CURRENT STATUS AND RESEARCH NEEDS RELATED TO BIOGENIC HYDROCARBONS

HEALTH AND ENVIRONMENTAL AFFAIRS API PUBLICATION NUMBER 309 JUNE 1992

> American Petroleum Institute 1220 L Street, Northwest Washington, D.C. 20005

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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 agriculatural 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 satellelite 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 exists 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; Arnts 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 alphapinene, beta-pinene, limonene, camphene, sabinene, myrcene, and $\Delta 3$ -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.

Compound	Plant species#	Compound	Plant species#
Propylene Butylene Isoprene Hydrocarbon C ₅ H ₁₀ 2-Methylbutane	8,9 1-12,15,16 (1-4)**,5-17 1,2,5-9,13-15 1-8 12	Chloroform Dimethyl sulphide Santene Cyclofenchene Bornilene	16 15 8,11 8-10,15 8-17
2,3-Deimethyl butadiene	8,13,14	Tricyclene α-Thujene	7,8*,9-10 9,10,13-17
Hydrocarbon C ₈ H ₁₂ Hydrocarbon C ₉ H ₁₀ Methanol	8,9 1,6,11,16 15	α-Pinene δ-Fenchene	(9,10,13,15,17)**,16 9,10,12
Ethanol 3-Hexene-l-ol	3-5,10,12-15	ε-Fenchene	9,12 7-17
Propanal	6	β-Fenchene	7-10,12
Isobutanal Crotonal Isobutenal Acetone	16 17 1-4,9,7 1-17	Camphene Sabinene B-Pinene	3,(7,9,10,12)*,*(8,11)** 13-17 12,13,15,17,(14,16)* 3,7-11,15
Butanone-2 Methyl vinyl ketone Pentanone-2	8,13-15 2,4 6,8,15	Myrcene 3-Carene α-Phellandrene	7-13,14*,15-17 7*,8-10,12-15,16*,17 3,8-11
Pentanone-3	5,7-10,15,16	β -Phellandrene	8-11,14
Furan 2-Methyl furan	6 1-5.12.13	α -Terpinene	8-10,17 3,8-10,13-15
3-Methyl furan	1-5,12,13	γ-Terpinene	9,13-15,17
Ethyl furan Vinyl furan Ethyl acetate 3-Hexene-l-ol acetate	1,2,4,8 1,2,4,8 9 1,4-8	Limonene Terpinolene 1,8-Cineol Fenchone	3,7-17 9-17 3,8,14 16*
Methyl (α-methyl) butyrate	14**	Thujone Camphor	16** 8
Methyl (α-methyl) capronolate Methyl chioride	14 14-16	p-Cymene Menthane	7-17 14

Ta	ał	ol	e 1	.1	. C	Organics in	V	olatile	Emissions	of	Ar	borec	ous l	Pl	ant	S
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#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).

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Source: Isidorv et al. (1985)

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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 studued. 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 µg/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
Abies fraseri (Fraser fir)	•	+ [.]			Rasmussen, 1972	•
Acer rubrum (red maple)	0.0 0.0 0	3.5 2.4 2.1	· A A A	9 9 1	Zimmermann, 1979 Zimmermann, 1979 Lamb et al., 1984	day, a night, b day, 24.4 ⁰ 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)	• •					
Carya aquatica (water hickory)	•	-0.4 -0.3	A A	4 4	Zimmermann, 1979 Zimmermann, 1979	day, a night, b
Carya cordiformis (swamp hickory)	0.0 0.0	-0.4 -0.2	A A	4 4	Zimmermann, 1979 Zimmermann, 1979	day, a night, b
Carya glabra (pignut hickory)	0	3.6	A	2	Lamb et al., 1984	day, 25.0 ⁰ C, c
Carya illinoensis (pecan)		۲ پ				
Carya ovata (shagbark hickory)						
Carya tormentosa (mockernut hickory)						
Cercis canadensis (eastern redbud)	+	•		3	Evans et al., 1982	
Comus florida (flowering dogwood)	0	7.8	A	1	Lamb et al., 1984	day, 27.3 ⁰ C, c
<i>Diospyros virginiana</i> (common persimmon)	0.0 0.0	0.0 0.0	A A	17 ⁻ 17	Zimmermann, 1979 Zimmermann, 1979	day, a night, b

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		Table	1.2 (Cor	ntinuec	l) .	· ·
Fagus grandifolia (American beech)	0	2.3	А	1	Lamb et al., 1984	day, 23.3 ⁰ C. .
Frazinus americana (american ash)			, .			
<i>Frazinus caroliniana</i> (Carolina ash)	0.0 0.0	0.0 0.0	A A	1 1	Zimmermann, 1979 Zimmermann, 1979	day, a night, b
Frazinus pennsylvanica (green ash)						
Ilex cassine (dahoon holly)	0.0 0.0	.0.0 0.0	A A	3 3	Zimmermann, 1979 Zimmermann, 1979	day, a night, b
<i>llex coriacea</i> (sweet gallberry)						
<i>Juniperus silicicola</i> (southern redcedar)						
Juniperus virginiana (eastern redcedar)						
Liquidambar styraciflua (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 ⁰ C
<i>Liriodendron tulipifera</i> (tulip popla r)	0	2.7	A	2	Lamb et al., 1984	day, 23.9 ⁰ C, c
Magnolia grandiflora (southern magnolia)						
<i>Magnolia virginiana</i> (sweetbay)						
Myrica cerifera (wax myrtle)	0 Q	· 6.3 4.4	A A	9 9	Zim ann, 1979. Zimiann, 1979	day night
Nyssa aquatica (water tupelo)						
Nyssa sylvatica (blackgum)	Ö	5.8	`A ^{``}	<u>1</u> -	Lamb et al., 1984	day, <u>2</u> 8.9 ⁰ C, c
Oxydendrum arboreum (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
Picea rubens (red spruce)	+.	+			Rasmussen, 1972	

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Table 1.2 (Continued)

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

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Table 1.2 (Continued)

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

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	8					
(sassafras)						
<i>Taxodium distichum</i> (baldcypress)	•	8.5 5.9	A A	20 20	Zimmermann, 1979 Zimmermann, 1979	day, a night, b
Taxodium distichum var. nutans (pondcypress)						
<i>Tsuga canadensis</i> (eastern hemlock)	0	1.3	A	2 ·	Lamb et al., 1984	day, 19.4 ⁰ C
Ulmus americana (American elm)	0.0 0.0	0.0 0.0	A A	1 1	Zimmermann, 1979 Zimmermann, 1979	day, a night, b

<u>Units</u>: A = g (g dry weight) ^{-1}h $^{-1}$; B = ppb min $^{-1}$ (g fresh weight) $^{-1}$ liter $^{-1}$; C = μ g m $^{-2}$ h $^{-1}$

<u>Comments</u>: a, corrected to 30^oC; b, corrected to 25^oC; 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 the 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, $\Delta 3$ -carene, limonene, tricyclene, and 1,8-cineole. The emission rates of alphapinene 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 $uE/m^2/s$, 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 (8-pinene, sabinene, myrcene, limonene, and 8-phellandrene), leaf alcohols and aldehydes (cis-1-hex-3en-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 CO_2 or O_2 ; 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 CO_2 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 CO_2 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 CO_2 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, CO_2 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 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 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 $CO(9\pm1\%)$, $CO_2(30\pm2\%)$, $HCHO(22\pm1\%)$, and the aldehydes(51\%): pