i> (pignut hickory)	0	3.6	A	2	Lamb et al., 1984	day, 25.0°C, c
<i>Carya illinoensis</i> (pecan)						
<i>Carya ovata</i> (shagbark hickory)						
<i>Carya tomentosa</i> (mockernut hickory)						
<i>Cercis canadensis</i> (eastern redbud)	+	-		3	Evans et al., 1982	
<i>Cornus florida</i> (flowering dogwood)	0	7.8	A	1	Lamb et al., 1984	day, 27.3°C, c
<i>Diospyros virginiana</i> (common persimmon)	0.0	0.0	A	17	Zimmermann, 1979	day, a
	0.0	0.0	A	17	Zimmermann, 1979	night, b

Table 1.2 (Continued)

<i>Fagus grandifolia</i> (American beech)	0	2.3	A	1	Lamb et al., 1984	day, 23.3°C, c
<i>Fraxinus americana</i> (american ash)						
<i>Fraxinus caroliniana</i> (Carolina ash)	0.0 0.0	0.0 0.0	A A	1 1	Zimmermann, 1979 Zimmermann, 1979	day, a night, b
<i>Fraxinus pennsylvanica</i> (green ash)						
<i>Ilex cassine</i> (dahoon holly)	0.0 0.0	0.0 0.0	A A	3 3	Zimmermann, 1979 Zimmermann, 1979	day, a night, b
<i>Ilex coriacea</i> (sweet gallberry)						
<i>Juniperus silicicola</i> (southern redcedar)						
<i>Juniperus virginiana</i> (eastern redcedar)						
<i>Liquidambar styraciflua</i> (sweetgum)	8.5 0.0 1.4	46.4 31.8 +	A A B	17 17 1	Zimmermann, 1979 Zimmermann, 1979 Rasmussen, 1972	day, a night, b 6 reps, 28°C
<i>Liriodendron tulipifera</i> (tulip poplar)	0	2.7	A	2	Lamb et al., 1984	day, 23.9°C, c
<i>Magnolia grandiflora</i> (southern magnolia)						
<i>Magnolia virginiana</i> (sweetbay)						
<i>Myrica cerifera</i> (wax myrtle)	0 0	6.3 4.4	A A	9 9	Zimmermann, 1979 Zimmermann, 1979	day night
<i>Nyssa aquatica</i> (water tupelo)						
<i>Nyssa sylvatica</i> (blackgum)	0	5.8	A	1	Lamb et al., 1984	day, 28.9°C, c
<i>Oxydendrum arboreum</i> (sourwood)						
<i>Persea borbonia</i> (redbay)	0.0 0.0	1.2 0.8	A A	2 2	Zimmermann, 1979 Zimmermann, 1979	day, a night, b
<i>Picea rubens</i> (red spruce)	+	+			Rasmussen, 1972	

Table 1.2 (Continued)

<i>Pinus clausa</i> (sand pine)	-	11.6	A	4	Zimmermann, 1979	day, a
	-	8.1	A	4	Zimmermann, 1979	night, b
<i>Pinus echinata</i> (shortleaf pine)	-	+			Rasmussen, 1972	
<i>Pinus elliotii</i> (slash pine)	-	6.4	A		Tingey <i>et al.</i> , 1980	-
	-	3.2	A	16	Zimmermann, 1979	day, a
	-	2.2	A	16	Zimmermann, 1979	night, b
<i>Pinus palustris</i> (longleaf pine)	-	5.9	A	28	Zimmermann, 1979	day, a
	-	4.1	A	28	Zimmermann, 1979	night, b
<i>Pinus rigida</i> (pitch pine)	0	10.7	A	1	Lamb <i>et al.</i> , 1984	day, 23.9°C
<i>Pinus serotina</i> (pond pine)						
<i>Pinus strobus</i> (eastern white pine)	0	8.8	A	6	Lamb <i>et al.</i> , 1984	day, 24.4°C
	0	2.0	B	1	Rasmussen, 1972	7 reps, 31°C
<i>Pinus taeda</i> (loblolly pine)	-	3.7	A		Arnts <i>et al.</i> , 1978	-
	-	1.2	A	5	Knoppel <i>et al.</i> , 1982	reps on 1 tree
	-	3.5	B	1	Rasmussen, 1972	7 reps, 31°C
	-	2580	C	18	Arnts <i>et al.</i> , 1978	met method
<i>Pinus virginiana</i> (virginia pine)	0	7.2	A	1	Lamb <i>et al.</i> , 1984	day, 28.3°C
<i>Platanus occidentalis</i> (American sycamore)	45.9	-	A	1	Lamb <i>et al.</i> , 1984	day, 32.2°C
<i>Populus deltoides</i> (eastern cottonwood)	+++	-		3	Evans <i>et al.</i> , 1982	
<i>Quercus alba</i> (white oak)	4.6	-	A	1	Lamb <i>et al.</i> , 1984	day, 26.9°C
<i>Quercus coccinea</i> (scarlet oak)	12.4	-	A	1	Lamb <i>et al.</i> , 1984	day, 25.0°C
<i>Quercus falcata</i> (southern red oak)						
<i>Quercus geminata</i> (scrub live oak)						
<i>Quercus incana</i> (bluejack oak)	43.9	0.2	A	7	Zimmermann, 1979	day, a
	0.0	0.2	A	7	Zimmermann, 1979	night, b
<i>Quercus laevis</i>	23.4	0.8	A	7	Zimmermann, 1979	day, a

(turkey oak)	0.0	0.6	A	7	Zimmermann, 1979	night, b
<i>Quercus laurifolia</i>	10.0	0.2	A	10	Zimmermann, 1979	day, a
(laurel oak)	0.0	0.1	A	12	Zimmermann, 1979	night, b
<i>Quercus marilandica</i>						
(blackjack oak)						
<i>Quercus minima</i>						
(dwarf oak)						
<i>Quercus myrtifolia</i>	14.6	0.2	A	1	Zimmermann, 1979	day, a
(myrtle oak)	0.0	0.1	A	1	Zimmermann, 1979	night, b
<i>Quercus nigra</i>	23.7	0.1	A	3	Zimmermann, 1979	day, a
(water oak)	0.0	0.1	A	3	Zimmermann, 1979	night, b
<i>Quercus phellos</i>	31.0	0.0	A	1	Zimmermann, 1979	day, a
(willow oak)	0.0	0.0	A	1	Zimmermann, 1979	night, b
<i>Quercus prinus</i>	2.2	-	A	8	Lamb et al., 1984	day, 20.0°C
(chestnut oak)						
<i>Quercus pumila</i>						
(runner oak)						
<i>Quercus rubra</i>						
(northern red oak)						
<i>Quercus stellata</i>						
(post oak)						
<i>Quercus velutina</i>	25.1	-	A	1	Lamb et al., 1984	day, 28.8°C
(black oak)						
<i>Quercus virginiana</i>	41.2	-	A		Tingey et al., 1979	-
(live oak)	9.1	0.3	A	18	Zimmermann, 1979	day, a
	0.0	0.5	A	21	Zimmermann, 1979	night, b
	1400	-	C		Tingey et al., 1981	day
	4	-	C		Tingey et al., 1981	night
<i>Rhizophora mangle</i>	-	.006	A	16	Zimmermann, 1979	day, a
(red mangrove)	..	.004	A	16	Zimmermann, 1979	night, b
<i>Sabal palmetto</i>	4.5	0.4	A	11	Zimmermann, 1979	day, a
(cabbage palmetto)	0.0	0.0	A	13	Zimmermann, 1979	night, b
<i>Salix caroliniana</i>	12.4	1.9	A	7	Zimmermann, 1979	day, a
(Carolina willow)	0.0	0.1	A	8	Zimmermann, 1979	night, b
<i>Sambucus simonil</i>	0	0	A	5	Zimmermann, 1979	day, night
(elderberry)						
<i>Sassafras albidum</i>	0	7.3	A	1	Lamb et al., 1984	day, 29.4°C

(sassafras)

<i>Taxodium distichum</i>	-	8.5	A	20	Zimmermann, 1979	day, a
(baldcypress)	-	5.9	A	20	Zimmermann, 1979	night, b
<i>Taxodium distichum</i> var. <i>nuttans</i> (pondcypress)						
<i>Tsuga canadensis</i>	0	1.3	A	2	Lamb et al., 1984	day, 19.4°C
(eastern hemlock)						
<i>Ulmus americana</i>	0.0	0.0	A	1	Zimmermann, 1979	day, a
(American elm)	0.0	0.0	A	1	Zimmermann, 1979	night, b

Units: A = $\text{g (g dry weight)}^{-1} \text{h}^{-1}$; B = $\text{ppb min}^{-1} (\text{g fresh weight})^{-1} \text{liter}^{-1}$; C = $\mu\text{g m}^{-2} \text{h}^{-1}$

Comments: a, corrected to 30°C; b, corrected to 25°C; c, total hydrocarbons, mostly monoterpenes; -, not measured; +, significant emission but not quantified; 0, emission was very low; 0.0, emissions were undetectable despite high sensitivity of analysis.

Bufler and Wegmann (1991) used open top chambers in a Norway spruce forest (*Picea abies* L. Karst) and measured emissions of alpha-pinene, beta-pinene, camphene, sabinene, myrcene, Δ^3 -carene, limonene, tricyclene, and 1,8-cineole. The emission rates of alpha-pinene and beta-pinene accounted for more than 80% of the total. These authors also reported that volatilization of oils in bark appeared to be a significant source in addition to the emissions from needle biomass. This may be a significant finding since most other studies report emissions in terms of needle or leaf biomass and inventories derived from these measurements are usually formulated using leaf biomass density factors. Hrutfiord et al. (1974) had earlier measured the composition of needle and cortex oils for Sitka spruce (*Picea sitchensis*) over a growing season. They reported that the needle oil composition was high in myrcene (30%), camphor (18%), and piperitone (28%), while the cortex oils contained mostly alpha-pinene (22%), beta-pinene (14%) and beta-phellandrene (38%). Oxygenated monoterpenes accounted for 45% of the needle oil composition, while hydrocarbon monoterpenes dominated the cortex oil. The composition of oil was lower in myrcene and higher in piperitone for older needles compared to younger needles. Hrutfiord et al. reported that cortex and needle oil becomes essentially identical in composition for older branches near the bottom of large trees. On a seasonal basis, needle oil from new growth is initially almost all myrcene with no detectable oxygenated species, but the myrcene content decreases rapidly with time.

For isoprene emitting hardwoods, Lamb et al. (1985) found that isoprene accounted for approximately 80% of the total emissions, and that total VOC emissions from non-isoprene emitters were a factor of two less than from isoprene emitters over the same range of temperatures. The emission rate of isoprene from hardwood species increased from 0.3 ug/g/hr at 12 °C to 50 ug/g/hr at 35 °C. Similar results have been reported in other studies of deciduous emissions (e.g. Zimmerman, 1979a; Winer et al., 1983). Evans et al. (1982) identified isoprene emitters from among 54 different species of young seedlings and concluded that isoprene is emitted from many trees and shrubs, but usually not from herbaceous or crop species. The emission rates obtained from these studies followed a lognormal distribution after correction to 28 °C and a light intensity of 1000 uE/m²/s, and Evans et al. thus compiled the emissions in terms of the geometric means of the measurements.

Arey et al. (1991) measured linalool as the dominate compound emitted from Valencia orange trees (*Citrus sinensis*). There was a strong seasonal effect with emissions a factor of ten higher during the spring blossom period than later in the growing season. The maximum emission rate was 13 ug/g/hr at 25 °C.

Ohta (1984) identified cis-1-hexen-1-ol (leaf alcohol) as the major emission from a temperature zone grass (*Miscanthus sinensis*) with a maximum emission rate of 15 ug/g/hr at approximately 24 °C. This may be a significant underestimate because it appears from the paper that the samples were collected 5 minutes after enclosure and steady state concentration levels were probably not achieved within this time. Hexenol has also been reported by a number of other researchers as a significant emission from grasses and crops (Winer et al., 1989; Lwande and Bentley, 1987).

Thompson et al. (1971) earlier reported twelve different compounds emitted from cotton plants (*Gossypium hirsutum* L., var. Deltapine Smoothleaf). Two isomers of bisabool accounted for 20 to 50% of the emissions, and trans-2-hexanol accounted for 5 to 10% of the total emission. Hatanaka et al. (1978) showed that specific enzyme activity levels in plants were related to the production of cis-3-hexenal and n-hexanal. Production of these oxygenated species was relatively high in dicotyledonous plants and low in edible leafy vegetables, fruits, and monocotyledonous plants. A total of 34 volatile compounds, including a number of sulfur and nitrogen-containing species were identified by Tollsten and Bergstrom (1988) in the headspace over whole and macerated rape and mustard plants (*Brassica* and *Sinapis* species). The identified compounds over whole plants included a number of terpenes (β -pinene, sabinene, myrcene, limonene, and β -phellandrene), leaf alcohols and aldehydes (cis-1-hex-3-en-1-ol, trans-hex-2-enal, and cis-hex-3-en-1-yl acetate), benzaldehyde, and low amounts of nitrogen and sulfur species (indole, phenylacetonitrile, dimethyl disulfide and dimethyl trisulfide).

As an interesting aside, Gelmont et al. (1981) reported the isoprene was the dominate endogenous hydrocarbon in human breath. The emission rate was estimated as 2 to 4 mg/day. This extrapolates to less than .001 Tg/yr in the U.S. which is negligible compared to inventory estimates of isoprene emissions from vegetation in the U.S.

1.3.2 Emission Patterns and Environmental Effects

It is well documented from the aforementioned field studies and from laboratory studies by Tingey and co-workers (Tingey et al., 1979, 1980, 1981), among others, that isoprene emissions increase with increasing temperature and light. Isoprene emissions in the dark can occur, but at very low levels. In contrast, it is generally believed that monoterpene emissions increase with temperature, but are not affected by light intensity. However, Yokouchi and Ambe (1984) reported that monoterpene emissions from red pine (*Pinus densiflora*) decreased by a factor of two in darkness compared to full sunlight. These authors noted that increased leaf temperature in sunlight might explain part of this effect. They argued that temperature acts through the vapor pressure curve of the monoterpene to increase volatility while light provides a pool of material through photosynthesis. This claim has not been substantiated in other studies.

Sanadze (1990) described the hypothesis that isoprene emission to the atmosphere is the result of two interrelated photosynthetic carboxylation schemes within the leaf chloroplasts. Monson and Fall (1989) used a leaf cuvette system to investigate the linkage between photosynthesis, photorespiration, and isoprene emission from aspen leaf. In this study, isoprene emissions occurred in the presence of either CO₂ or O₂; the presence of both gases was not a requirement for isoprene emission. The authors interpreted this to imply that isoprene emissions are not related to photorespiration. The results indicated that elevated CO₂ levels inhibited isoprene emissions, and that a light generated reductant or ATP is required for isoprene to be emitted. The yield of isoprene as a percent of the assimilation of CO₂ increased from 0.4% at 20 °C to 8.4% at 42.5 °C. For comparison, in a global emission inventory of

isoprene, Zimmerman et al. (1978) estimated from a U.S. inventory of emissions that isoprene emissions were 0.7% of the net primary productivity of vegetation. Also, Gay (1987) compared the carbon uptake predicted from a simple photosynthesis model to the isoprene emissions predicted from empirical temperature-emission curves applied in an inventory of emissions for the U.S. The isoprene emission represented 0.2% of total carbon uptake predicted in this study. These estimates provide measures of the linkage between the dynamics of photosynthesis to isoprene emission mechanisms in vegetation.

In earlier work, Tingey et al. (1981) demonstrated in a series of growth chamber tests, that isoprene emissions were a normal plant product and were not induced due to the effects of stress upon a plant. Juuti et al. (1990) measured emissions from Monterey pine and observed no effects due to changes in CO₂ levels, the presence of elevated ozone, or increased wind speed. However, rough handling of the branches increased emissions by factors of 10 to 50 times. Lamb et al. (1985) measured alpha-pinene emissions from wet and dry branches of Douglas fir (*Pseudotsuga menziesii*) and found that the emission rate was a factor of two higher from wet branches than from dry branches over the same temperature range. In both cases, the emissions were strongly correlated with temperature.

Guenther et al. (1990) have recently reported extensive emission rate measurements of isoprene and monoterpene emissions from leaves of *Eucalyptus globulus* using a leaf cuvette method. Isoprene emissions fluctuated less than 3% on an hourly basis and less than 14% from day to day. Leaf-to-leaf variations were much higher at 62%. These fluctuations were also observed for CO₂ uptake over time and from leaf-to-leaf. Leaf age was an important factor in these variations. An empirical model of isoprene emissions which accounted for the effects of relative humidity, light intensity, CO₂ assimilation, and leaf temperature was developed using the measured data. The fit of the model to the data was reasonably good (within 10% of observed for 62% of the values). Tests of the model against an independent data set are needed. It is not clear how general the empirical constants will be for different species or for real-world conditions.

Seasonal effects in emissions have been reported by Flyckt (1980) for isoprene emissions from red oak and by Arey et al. (1991) described previously for orange trees in blossom. Dilts et al. (1990) recently found significant changes in emissions over the course of a growing season for English oak which were not explained by changes in temperature or light intensity. Beyond these few studies, however, there are no long term efforts to measure seasonal effects upon emissions. Similarly, there are no systematic efforts to determine the effects of stress or disease upon vegetation under real world conditions.

This overview of the literature indicates that emission rate data exists for a wide variety of species, but for a relatively limited number of compounds: isoprene, a number of the dominate monoterpenes, and a few oxygenated species. From these data it appears that isoprene is the single dominant compound emitted from vegetation, the dominate terpene emissions are distributed among several monoterpenes, and emissions of identified oxygenated compounds may be significant for some types of vegetation. The available emission rate data includes data sets with relatively complete measurements of environmental parameters as well

as other data sets with only limited parameter information. Because of the different species, different locations, and different methods used in these measurement programs, it is difficult to envision a single compiled data set describing emission rates and related parameters. The question of scaling individual branch sampling to small scale flux estimates and from there to regional flux predictions has been discussed by Hicks (1989), but no attempts to demonstrate experimentally the scale up of emissions have been reported. This remains a serious question concerning the utility of emission rate data.

In addition to the compounds for which emission rate data exist, there is a much longer list of compounds which have been identified as being volatile components in plant biomass, but for which no quantitative emission rate information is available. There is work in progress dealing with the biochemical mechanisms for release of volatiles from vegetation. There is the beginning of a foundation for modeling isoprene emissions in terms of vegetation biochemistry. Terpene emissions seem to be directly related to oil composition and compound vapor pressure, but the formation mechanisms of the oil reservoirs has not been addressed in the context of volatile emissions.

1.4 AMBIENT BIOGENIC VOC CONCENTRATION MEASUREMENTS

Efforts to identify the dominate VOC emissions by investigating diurnal concentration patterns have been reported in a number of studies. Arey et al. (1991) in the study of linalool emissions mentioned previously found a good correlation between ambient linalool concentrations and measured emission rates in an orange grove. Clement et al. (1990) measured monoterpene concentrations at two heights within a maple forest (*Acer saccharum*) in Quebec. Limonene was the dominate monoterpene, but it was emitted from understory species and not maple. This underscores the potential importance of understory species in forest emissions. Emissions from secondary vegetation in a forest may be incorrectly assigned to the dominate tree species if direct emission measurements are not made. The monoterpene concentrations in the maple forest were at a maximum at night and at a minimum during the day. This concentration pattern has been reported by others (Bufler and Wegmann, 1991; Petersson, 1988) and is probably related to the continued emission of terpenes in the dark into a very stable atmosphere where dilution is minimized compared to daytime conditions. The terpene concentrations were slightly higher near the ground than in the canopy, and the authors suggested that this might be due to decomposition of leaf litter on the forest floor.

Martin et al. (1991) found an early evening maximum isoprene concentration associated with the onset of a stable surface inversion in a deciduous forest clearing followed by a sharp decline in concentration during the night. The rapid decline may be related to deposition of isoprene since it appears too rapid to be accounted for by chemical degradation. It appears from this literature review that the deposition of biogenic VOC's has not been investigated in any fashion. The general diurnal pattern of isoprene concentrations measured by Martin et al. followed a rapid increase of isoprene concentration in the early morning, then a slow rise through midday and a slow decrease in the late afternoon. This was followed by the early evening maximum described above and then low levels were observed through the night.

Typical maximum concentrations reached 5 ppbC during midday and 8 ppbC in the early evening.

Yokouchi and Ambe (1988) measured isoprene and monoterpene concentrations in an agricultural area of Japan during both rainy and clear midsummer conditions. Maximum isoprene concentrations during wet and clear days were 4 ppbC and 4.8 ppbC, respectively, but the average daily concentrations of isoprene were much higher on clear days versus cloudy days. Monoterpene concentrations were dominated by alpha-pinene with maximum wet and dry day concentrations of 21 ppbC and 22.8 ppbC, respectively. The average daily monoterpene concentrations were similar on clear and cloudy days, but clear nights produced monoterpene concentrations higher by a factor of 10 compared to cloudy nights. The ratio of alpha-pinene to beta-pinene increased from about 1 on high ozone days to about 4 on low ozone days.

These measurements of ambient concentrations of biogenic VOC's present a reasonably consistent picture of both isoprene and monoterpene diurnal concentration patterns. Isoprene clearly increases during the morning to maximum values during periods of maximum solar radiation and temperature and decreases at night. This pattern can be perturbed somewhat by the formation of a stable surface inversion in the evening. It appears that the rapid decrease in isoprene concentrations in the evening may be related to deposition. In contrast to isoprene concentrations, terpene concentrations tend to be lower during the day than at night primarily because of greater dilution during the day and low mixing at night. This implies that the daytime terpene sources are not as large as daytime isoprene sources. Changes in the ratios of terpenes with changes in ozone concentration are indicators of the different reactivity of terpenes in the atmosphere which may provide a powerful tool for evaluating chemical kinetic mechanisms proposed for terpene oxidation.

1.5 BIOGENIC EMISSION INVENTORIES

Efforts to compile emission inventories of biogenic emissions have paralleled modeling studies because of the need for temporal and/or spatial emission descriptions as input to models. U.S. emission inventories have been reported by Zimmerman (1979b), by Lamb et al. (1987), Gay (1987), and Lamb et al. (1990). The last three studies developed inventories on a county spatial scale, while the last two studies provided hourly estimates for typical diurnal periods for each month. The work by Gay (1987) and Lamb et al. (1990) introduced the use of a forest canopy model and leaf energy balance as a way to account for canopy effects upon leaf temperature and photosynthetic radiation. These studies provided the basis for a gridded inventory system developed for EPA use and described by Pierce et al. (1990). Regional or urban inventories have been developed by Zimmerman (1979a) for Tampa Bay, FL, by Winer et al. (1983) for the Los Angeles basin, by Salop et al. (1985) for a portion of Virginia, and by Flyckt et al. (1980) for Pennsylvania state. Global emission inventories of biogenic hydrocarbons have recently been developed by a number of groups including Dignon and Logan (1990), Allwine et al. (1990), and Turner et al. (1991). These global estimates use gridded land use data with gridded climatological data with various emission rate algorithms to estimate isoprene emissions. Allwine et al. (1990) also predicted emissions for alpha-pinene,

other identified monoterpenes, and the sum of other paraffins, olefins, and aromatics. The work by Turner et al. relies upon satellite imagery to determine the distribution of foliar density.

In these inventories, emission rate measurements from enclosure samples are used to develop simple emission algorithms which account for the effects of temperature and, for isoprene, light, upon the emission rate. Data collected in the Tampa Bay study by Zimmerman (1979a) are the primary source of data in all of the studies except the site specific work by Flyckt et al. and Winer et al. and in all cases, except for that of Gay and Lamb et al., ambient temperature data are used to drive the emission rate algorithms. Land use data in these inventories were derived from a number of sources, but there has been no rigorous attempt to intercompare land use areas among different inventories. Similarly, biomass density factors were derived from the literature in most cases, and intercomparisons of these data have not been reported.

1.6 ATMOSPHERIC CHEMISTRY OF BIOGENIC VOCs

Westberg and Rasmussen (1972) initially demonstrated the very reactive nature of isoprene and a number of monoterpenes in the presence of sunlight and nitrogen oxide. Since that early work, there has been a considerable number of smog chamber studies to determine rate constants of the oxidation of biogenic hydrocarbons with photochemical oxidants and to investigate the products of the oxidation reactions. The rate constants continue to be refined and information concerning the products and their yields is becoming available. At the same time, detailed chemical mechanisms have been formed for isoprene, and the initial products from the oxidation of monoterpenes such as alpha-pinene and beta-pinene have been suggested. These kinetic mechanisms have been included in a number of computer modeling studies to determine the relative importance of biogenic versus anthropogenic hydrocarbons for the formation of ozone downwind of urban areas. More recently, measurements of ambient concentrations of isoprene and monoterpenes and their expected oxidation products have been conducted so that the predicted behavior of biogenic VOC's in the atmosphere can be evaluated against atmospheric measurements. Recent results in each of these areas are discussed below; abstracts of the compiled literature are given in the appendix.

Atkinson (1990) presented a comprehensive review of the gas phase chemistry of tropospheric organics. For isoprene, oxidation by hydroxyl radical occurs via addition to the double bonds to produce either methyl vinyl ketone and formaldehyde or methacrolein and formaldehyde. The ratio of rates leading to methacrolein versus methyl vinyl ketone are calculated to be 34/66 at room temperature. Atkinson further noted, however, that these products do not account for the entire reaction process; Gu et al. (1985) measured methyl vinyl ketone (16%), methacrolein (23%) and 3-methylfuran (5%), and Tuazon and Atkinson (1989) measured methyl vinyl ketone (29%), methacrolein (21%), 3-methylfuran (4.4%), and formaldehyde (59%) as reaction products. Rate constants for reaction with OH, NO₃ radical, and ozone were reported for isoprene, alpha-pinene, and beta-pinene.

Additional reaction rate data for alpha-pinene and beta-pinene with ozone and OH have been reported by Hatakeyama et al. (1989,1991). These authors found that the major reaction products of alpha-pinene with ozone were CO($9\pm 1\%$), CO₂($30\pm 2\%$), HCHO($22\pm 1\%$), and the aldehydes(51%): pinonaldehyde and nor-pinonaldehyde. The reaction products of beta-pinene with ozone were CO₂($27\pm 2\%$), HCHO($76\pm 2\%$), and 6,6-dimethylbicyclo[3.1.1]heptan-2-one($40\pm 2\%$). Aerosol yields in these reactions were relatively constant over the terpene concentration range 10 to 100 ppb at $18.3\pm 1.1\%$ and $13.8\pm 0.8\%$ for alpha-pinene and beta-pinene, respectively. For OH oxidation, these authors reported that the major oxidation product for alpha-pinene in the presence of NO was pinonaldehyde ($56\pm 4\%$) and the major products for beta-pinene in the presence of NO were 6,6-dimethylbicyclo[3.1.1]heptan-2-one($79\pm 8\%$) and HCHO ($54\pm 5\%$). The latter yield evidently suggests that some of the HCHO is a secondary product of the oxidation. In the absence of NO the yields were decreased and enhanced aerosol formation was observed.

Kotzias et al. (1990) conducted chamber experiments of the oxidation of alpha-pinene, beta-pinene, and limonene via ozone under dark conditions in the presence of SO₂/NO₂ and beta-pinene in the presence of SO₂ alone. In the latter case, oxidation rates of SO₂ were in the range 6 to 15% after four hours, and greater oxidation of SO₂ occurred with low relative humidity levels. Nopinone was identified as the dominate volatile terpene oxidation product. Adding NO₂ to the system cause significant degradation of the terpenes--approaching 95% in one hour for limonene and 90% in 4 hours for alpha-pinene--and less oxidation of SO₂ than in the case without NO₂. Nopinone and pinonaldehyde were the main volatile products from alpha-pinene and beta-pinene oxidation, but an unknown compound appeared to the dominate product of limonene oxidation. The change in oxidation rates was explained through the effects of nitrate radical and a larger source for Crigee intermediates.

Reaction rate constants for gas phase oxidation of sabinene and camphene due to OH, NO₃, and ozone were measured by Atkinson et al. (1990). The results indicated that NO₃ and ozone oxidation of the terpenes were less than 5% of the rate associated with OH. In comparison to OH oxidation of isoprene, the rates constants for sabinene and camphene were factors of 1.16 and 0.525 times the isoprene rate constant.

Nolting et al. (1988) described the development and testing a smog chamber designed specifically for the study of terpene oxidation and aerosol formation. The chamber was tested by measuring rate constants for a number of alkanes and alkenes for comparison to the literature. Initial application of the system involved measurements of alpha-pinene and beta-pinene oxidation by O₃ and OH which compared well with literature results.

Hooker et al. (1985) used a ¹⁴C radiotracer method to examine the carbon mass balance of alpha-pinene oxidation products among gas phase, aerosol phase, and wall losses in a smog chamber. Mass balance results accounted for between 79% and 97% of the carbon for realistic ambient starting concentrations for ozonolysis and photochemical mixes.

Reports of ambient measurements of the oxidation products of isoprene and terpene have only recently appeared in the literature. Pierotti et al. (1990) measured methacrolein

(MAC) and methyl vinyl ketone (MVK) concentrations at California forests including California live oak (*Quercus agrifolia*) and sycamore (*Platanus racemosa*), eucalyptus groves, and groves of date palms (*Phoenix dactylifera*). Maximum concentrations were measured in midsummer and minimum concentrations were measured in early spring. Significant linear correlations existed between isoprene and each of the two oxidation products. Enclosure measurements indicated that neither MAC nor MVK were emitted directly from vegetation. Comparison of the measured concentrations with photochemical model calculations indicated that the kinetic mechanisms for moderate NO_x concentrations were not consistent with the observations. The work by Martin et al. (1991) in a mixed hardwood forest, mentioned previously, included diurnal measurements of isoprene, MAC, MVK, HCHO, and several organic acids. These data showed a strong correlation between isoprene and each of the carbonyls, but the slopes of the correlations for MAC and MVK were different than reported by Pierotti et al. (1990).

Helmig et al. (1990) obtained continuous measurements of peroxyacetyl nitrate (PAN) at a forest site over a one year period. Concentrations were lower within a spruce forest than above the canopy. Typical concentrations were less than 0.2 ppb, but episodic concentrations reached 4.6 ppb. The results indicated that long range transport of PAN was more important than local production within or above the forest. It was concluded that biogenic hydrocarbons did not contribute to the maximum PAN concentrations. Gunz and Hoffman (1990) measured carbonyl and carboxylic acid concentrations in snow samples from central and southern California mountains. Formaldehyde and acetaldehyde were the dominant species, and the maximum concentrations were measured in areas with widespread deciduous and coniferous forests, but the possibility of transport from agricultural and urban areas was not eliminated as a source of the aldehydes. Organic acid contributions to the total free acidity averaged 43%. Clairac et al. (1988) measured the physical properties and chemical composition of aerosols in an equatorial region of Africa during a period with minimal biomass burning. The results show that the forest was a source of fine particles produced by gas-to-particle conversion and by mechanical processes. Half of the carbon was in the form of submicron particles believed to be derived from gas phase photochemistry.

The measurements of rate constants and the recent measurements of product concentrations in the atmosphere provide the basis for developing kinetic mechanisms and photochemical models in the first case and the basis for testing these models in the second case. There have been a number of kinetic mechanisms developed and a large number of photochemical modeling studies related to biogenic hydrocarbons. In the latest version of the carbon bond mechanism (CB-IV), isoprene is treated explicitly, while a terpene is modeled using a lumped structure approach where the structure is represented by a combination of OLE and PAR surrogates for the double and single bonded carbons. The primary products of isoprene oxidation are modeled to be MAC, MVK, and HCHO. Evaluation of the chemical mechanisms versus smog chamber studies indicated significant improvement over previous versions of the model. For isoprene, ozone concentrations were overpredicted by only $6 \pm 23\%$, PAN concentrations were overestimated by $10 \pm 22\%$, and HCHO concentrations were estimated to within $1 \pm 18\%$.

Calvert and Madronich (1987) developed a detailed chemical mechanism covering 26 alkanes, two alkenes, five aromatics, isoprene and alpha-pinene. The predicted initial products of isoprene oxidation in a realistic atmospheric mix were MAC (25%), MVK (25%), and HCHO (50%). The authors further noted, however, that these products have short lifetimes in the atmosphere and that these are also products of common aromatics as well so that the products are not necessarily unique markers of isoprene laden air masses. For the terpenes, the products of oxidation are unique and should be useful short term markers in the atmosphere.

Different chemical kinetic mechanisms have been compared by Dodge (1989) and by Derwent (1990). While Derwent did not explicitly discuss biogenic VOC chemistry, Dodge included simulations where isoprene emissions varied diurnally. There were some differences among the different simulations, but Dodge concluded that overall the three mechanisms showed good agreement in the treatment of rural atmospheric chemistry.

Questions concerning the importance of biogenic hydrocarbons in the formation of ozone within or downwind of urban areas have been addressed in a number of air quality modeling studies (e.g. Lurman et al., 1984; Trainer et al., 1987; Chameides et al., 1988). Methods have ranged from the use of simple box models to Lagrangian chemical reactor models to fully three dimensional Eulerian grid models. The influence of biogenic hydrocarbons in the Regional Acid Deposition Model (RADM) (Chang et al., 1988) and the Regional Oxidant Model (ROM) (Roselle and Schere, 1990) have been of particular interest. Similar concern for the importance of biogenic VOC's in formation of CO and tropospheric ozone on a global basis has been addressed through tropospheric chemical models (Lopez et al., 1989; Jacob and Wofsy, 1988; and Atherton and Penner, 1990).

Lin et al. (1988) employed a photochemical box model to investigate the nonlinear dependence of ozone formation upon precursor concentrations. The results indicated that the composition of hydrocarbons, the ratio of VOC/NO_x, and the background concentrations of biogenic VOC's, CO, and CH₄ all are important in determining the nonlinearity of ozone formation with respect to NO_x loss. Atherton and Penner (1990) performed a similar study using a photochemical box model to investigate the importance of odd nitrogen species beyond those normally included in models: NO, NO₂, PAN, HNO₃, and NO₃⁻ (particulate nitrate). The shortfall of odd nitrogen was defined as the ratio of other nitrogen species to the sum of the above compounds. For cases with biogenic VOC's, the nitrogen shortfall was 0.25 with background isoprene and pinene emissions and 0.45 with high pinene emissions. In comparison, the shortfall varied between 0.02 to 0.33 for various urban simulations. The implications from this work are that incorrect specification of odd nitrogen chemistry may be a significant source of error in chemical modeling studies of biogenic emissions.

Jacob and Wofsy (1988) compared photochemical model predictions against isoprene and ozone concentrations measured over the Amazon forest. The results were in good agreement with observations and showed that biogenic isoprene and NO_x can supply most of the ozone observed in the boundary layer. In agreement with the suggestion made previously

about the dry deposition of isoprene at night, the model comparison with observations indicated the importance of dry deposition.

Lopez et al. (1989) modeled the vertical profiles of photochemical species in a Lagrangian air parcel moving over homogeneous land cover. For cases with terpene emissions into an air mass with low NO_x, ozone was depleted, while emissions into an air mass with high NO_x caused an enhancement of ozone. The degree of change was larger for alpha-pinene emissions than for isoprene emissions.

The effects of biogenic emissions upon the urban plume of London was investigated by MacKenzie et al. (1991) using a detailed photochemical expanding air parcel model. The results seemed quite similar to the early work by Lurmann et al. (1984) since the predicted effect of adding biogenic emissions increased the ozone concentrations by about 8 ppb.

The sum of these modeling studies have provided insight into the role of biogenic VOC's in atmospheric chemistry. However, until a better understanding of the biogenic emission fluxes is obtained, the identity of important biogenic species is clarified, and more complete chemical mechanisms are compiled, the modeling results provide an incomplete and uncertain picture of biogenic VOC's in the atmosphere.

1.7 CURRENT BIOGENIC STUDIES

The NOAA ROSE (Rural Oxidants in a Southeastern Environment) program recently completed a 2 month field study in an Alabama pine plantation designed to measure precursors and products related to ozone formation in the southeastern U.S. The programs included sampling of biogenic emissions, measurements of VOC reactant and product concentrations, and performance of vertical profile tracer flux studies. Similar work was performed in the predecessor to ROSE which was conducted in Scotia, Pennsylvania, in 1988 (see Martin et al., 1991). The unique feature of the ROSE program is the combined measurement of essentially all carbon and nitrogen species thought to be important in ozone air chemistry along with detailed boundary layer meteorological measurements and vertical transport tracer studies. In ROSE 1990, this included diurnal sampling of VOC emissions using a vegetation enclosure method of all the dominant vegetation types in the area as well as diurnal sampling of the concentrations of isoprene, the terpenes, and their expected oxidation products in the atmosphere. More than 200 enclosure samples were collected along with measurements of pertinent environmental parameters during the study. Compound fingerprints from each species sampled were obtained using a GC/MS system located on site. A data meeting of all participants was held in January, 1991. Initial presentation of results occurred in a special session at the fall 1991 meeting of the American Geophysical Union.

The SOS (Southeast Oxidant Studies) program is a broad plan under development by a consortium of universities and EPA laboratories. A large aspect of SOS will deal with biogenic emissions (Southern Oxidants Research Program on Emissions and Effects, SORP-EE) while other parts of SOS are directed at intensive field studies of ambient reactant and product gases. The proposed SORP-EE emissions activities are extremely broad at this point.

As one component of the work, the NCAR Trace Gas Biogeochemical section has proposed to measure biogenic emission rates and perform biomass surveys at a number of sites. Measurements of vertical profiles of hydrocarbon concentrations will be made at each site using the NCAR tethered balloon sampling system.

The OTER (Oregon Transect Ecosystem Research) project is a NASA effort to use ecosystem models with remotely sensed observations of ecosystem variables as a way to predict ecosystem response and feedback to global warming. The OTER project covers six sites along a line from coastal Oregon over the Cascade Mountains to the high central desert of Oregon. Initial EPA plans to incorporate biogenic emission measurements by Washington State University (WSU) within the OTER framework have been eliminated. However, alternate funding were obtained for a scaled back set of measurements during 1991 at one of the OTER sites. The emphasis in the emissions measurements was to collect diurnal emission profiles during two field visits through the growing season in conjunction with careful measurement of key photosynthesis and environmental variables. As a predecessor to the WSU OTER study, Dilts et al. (1990) have completed a one year study of emissions from English oak in Pullman, WA where enclosure samples were collected on an hourly basis through a diurnal period and environmental parameters were measured continuously (photosynthesis rate, leaf and air temperature, moisture level, and photosynthetic active radiation). These diurnal sampling profiles were repeated approximately twice weekly during the growing season beginning in the fall, 1989, and continuing through the fall, 1992.

The BOREAS (Boreal Ecosystem-Atmosphere Study) sponsored by NASA is an extensive multi-year field measurement and modeling program that is designed to improve our understanding of carbon cycling in boreal forests and to investigate how the fluxes of radiatively active trace gases from terrestrial ecosystems will influence future climate scenarios. The study area will be at two boreal forest sites in central Canada. Preliminary field measurements will be made during 1993 and several intensive study periods will be completed during 1994.

The SJVAQS/AUSPEX are two joint projects being conducted in the San Joaquin valley of California. Like SOS, these are broad field measurement and modeling efforts to obtain quantitative information about ozone formation and transport. In terms of biogenic emissions, the unique feature of this work is the importance of emissions from a variety of agricultural crops. Winer et al. (1989) recently completed a comprehensive survey of emissions from crops and natural vegetation in the San Joaquin valley. These data and results from additional measurements will be used as the basis for a gridded emission inventory of emissions being developed by the Desert Research Institute (DRI) for the project. The inventory will make use of satellite data to map vegetation cover, and it will include methods to predict emissions for specific times using emission models with measured meteorological conditions.

The EPA Air and Energy Engineering Research Laboratory (AREEL) is funding work to improve biogenic hydrocarbon emission inventories. The NCAR TGB section will be involved in reviewing the Tampa Bay emissions data to identify compounds lumped into the

"other hydrocarbon" categories more specifically. Results from the ROSE sampling program will be used along with the laboratory measurements by Guenther et al. (1990) to test and improve the physiological emission rate model. In addition, the use of satellite data to determine biomass distributions over time will also be investigated through this program.

Together, these current programs represent a substantial effort to improve our understanding of biogenic emissions. Many of the uncertainties associated with estimating biogenic emission rates and identifying important VOC species should be resolved as these programs proceed, and new methods for the development of inventories will be available.

2.0 CRITICAL REVIEW OF THE LITERATURE

2.1 INTRODUCTION

As a result of the Clean Air Act of 1990, development of plans to control ozone formation in non-attainment regions must account for the emission of reactive hydrocarbons from vegetation, and models used to test control strategies must address the photochemistry of these biogenic gases. However, the inventory models used to estimate biogenic emissions contain large uncertainties and there is still an incomplete understanding of the oxidation mechanisms of biogenic hydrocarbons in the atmosphere. In this chapter, selected papers from the literature are critically reviewed. These papers were selected as representative of the state-of-the-art in each of several areas including biogenic emissions modeling, emission rate measurements, and atmospheric chemistry related to biogenic hydrocarbons. The purpose of this critical review is to highlight the major areas of uncertainty in each area and to identify gaps where additional information or work is needed. This analysis will thus provide a basis for the development of a detailed research plan to answer the major questions concerning the role of biogenic hydrocarbons in the formation of photochemical oxidants.

There are several current large-scale studies underway which have a significant biogenic VOC component. Because reports and papers from these efforts, the Lake Michigan Oxidant Study and the San Joaquin Valley Air Quality Study, are not yet available, these studies are not considered at this time. This review includes available papers and reports selected as being representative of current studies. The review is designed to be critical in the sense that it identifies key assumptions, lack of data, or incomplete understanding that limits our confidence in emission estimates, emission measurements, or predictions of atmospheric fate.

2.2 EMISSION INVENTORY SYSTEMS

The central emission inventory model being used for ozone control purposes in the U.S. was developed as part of the National Acid Precipitation Assessment Program (NAPAP) by Washington State University (WSU) (Placet et al., 1990; Lamb et al., 1991). This model was subsequently compiled for implementation on a personal computer as PC-BEIS (Biogenic Emission Inventory System) by Pierce and Waldruff (1991) (see also Pierce et al., 1990, and the user's guide, Pierce, 1990). This system is being used as the starting point for inventory systems now being developed as part of the Lake Michigan Oxidant Study (LMOS, Heiler et al., 1990) and as part of the San Joaquin Valley study (SVJAQS/AUSPEX, Ranzieri et al., 1990). In Europe, the NAPAP inventory methods are also being used as a starting point for the development of European biogenic emission inventories (Veldt, 1991).

The WSU and PC-BEIS inventory models are essentially the same with some differences in implementation. The key features of both include the use of geometric mean emission rate factors derived from Zimmerman's Tampa Bay study (Zimmerman, 1979a), the use of forest biomass density factors from Zimmerman's work (Zimmerman, 1979b), the



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application of modified curves of emission rate-temperature-light from Tingey's chamber work (Tingey, 1981), and incorporation of county land use data from the Geoecology Data Base (Olsen, 1980). A simple semi-empirical forest canopy model/leaf energy balance is used in both systems to account for the attenuation of sunlight by the canopy and to calculate resulting leaf temperatures (Lamb et al., 1991). PC-BEIS uses hourly ambient temperature, ambient relative humidity, wind speed, and cloud cover to calculate emissions for a specified county for a specified day.

Emission fluxes are calculated for isoprene, alpha-pinene, other identified monoterpenes, and other hydrocarbons. While PC-BEIS calls the latter category 'unidentified', as Lamb et al. (1991) describe, other hydrocarbons were originally identified by Zimmerman in terms of paraffins, other olefins (besides isoprene and specific terpenes), and aromatics. In the original work, Zimmerman reported that 85% of all emissions were identified in terms of specific compounds, but for purposes of reporting, minor species were lumped in the three categories given above. Unidentified species were categorized according to the chromatographic peak retention time. In terms of the classes used in the inventory system, most of the other hydrocarbons are listed as paraffins and aromatics as shown in Table 2.1 from Lamb et al. (1991).

Table 2.1. Composition of Other VOC emissions (geometric mean emissions at 30 °C) derived from emission rate measurements in Tampa Bay, FL).

Class	Paraffins	Other Olefins* (ug/g/hr)	Aromatics	Total
High Isoprene	0.88	0.15	0.79	15.8
Low Isoprene	0.73	0.07	0.64	7.74
Non Isoprene	0.77	0.12	0.65	1.96
Coniferous	0.74	0.25	0.36	4.26

* olefins besides isoprene and selected terpenes

This breakdown does not agree with the assumption by Pierce et al. (1990) that the other hydrocarbon class is 45% paraffin, 45% olefin, and 10% aromatic.

In spite of the identifications reported by Zimmerman, the fact remains that the exact identity and the quantity of other VOC emissions are largely uncertain. These constitute a significant uncertainty in the current inventory system. As indicated in the first chapter, several workers have identified a wide range of other compounds, including oxygenated VOC, as volatile emissions from plants. However, there has been no systematic effort to develop

usable emission fingerprints for large classes of vegetation suitable for use in an inventory scheme.

For a particular emission class, emission rates in the inventory system are calculated as the product of an emission rate factor and an algorithm derived from Tingey's chamber work to account for the light (for isoprene, only) and temperature conditions. In the development of the inventory, emission rate factors for trees were calculated from the raw Tampa Bay data in terms of geometric means for the following classes: deciduous high isoprene emitters, deciduous low isoprene emitters, deciduous non-isoprene emitters, and coniferous terpene emitters. The calculation involved correction of the raw data to 30 °C using Tingey's curves and then calculation of the geometric mean of all emission rates in each class. There are four aspects to the calculation of the emission rate factors which introduce uncertainties into the inventory. First and foremost, all of the emissions data are for species measured in only one location: Tampa Bay, FL. Lamb et al. (1987) compared these data with results from a variety of other studies across the U.S. and found that there was general agreement between the slope of emissions versus temperature as well as for the magnitude of the emissions. However, there was still a factor of two to three scatter among all of the data points from that comparison.

Second, Lamb et al. (1991) pointed out the difficulty of choosing between the use of geometric means to represent emissions as opposed to arithmetic means. Geometric means were initially selected as representative of the central tendency of emission because the frequency distribution of the raw emission data corrected to 30 °C showed a log-normal distribution. However, it can be argued that arithmetic means are more appropriate because an arithmetic mean multiplied by the number of samples returns the total summed emission rate and thus better represents the presence of outliers. For the U.S., the use of geometric mean emission rate factors yields a total annual emission of 28 Tg/yr while the use of arithmetic mean factors yields a total annual emission of 47 Tg/yr. The uncertainty due to the selection of mean emission rate factors cannot be reduced without a more definitive comparison of individual enclosure samples with total flux measurements from a forest.

Third, the inventory corrects for temperature and light effects upon emissions using Tingey's curves derived only from measurements for slash pine and live oak. The representativeness of these curves for a wide variety of species has not been fully determined. As indicated above, comparison of data from a variety of U.S. studies showed general agreement in terms of the slope of the emission rate-temperature relationship and this included Tingey's results. Guenther et al. (1991) have recently introduced a different model of the emission rate process which addresses the effects of light and temperature as well as the effects of humidity and carbon dioxide levels. Further work to determine the representiveness of either the Tingey model or the Guenther model is required.

Fourth, the correction algorithm for temperature and light is given in terms of four emission rate-temperature curves corresponding to 100, 200, 400 and 800 $\mu\text{E}/\text{m}^2/\text{s}$ light intensities. In the WSU inventory the curve for 400 $\mu\text{E}/\text{m}^2/\text{s}$ is used as the basis for normalization of the emission rate data, while in PC-BEIS the 800 $\mu\text{E}/\text{m}^2/\text{s}$ curve is employed.

Lamb et al. (1991) found in the Tampa Bay emission rate data that the raw data most closely followed the $400 \text{ uE/m}^2/\text{s}$ curve. During the collection of the data, the observer also recorded a light index based upon the perceived light level at the sampling location. The average light conditions from these data represented shaded conditions. As a result, Lamb et al. assumed that the mean emission rate factors corresponded to the $400 \text{ uE/m}^2/\text{s}$ curve. Normalizing the raw emission rate data using either the 400 or $800 \text{ uE/m}^2/\text{s}$ curve has the effect of changing the calculated emissions for a given light level. For the annual U.S. inventory, Lamb et al. (1991) calculated a total emission of 28 Tg/yr assuming the mean emission rate factors corresponded to conditions with $400 \text{ uE/m}^2/\text{s}$ light intensity. Assuming that the emission rate factors corresponded to conditions with $800 \text{ uE/m}^2/\text{s}$ light intensity yielded a total U.S. annual emission of 22 Tg/yr .

One missing feature in the current inventory is the lack of consideration for the emission of isoprene by spruce trees and the corresponding dependence of the emissions upon light. Evans et al. (1985) reported upon the differences in light effects between two species of spruce. Field measurements of isoprene emissions from spruce do not appear to be available in the literature.

In summary, the basis for the current inventory system are the Tampa Bay vegetation enclosure data and the empirical curves from a set of growth chamber measurements using one deciduous and one coniferous species. It is clear that this is an insufficient data set and that more work is required to develop more robust emission rate factors and emission rate models. Validation of selected factors and models is required for a variety of species in a variety of locations.

This conclusion applies even more strongly to the methods used to estimate emission rate factors for agricultural crops. In this case, a relatively small number of measurements were used to calculate total hydrocarbon mean emission rate factors for different crops. The composition of these total emissions was then largely assumed following compositions originally used in the EPA BESS emission procedure (a fore-runner to the current PC-BEIS system). The result is that the uncertainties in the emission rates and in the composition of emissions from agricultural crops are extremely large. Winer et al. (1989) and Arey et al. (1991a and b) have recently reported emission rate measurements for a number of California crops. This type of data should be used to refine the emission rate and compositions used in the inventory system. For example, the measurements for California crops exhibited very little or no isoprene emissions. Yet, it is assumed in the emission inventory system that emissions from crops include a significant fraction of isoprene. In addition, the emission rate measurements from California indicate that oxygenated species, such as hexenol, can be a significant component of the emission fingerprint. These types of findings need to be incorporated into future inventory estimates.

For forested areas, environmental conditions are affected by the forest canopy so that leaves in the upper canopy receive direct sunlight while those in the lower canopy are shaded. Leaf temperatures in the upper canopy can thus be as much as 10°C above ambient, while leaf temperatures in the lower canopy can be cooler than ambient. At night the situation may be

reversed due to radiative cooling of exposed leaves. To account for these effects, Lamb et al. (1991) developed a simple set of vertical scaling relationships which empirically describe the vertical profile of ambient temperature, solar radiation, humidity, and wind speed as a function of the above canopy ambient values. In turn, the local conditions in the canopy are used in a leaf energy balance to yield leaf temperature in a way that accounts for absorbed solar radiation, radiative cooling, and sensible and latent heat fluxes from a leaf. The local leaf temperature and available solar radiation are then used as input to the empirical emission algorithms, and emission fluxes are calculated for each of 8 different layers from the ground to the canopy top.

This simple forest canopy model is an empirical description of the canopy dynamics. While it captures the essence of the canopy effects upon solar radiation and leaf temperature, it makes no attempt to account for the feedback of vegetative activity upon the canopy environment, and it represents all forests in terms of either an idealized deciduous or coniferous canopy with a fixed canopy height and a fixed vertical biomass distribution.

Chuang et al (1991) have calculated the U.S. inventory with and without the forest canopy model in place. Isoprene emissions were 50% lower using the canopy model, while terpene emissions were only 6% less using the canopy model. These results suggest that the attenuation of solar radiation is a much more important effect upon emissions than modification of leaf temperatures.

Lamb et al. (1991) compared average leaf temperature measurements in a semi-open deciduous canopy with predictions from the forest canopy model. On an average diurnal basis, the model duplicated the observed profile to within 1 to 2 °C during the midday and nighttime periods, but the differences between model and measurements was 3 to 4 °C during the transition periods from day to night and night to day.

The forest canopy model appears to be an important component of the inventory process for isoprene emissions, but it has not been evaluated against comprehensive measurements. In particular, vertical profiles of the environmental parameters and corresponding emission rates must be measured in order to fully test the model. This type of program is being planned by EPA for a deciduous forest during the summer 1992 (Geron, EPA, personal communication, 1991). There is similar work being conducted in Europe; preliminary results are noted in a later section.

In order to convert emission rates calculated from the emission algorithms to emission fluxes from a forest and to extrapolate these fluxes to a county spatial scale, biomass density factors and land use classes must be specified. Land use classes include oak forests, other deciduous forests, coniferous forests, scrublands, grasslands, urban areas, inland waters, and agricultural crops. In PC-BEIS, agricultural crops are further classified in terms of approximately 15 different crops.

In the emission inventory model, biomass density factors are assumed based upon literature data for each emission class. This assumption includes the specification of the mix

of tree types within an emission class (or forest) as well as the magnitude of the biomass density for each tree type within that forest. For example, it is assumed that an oak forest actually consists of a mix of high, low, and no isoprene emitting trees and coniferous trees. The relative contributions of each type are given in terms of the biomass density for each type.

Obviously, assuming a distribution of biomass densities for a given forest type and applying this distribution across the U.S. introduces considerable uncertainty into the final calculation for any specific location. While the range of biomass densities for a given age and type of forest appears to be relatively small ($\pm 30\%$, see Lamb et al., 1987; and Veldt, 1989), the distribution of forest ages is not addressed in any way within the inventory. This is an uncertainty which needs further evaluation. Similarly, the application of a specific distribution of biomass density factors for a forest type ignores differences associated with different tree species within that forest type. Veldt (1989) has also suggested that for some species, such as *Picea abies* (Norway spruce), biomass density can be correlated with latitude.

Currently land use data from the Geoecology Data Base are used to specify the fractional county area for each of the eight land use types. The Geoecology Data Base is a composite of a wide variety of data sources compiled prior to 1980. Chueng et al. (1991) found agreement to within approximately 10% for major land types (coniferous forests, scrublands, and agricultural) between the Geoecology Data Base and land use information derived from a very recent detailed vegetation map for the state of Idaho. For minor land types, such as deciduous forests and inland waters, differences exceeding a factor of six existed for Idaho. The accuracy of this land use data needs further evaluation for other portions of the country. In addition, an effort to update the land use data to account for changes in land use is also needed.

Beyond further evaluation of the individual components of the inventory model, direct validation of the overall inventory procedure is also missing. Direct validation of an inventory requires a method which relates measured ambient concentrations of isoprene and the terpenes to predicted emission rates for a region. Martin et al. (1992) have compared emission fluxes obtained using an atmospheric tracer method with emission fluxes estimated using the inventory emission algorithm. The fluxes derived from the tracer/isoprene measurements were in relatively good agreement with fluxes derived directly from the isoprene emission algorithm in the inventory model. However, as Martin et al. indicate, the observed emission fluxes from the forest actually represent an upper bound to the predictions since the emissions are predicted in the absence of any canopy effects which have the tendency to reduce isoprene emissions due to shading of leaves within the canopy. At any rate, this is a test of the model at a relatively small scale. Similar efforts are needed at a larger scale where the combined effects of different forest and land types might be observable.

2.3 EMISSION RATE MEASUREMENTS

Arey et al. (1991a) conducted a comprehensive survey of biogenic VOC emissions from vegetation in the San Joaquin Valley of California. This work is worthwhile to review.

because of the emission data reported for crops and because the methods are representative of current capabilities for emissions measurements.

Emissions were measured for 17 crops and three natural species which occur in the San Joaquin Valley. Measurements were made using a dynamic flow through enclosure system where humidified zero air tagged with ambient levels of carbon dioxide is passed through an enclosure. Gas samples were collected after three chamber residence times (10 minutes) using either Tenax-GC or Tenax-GC/Carbosieve (for isoprene quantification) adsorbent tubes. It should be noted that measurement at 3 residence times should yield emission estimates to within 95% of the steady state value if the chamber is well-mixed. In addition, the effective velocity of air through the chamber is probably much less than 1 m/s if the chamber is cylindrical with a diameter of approximately 0.5 m.

This sampling approach is quite reasonable and provides for an atmosphere containing representative levels of moisture and CO₂. Close control to maintain specific levels of moisture or CO₂ is not used. Guenther et al (1991) found weak dependence of isoprene emissions upon humidity and CO₂ levels, but the importance of these parameters upon terpene emissions is not well established. Arey et al (1991a) did not describe methods used to monitor leaf or enclosure temperatures nor were light levels or the actual humidity levels reported for any of the measurements. It is a weakness in many recent papers that this type of information is not included routinely with reported emission rate measurements.

For each species tested, samples were collected five times during the daytime (0900, 1030, 1200, 1330, and 1430 PDT) from as many as three different plants while the 0900, 1200, and 1430 samples were collected from the same plant. This is a reasonable survey approach which attempts to address both diurnal variability as well as plant to plant variability. However, only the mean emissions were reported and the variability in emissions and any diurnal effects were not described in the paper. Some of this information is available in the report by Winer et al. (1989). It is probably a weakness of this type of diurnal sampling scheme that no samples were collected at night. It is generally believed that terpene emissions are not light dependent. However, sampling some or all of the species at night would provide a wider temperature range and also test for any anomalous behavior in agricultural crops. It should also be noted that Steinbrecher (Fraunhofer-Institut Fur Atmospharische Umweltforschung, IFU, personal communication, 1991) has recently found a weak light dependence of terpene emissions from spruce. Further work is needed to corroborate this finding and to look for similar behavior in other species.

The adsorbent tube samples were analyzed using a combination of GC/MS to determine compound identities and GC/FID to obtain quantitative emission rate measurements. Details concerning the analysis of blank tubes and testing for breakthrough were not given, although it was stated that terpene recovery efficiencies were 100%. More than a dozen terpenes were identified as measurable emissions from agricultural crops, but isoprene was not measured as an emission from any of the agricultural crops. Sesquiterpenes were identified in the emissions from approximately one third of the species tested. In some cases, the sesquiterpene emissions were larger than the terpene emission rates. Oxygenated species, including cis-3-

hexen-1-ol, 3-hexenylacetate, and others, were also measured and described in a separate paper (Arey et al., 1991b).

While the species tested are important in terms of acreage planted in the San Joaquin Valley, only alfalfa, cotton, and sorghum are crops which appear in a list of the top 15 crops planted in the U.S. For these species, the measured total emission rates are compared to the emission rates used in PC-BEIS in Table 2.2.

Table 2.2. Comparison of measured VOC emission rates from Arey et al. (1991a) and those used in PC-BEIS for three agricultural crops.

Crop	Measured Emission Rate* (ug/g/hr)	PC-BEIS Emission Rate (ug/g/hr)	Tg/yr**
Alfalfa	0.26	0.0117	0.155
Cotton	0.74	0.24	0.0528
Sorghum	0.07	0.0123	0.0131

* corrected to 30 °C using the Tingey temperature relationship for monoterpenes.

** annual emissions for U.S. based upon measured emission rates at 30 °C.

Obviously, there is a very large difference between the measured values and the emission factors used in the inventory. In addition, it is assumed in the inventory model that these crops have an emission composition which includes 20% to 50% isoprene, while no isoprene emissions were measured from these crops. To keep these errors in perspective, however, the annual total emissions from these crops are also listed in Table 2.2. The annual values are very small compared to emissions from other sources. Even so, further emissions data are needed for all important crops in the U.S.. Surveys using methods like those described by Arey et al. (1991a) should be conducted in different regions of the country covering the dominant U.S. crops.

Enders et al. (1991) have recently described the overall approach and preliminary results from a large cooperative European study of biosphere/atmosphere interactions in a mature coniferous forest (*Picea abies*, Norway spruce). This work is briefly described here because it introduces a significant and ongoing effort. The overall objectives of the measurement program includes: determination of emission/deposition rates and ambient concentrations, studies of emission mechanisms, comparison of fluxes and emission rate measurements (i.e. gradient versus enclosure measurements), studies of photochemistry, and studies of mesoscale and microscale meteorological processes on local sources and sinks of

important trace gases. The gases of interest include nitrogen compounds, oxidants, volatile organic compounds, and reduced sulfur species.

The experimental design involves ambient concentration, meteorological, and emission measurements along a 51 m tower in a spruce forest located in a German National Park 'Bayerischer Wald'. A significant aspect of the emissions measurements is the intercomparison of different enclosure systems operated by different groups at the same location. In preliminary results from one afternoon, two methods gave emission rates of alpha-pinene which differed by as much as a factor of four. The authors reported gradient measurements of formic and acetic acid which suggested a surface source of formic acid and a sink for both gases within the canopy. The authors also pointed out that the NMHC/NO_x ratios can vary from 0.3 to 20 depending upon time and height; this implies that the production or destruction rates for different compounds can vary considerably depending upon conditions. A significant aspect of this range of values is the effect of the diurnal stratification pattern which was observed within the forest canopy where daytime stable and nighttime unstable temperature gradients occur within the forest canopy.

2.4 ATMOSPHERIC CHEMISTRY

Biogenic hydrocarbons contribute to atmospheric chemistry in the following ways:

1. In the presence of the oxides of nitrogen and sunlight, they can enhance ozone production.
2. Oxidation of the monoterpenes produces aerosols which affect visibility.
3. Organic acids are undoubtedly produced during the oxidation of biogenic hydrocarbons. These acids can contribute to acidic deposition in rural areas.
4. Biogenic hydrocarbons can influence atmospheric OH levels directly and/or indirectly. The direct link occurs through their reaction with OH and the indirect component lies in their oxidation to CO, which in itself plays an important role in controlling OH concentrations in the atmosphere.
5. Organic nitrates (PAN, etc.) produced during the oxidation of biogenic hydrocarbons may provide a temporary reservoir for NO_x.

Most of these biogenic effects have been addressed in a modeling study by Jacob and Wofsy (1988). They simulated the chemistry occurring over an Amazon forest during the dry season with a photochemical model. Results from the modeling exercise were compared with field measurements in the Amazon during the NASA sponsored ABLE-2A experiment. The model indicates that ozone production in the boundary layer is controlled by the availability of NO_x and independent of the isoprene source strength. This is due to the very low levels (~30 pptv) of NO_x present in the Amazon boundary layer. Jacob and Wofsy further conclude that it would take isoprene emission fluxes much larger than expected for isoprene to act as a

significant ozone sink. Their study indicates that 1) high concentrations of NO_y species (primarily PAN-types) are produced, 2) photooxidation of isoprene could account for a large fraction of the CO enrichment observed in the boundary layer, and 3) the oxidation of isoprene could be an important source of organic acids in the atmosphere. The ambient concentrations of O_3 , CO, NO_y and organic acids predicted by the Jacob and Wofsy model agree very well with levels observed in the Amazon boundary layer. This lends credibility to the photochemical model employed. However, it is recognized that the atmospheric chemistry of intermediate species such as carbonyls, alcohols, peroxides, organic acids and organic nitrates is poorly understood. In most cases, model predicted concentrations of carbonyl intermediates don't agree very well with measured concentrations.

Hatakeyama, et al. (1991) have studied the oxidation of alpha- and beta-pinene in the laboratory for purposes of defining the conversion to CO. In addition, their study provides some information concerning ozone and aerosol production when the two monoterpenes react with hydroxyl radical. They report a gas-phase product yield of 55% when monoterpenes react with OH in the presence of NO_x . In the absence of NO_x the yield of gas-phase products is significantly lower. Hatakeyama and co-workers hypothesize that under 15% of the monoterpene emitted into the atmosphere is converted to carbon monoxide. They estimated that the reaction of monoterpenes with OH produces ~52 Tg of CO annually. When this is combined with the 172 Tg of CO generated in terpene-ozone reactions, 224 Tg of CO are produced annually from terpene oxidations. The 224 Tg/yr is about 40% of the 560 Tg/yr of CO that is estimated to be produced in the atmosphere from biogenic hydrocarbon oxidation (Logan et al. 1981). The other 60% presumably is generated via the oxidation of isoprene.

As is the case with many of the biogenic hydrocarbon issues, the Hatakeyama et al. CO production estimate is highly uncertain. The primary cause of uncertainty relates to the polar nature of the highly oxygenated intermediate products of biogenic hydrocarbon oxidation. A large and varying fraction of these intermediates are undoubtedly deposited by wet and dry processes, and thus removed from the CO production pathway. This is not to say that the work of Hatakeyama is futile. It provides a base on which future studies can build.

Kotzias and co-workers (1990) have conducted laboratory studies to help better understand the mechanism of terpene degradation in the presence of SO_2 , NO_2 and O_3 . The concentrations employed in this laboratory study were somewhat higher than those observed in the real atmosphere (i.e. hundreds of ppbv vs < 10 ppbv) but more realistic than many earlier studies. Their yield of organic products was very low (a few percent) so the study provides little insight into reaction mechanisms. However, some information about the oxidation mechanism was achieved by manipulating the presence/absence of H_2O and NO_2 . Examination of the reaction kinetics and inorganic product yields appears to confirm that 1) NO_3 is a more reactive oxidant than O_3 and 2) water scavenges the initial O_3 -terpene adduct (Criegee Intermediate) which presumably leads to organic acid formation. It would have been helpful if the presence of organic acids could have been confirmed, however, the mode of sample collection (Tenax/charcoal) precluded analysis for highly oxygenated products.

The Kotzias et al. work indicates that the nighttime oxidations of terpenes may assist in the conversion of SO_2 to sulfate. However, the importance of the terpene contribution is difficult to judge because of the multitude of competing reactions that may interfere with the SO_2 -sulfate oxidation process. Possibly the most interesting information reported in the Kotzias et al. paper is the tentative identification of a nitrate product of beta-pinene oxidation. As indicated previously, organic nitrates can serve as sequestering agents for NO_x and thus may play an important role in controlling the oxidizing capacity of the atmosphere. For example, if the organic nitrate reported by Kotzias and co-workers is formed at night, it will be transported along the wind trajectory and following sunrise will likely photodecompose, resulting in the return of NO_x to the air mass.

In summary, our present understanding of biogenic hydrocarbon chemistry in the atmosphere is limited. Oxidation rates with OH , O_3 and NO_3 are established, but the actual degradation pathways and ultimate product yields are poorly understood. Ozone formation from biogenic hydrocarbons is a non-linear process which depends on hydrocarbon structure, HC/NO_x ratio, sunlight intensity, plus other physical parameters. The reaction of ozone with biogenic hydrocarbons obviously destroys ozone; however, stable intermediate products that are formed may react with hydroxyl radical to generate ozone. Thus, the net effect on ozone levels will depend on a multitude of variables. Like the production of ozone, aerosol generation resulting from biogenic hydrocarbon oxidation is difficult to quantify. It does appear that a larger fraction of the oxidized hydrocarbon will be transformed to aerosol in atmospheres deficient in NO_x . Photochemical oxidant models predict enhancements in atmospheric carbon monoxide, organic acids and organic nitrates when biogenic hydrocarbons are oxidized. Recent field and laboratory studies seem to confirm the presence of elevated concentrations of these species in forested environments. However, much more work will be required to quantify the link between biogenic hydrocarbons and their oxygenated products.

2.5 SUMMARY SORP-EE BIOGENIC EMISSIONS WORKSHOP RALEIGH, NC OCTOBER 24 AND 25, 1991

Approximately 40 scientists attended this two day workshop. The first day consisted of invited presentations on topics relevant to the biogenic emissions issue. Considerable discussion accompanied each of the presentations. Near the end of day 1, several working groups were formed to review specific issues and make recommendations concerning future research needs. The working groups addressed topics that included emission factors, atmospheric chemistry, flux studies and mechanisms of biogenic emissions. Most of the discussion addressed VOC emissions; however, NO_x emissions from soils were considered as well.

Among the biogenic VOC's, isoprene was judged to be by far the most important precursor of ozone in the eastern United States. In order to quantify its contribution to oxidant formation, a better understanding in each of the following areas will be required:

1) Emission Mechanism -- The ultimate goal of mechanistic studies should be linking isoprene emissions to photosynthesis. This should consist of laboratory studies designed to establish the linkage between the physiology of isoprene production and its release by vegetation. The

affects attributable to environmental factors (i.e. of water stress, nutrient influences, temperature effects, etc.) should be clearly defined in laboratory studies as well. Laboratory results must then be confirmed through field experiments.

2) Emission factors -- Field measurements should be concentrated on vegetation types that emit the highest levels of isoprene, monoterpenes and oxygenated VOC's. When enclosure chambers are employed, they should be rigid structures with humidity, temperature and CO₂ controlled at levels equivalent to ambient conditions. Whole air-GC/FID methods are recommended for hydrocarbon collection and analysis. The use of solid adsorbents may be required for collection and recovery of oxygenated hydrocarbons.

3) Flux Estimates -- Direct methods for determination of regional biogenic fluxes are needed. This will require vertical profiling above the forest canopy. One or more blimp-type sampling platforms were suggested for this airborne sampling. It was pointed out that the influence of the forest canopy on emission fluxes needs to be better defined. The canopy is known to influence ambient temperature and sunlight intensity, both of which strongly affect isoprene emissions.

4) Atmospheric chemistry -- Isoprene chemistry is fairly well understood. Its reactivity toward atmospheric oxidants and the formation of oxygenated products have received considerable attention recently. At this time, the biggest uncertainties are concerned with the ultimate fate of the oxygenated products produced in the initial oxidation stage. As the initial oxygenated products, such as methacrolein and methylvinyl ketone, undergo further oxidation, even more highly oxygenated species are formed (e.g. methylglyoxyl, hydroxyacetaldehyde, hydroxyacetone, etc.). How much of these polar intermediate species are removed by wet and dry depositional processes and what fraction gets further oxidized to CO and CO₂ is uncertain. Not much aerosol production is expected from isoprene.

Monoterpene chemistry in the atmosphere is very poorly understood. Analytical methods are needed that can provide information about gaseous and aerosol products produced in monoterpene oxidation reactions.

The initial NO_x emissions studies, carried out by TVA in the southeast, indicate that biogenic NO_x emissions may be quite significant. Their studies show that emissions from forest soils are relatively low, but NO_x emissions from cultivated soils can be large. Additional studies will be required to better define the magnitude and variability of biogenic NO_x emissions in agricultural areas.

Future research needs identified at the workshop are summarized below:

- ◆ Improved emission factors -- Quantification of inter- and intra-species variability; influence of environmental stress factors on emissions.
- ◆ Improvements in current land-use data bases.
- ◆ Assessment of the accuracy of current flux estimates by utilizing a variety of measurement methods.

- ◆ Laboratory studies designed to understand the link between isoprene emissions and plant physiology.

3.0 RESEARCH NEEDS AND PLANNING

3.1 INTRODUCTION

The emission and fate of biogenic hydrocarbons remain uncertain terms in our understanding of the formation of ozone within and downwind of urban areas. In order to develop effective control strategies to reduce ozone pollution, additional research is needed to determine the importance of naturally emitted hydrocarbons relative to anthropogenic emissions. In this chapter, a research plan is outlined to address the uncertainties which remain in the following areas:

- Emission rate measurements
- Emission rate mechanisms and models
- Emission inventories
- Ambient concentration measurements
- Chemical oxidation mechanisms and models

In this chapter, the uncertainties in each of these areas are listed and steps are suggested for reducing these uncertainties. This research plan is based upon the literature review completed previously. However, it must be recognized that several large programs are currently underway which incorporate efforts to measure and model biogenic emissions and chemistry. Studies related to the San Joaquin Valley Air Quality Study, to the Lake Michigan Oxidant Study, to the Southeast Oxidant Study, to the NOAA Rural Oxidants in a Southeast Environment program, and to recent EPA sponsored biogenic emissions research are all in progress. These programs include varying aspects of the research plan described. Consequently, the research plan outlined in this report will need to be revised as results become available from these different programs.

3.2 UNCERTAINTIES AND RESEARCH PRIORITIES

The overall goal of biogenic hydrocarbon research is to determine quantitatively the production of ozone due to biogenic emissions under realistic scenarios and, in turn, determine the implications of biogenic hydrocarbon burdens with respect to ozone control strategies. To accomplish this goal, the ambient concentrations of biogenic hydrocarbons, the identity of these gases, and the chemical oxidation mechanisms of these species must be known. To address the first two requirements, detailed ambient measurements must be made and/or detailed emission inventories must be compiled for use in air quality models. To address the third requirement, a combination of smog chamber studies and ambient measurements of reactants and products related to hydrocarbon photochemistry must be conducted.

2. Rank these vegetation types according to region, land area, and, probably, by some measure of regional ozone potential. Identify vegetation types where accurate and complete emission rate data are already available and those where no or little information exists.
3. Conduct regional emission rate surveys of the dominant vegetation types with an emphasis upon accurate emission rate measurements, identification of all of the emitted compounds, and collection of peripheral vegetation and environmental data. These supporting data should include leaf temperature, photosynthetically active radiation (PAR), humidity, leaf area, leaf biomass, some measure of water stress, an indication of plant health or injury, photosynthesis rate, transpiration rate, and some measure of leaf biochemical levels (storage of terpenes or isoprene precursors, for example). Descriptions of the ecosystem should also be included in terms of the general vegetation types, elevation, soil type, etc. The sampling survey should include some diurnal pattern measurements of the most important species and it should include re-visiting some locations at different times of the year to identify seasonal effects.
4. Correlate measured emission rates with respect to measured environmental data within and across regions and examine the data for diurnal and season effects. Compile the emission rate and peripheral data for the purpose of testing emission rate models as indicated in the next section.

These data will form a national data base of emission rate measurements in a consistent format with sufficient supporting information to make the data very valuable for developing and testing emission rate models.

3.4 EMISSION MECHANISMS & MODELING

Current emission rate algorithms remain almost purely empirical in nature and do not reflect any fundamental understanding of the biochemical processes responsible for isoprene and terpene emissions. Continued fundamental research aimed at addressing the biochemistry of the leaf (needle) is required. At the same time, additional laboratory studies of emission rate versus different environmental variables for a wide range of dominant U.S. vegetation and crops should be conducted. Both of these types of efforts will complement the field measurements by providing emission rate data under controlled conditions which can be compared to field measurements. The following tasks should be addressed:

1. Laboratory studies of isoprene formation and release in leaves of dominant deciduous and spruce (isoprene emitting) needles. It has been observed that isoprene continues to be emitted even when photosynthesis stops so that identification of isoprene precursors should be achieved.
2. Laboratory studies of terpene volatilization from dominant conifer species and those deciduous species which release terpenes. Terpene storage levels in needles should be

sets and, more recently, from remotely sensed data are then used to extrapolate the predicted fluxes to county or gridded spatial scales. These county or gridded emission rates are then used in regional air quality models to predict grid average ambient biogenic hydrocarbon concentrations and, in turn, ozone formation for specific scenarios. This general approach is now being enhanced by incorporating satellite data as a basis for specifying vegetation coverage/land use, leaf area or biomass density, surface temperatures, and available solar radiation. The use of remotely sensed data will allow for continued adjustments to current vegetation coverage and for describing vegetation and environmental conditions for specific time periods. Further work is required to determine the accuracy of existing inventory systems and, with a slightly longer time frame, to develop a complete inventory system based upon remotely sensed data and validated against ground-truth surveys and measurements. The following tasks are required:

1. Evaluate the accuracy of current land use data and compile updated land use and vegetation coverage data using a combination of current vegetation data bases and remotely sensed data.
2. Evaluate the accuracy of current biomass density or leaf area index data using literature biomass density studies and remotely sensed data, and develop improved biomass density or leaf area factors.
3. Develop algorithms for deriving vegetation coverage, vegetation type, leaf area, surface temperature, and solar radiation from remotely sensed data and ground-truth measurements.
4. Combine emission mechanism and canopy models with the satellite algorithms to develop a complete emission inventory system.
5. Validate existing and new emission inventory systems using ambient hydrocarbon concentration measurements. This will require use of a diffusion or air quality model (which must also be evaluated). It should be possible to obtain validation data for specific locations and conditions from areal flux measurements based upon vertical profile measurements and/or atmospheric tracer flux studies.

This last task and the field studies required are the most critical elements required to achieve the overall goal of predicting biogenic hydrocarbon emissions and concentrations with a specified level of uncertainty. Direct evaluation of the inventory procedure must be accomplished in order to have confidence in the use of the inventory and ultimately in ozone control strategies.

3.6 AMBIENT MEASUREMENTS

The atmospheric concentrations of biogenic hydrocarbons must be known in order to predict ozone formation rates in rural areas. In addition, ambient concentration measurements are needed for the direct validation of emission inventory models and also for chemical

oxidation models. In the latter case, measurements must include both primary emissions and secondary reaction products associated with biogenic hydrocarbons. Ambient concentration measurements also provide a basis for comparison between biogenic and anthropogenic hydrocarbon burdens in areas within and downwind of urban areas, and on a regional basis. Measurement of carbon isotope ratios may provide another method of evaluating the relative importance of anthropogenic and biogenic organic species. These types of ambient measurements are required in each region of the country and the measurements should be coordinated with other regional air quality studies. This coordination will provide the type of detailed data required for validating emission inventory models (both biogenic and anthropogenic) and chemical oxidation models, as well as general air quality models.

In order to obtain these measurements, further work is required to develop analytical methods capable of measuring both reactants and products (both gas phase oxygenated species and aerosols) at low ambient levels with small time resolution. This work should be coordinated with modeling and smog chamber studies so that products predicted to occur can be measured in the atmosphere. The following tasks are required:

1. Develop analytical methods to measure oxygenated emissions and photochemical products.
2. Develop and test methods to measure carbon isotope signatures specific to biogenic hydrocarbons at ambient levels.
3. Conduct routine and specialized measurements of biogenic and anthropogenic hydrocarbon concentrations in different regions of the country during different seasons as a basis for evaluating emission inventory and chemical oxidation models. Measurements are needed in southern pine and deciduous forests, in northeast deciduous forests, in midwest agricultural regions, and in northwest conifer forests. These measurements should include isoprene, identifiable terpenes, oxygenated emitted species, and oxygenated photochemical products. The latter may be included only in specialized photochemical studies. Carbon isotope studies should be included where possible.
4. Compile the results from these regional monitoring studies and examine the data in terms of diurnal and seasonal patterns within and across regions and ecosystem types. Develop relative atmospheric burdens between biogenic and anthropogenic hydrocarbons. Examine chemical oxidation products for patterns consistent with the primary biogenic and anthropogenic hydrocarbon concentrations.

This survey of ambient hydrocarbon concentrations is an essential part of the validation of emission inventory and chemical oxidation models. Coordination of these ambient measurements with other emission field study efforts will enhance the overall impact of these measurements.

3.7 CHEMICAL MECHANISMS & MODELING

A great deal of uncertainty remains in the chemical mechanisms by which natural hydrocarbons are oxidized in the atmosphere. Recently, some progress has been made in the understanding of isoprene oxidation; however, the chemical fate of monoterpenes in the atmosphere is still poorly defined.

3.7.1 Atmospheric Isoprene Oxidation

Isoprene is initially oxidized by hydroxyl radical and/or ozone to formaldehyde, methacrolein and methylvinylketone (see Fig. 3.1). The ratio of these three carbonyls will vary somewhat depending on which of the oxidants is dominant, but for the most part, the kinetics and mechanism of this first step in the oxidation of isoprene is understood. The presence of formaldehyde, methacrolein and methylvinylketone in the ambient atmosphere has been confirmed in forested regions with deciduous vegetation (Martin et al., 1991; Pierotti et al., 1990). The pathways by which these first-stage carbonyls undergo further oxidation are not as well defined. The kinetics of methacrolein and methylvinylketone reactions with hydroxyl and ozone have been characterized, but the product distribution under atmospheric conditions is not well understood. Laboratory studies have suggested that species such as hydroxyacetone, methylglyoxyl, hydroxyacetaldehyde, peroxyethacryl nitrate (MPAN) and methacrylic acid should be present in forested environments.

The product distribution is expected to be dependant on ambient NO_x levels. At higher NO_x concentrations (ppb range) NO will be converted to NO_2 via reaction with organoperoxy radicals. This process contributes to a build up of ozone and is expected to lead to the hydroxycarbonyl and nitrate products mentioned earlier. At relatively low NO_x levels (ppt range) radical-radical reactions will become competitive and the peroxy radical derivative of methacrolein and methylvinylketone may yield organic acids and organic hydroperoxides.

Ambient measurement campaigns have confirmed the presence of MPAN, and it is expected that measurement techniques can be developed for determination of the other oxidation products of methacrolein and methylvinylketone. Hydroxyacetone has a relatively long atmospheric lifetime (~5 days) and should serve as an indicator of isoprene oxidation. As indicated in Figure 3.1, Stage II oxidation products (i.e. methylglyoxyl, hydroxyacetaldehyde, etc.) can react further to produce more highly oxidized species such as pyruvic acid. Gaseous pyruvic acid has been measured in rural environments at concentrations that are compatible with proposed isoprene oxidation mechanisms.

Recent smog chamber studies at Caltech and UC-Riverside have helped to elucidate the primary atmospheric oxidation pathways of isoprene. If the smog chamber results adequately represent the ambient atmosphere, isoprene will react mainly with hydroxyl radical during the midday period to give formaldehyde, methylvinylketone (36%), methacrolein (25%), other carbonyls (21%), alkylnitrates (14%), and 3-methylfuran (4%). A smaller fraction of the isoprene will react with ozone yielding similar products--methylvinylketone (26%),

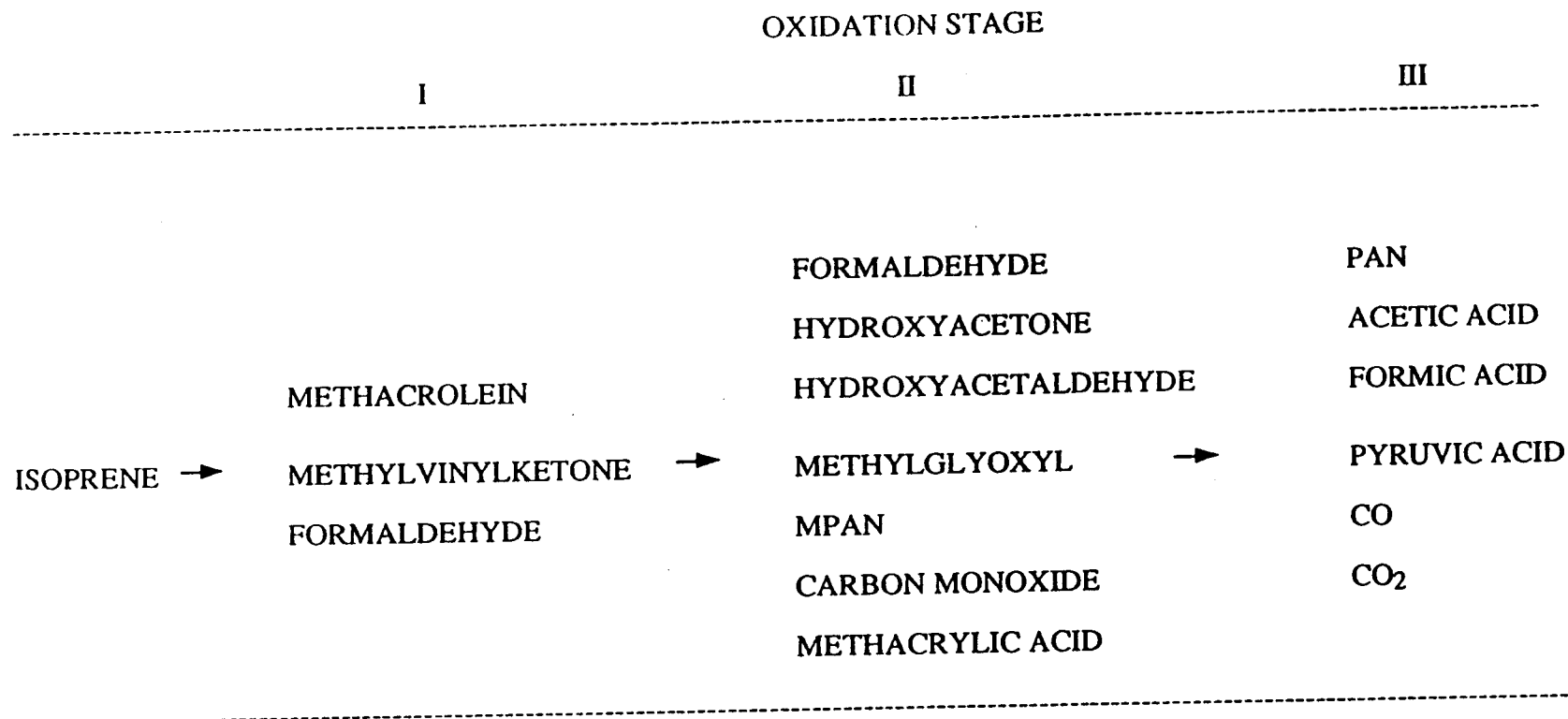


Figure 3.1. Isoprene Oxidation Products

methacrolein (67%) and formaldehyde. A small amount of the reacted isoprene probably ends up in the aerosol phase. The exact amount is rather uncertain, but probably is less than one percent.

Paulson and Seinfeld (1992) have developed a mechanism that appears to accurately predict product concentrations when OH is the primary oxidant and NO_x levels are relatively high. Under low NO_x conditions, the Paulson and Seinfeld mechanism underpredicts organic product and ozone yields.

Several uncertainties remain concerning the atmospheric oxidation of isoprene. The main issues can be summarized as follows:

1. The atmospheric fate of the 2-propenyl radical produced when methacrolein reacts with hydroxyl radical is unclear. This is especially true under conditions of low NO_x . This intermediate radical species can dissociate through a pathway that produces methylglyoxyl or one that yields formaldehyde. The amount of CO that is ultimately produced in the isoprene photooxidation may also depend on the fate of the 2-propenyl radical. Laboratory studies are needed that can produce this radical independent of the usual isoprene oxidation mix in order to examine its fate under various simulated atmospheric conditions.
2. The isoprene reaction has been shown to produce significant quantities of hydroxyl radical and oxygen atoms (O^3P). The mechanism by which these species are formed is not understood. One pathway that has been suggested involves the reaction between the Criegee-type radicals produced in the ozone-isoprene reaction and water (Rxn. 1).



Earlier studies had assumed that the reaction between the Criegee biradical and water would produce an organic acid, which in the case of Reaction 1 would be methacrylic acid. Laboratory studies that will define the fate of the Criegee radicals under atmospheric conditions are clearly needed.

3. Measurements in forested environments have shown a strong correlation between the ambient concentrations of low molecular weight organic acids (e.g. formic and acetic) and isoprene. Studies are needed that will confirm whether or not the photooxidation of isoprene is a source of these acids.
4. The amount of CO that results from the atmospheric oxidation of isoprene is not well defined. Most mechanisms proposed to date predict between 3 and 4 molecules of CO are ultimately produced for each isoprene oxidized. Whether or not the portion of this CO that results from continued oxidation of multi-oxygenated intermediates such as hydroxyl carbonyls makes it to CO in the atmosphere will be difficult to establish. These highly polar compounds may well be removed by atmospheric depositional processes before they are oxidized to CO.

5. The mechanistic pathway by which isoprene is oxidized when it reacts with nitrate radical is poorly understood. The isoprene- NO_3 reaction is fast; however, it may not serve as a major atmospheric sink for isoprene. NO_3 is a nighttime species, and isoprene is present primarily in the daytime. Consequently, the only time they may coexist at appreciable concentrations would be following sundown in the early evening hours. There are insufficient ambient measurements of NO_3 in forested regions to judge whether or not it serves to remove isoprene from the atmosphere. Simultaneous measurements of isoprene and NO_3 , as well as a knowledge of the products formed when these species react, is needed.

3.7.2 Atmospheric Monoterpene Oxidation

The monoterpenes react with atmospheric oxidants in a manner similar to that described for isoprene. Reaction with hydroxyl radical and ozone produces intermediate carbonyl species that can react further to give more highly oxidized organics as well as CO and CO_2 . In general, defining the pathways by which monoterpenes degrade in the atmosphere is much more difficult than for isoprene. With the 10-carbon monoterpenes, acyclic, monocyclic, bicyclic and tricyclic structures exist. In many cases, first-stage oxidation products of the monoterpenes contain more than one oxygenated functional group. These species are polar, relatively high molecular weight (C_8 - C_9) compounds that are difficult to isolate and identify by conventional means. Consequently, little definitive information exists concerning oxidation pathways for monoterpenes. Aerosol production during monoterpene oxidation is enhanced over that encountered with isoprene because of the lower volatility of the oxygenated intermediates. Thus, for each monoterpene, it is necessary to determine what the branching ratio is between gaseous and aerosol products.

Alpha and beta-pinene are the dominant monoterpenes emitted into the atmosphere, with lesser amounts of limonene and several other C_{10} terpenes reported in emission studies. Laboratory smog chamber studies have confirmed the highly reactive nature of these monoterpenes toward atmospheric oxidants. In smog chambers, the monoterpenes produce ozone and aerosols when photooxidized in the presence of NO_x . As with isoprene, the dominant daytime oxidation pathways for monoterpenes are closely coupled--the monoterpene-OH reaction produces ozone; and the monoterpene-ozone reaction yields radicals including OH. This adds to the difficulty of defining discrete degradation pathways for the monoterpenes.

Alpha-pinene oxidation has been studied in smog chambers for many years. Alpha-pinene reactivity and ozone production have been defined, but the oxidation pathway remains illusive. Intermediate products of alpha-pinene photooxidation are difficult to isolate, which results in very poor carbon balances in smog chamber experiments. Without a knowledge of oxidation products, it is difficult to assign oxidation mechanisms with any degree of certainty. New analytical techniques must be developed that will allow identification of oxygenated intermediates before much progress can be made at understanding the mechanism of alpha-pinene photooxidation.

Beta-pinene is not quite as complicated as alpha-pinene because the main point of attack consists of an exo olefinic bond, which when oxidized yields mono-oxygenated products (nopinone and formaldehyde). Nopinone can be detected using a gas chromatographic procedure and, indeed, has been shown to be present in smog chamber photooxidations involving beta-pinene. It has also been reported in ambient forested environments. Nopinone is relatively inert toward ozone but certainly reacts with hydroxyl radical. Products from the nopinone-OH reaction have not been characterized and will undoubtedly be polar, oxygenated species that are difficult to isolate and identify with certainty. Thus, a complete description of the beta-pinene photooxidation pathway cannot be confirmed until better product information becomes available. Beta-pinene, like alpha-pinene, produces aerosol during the photooxidation process. Recent reports have estimated that a significant fraction of the reacted beta-pinene ends up in the aerosol phase (Pandis et al., 1991). Once again, this complicates an understanding of the overall beta-pinene oxidation mechanism.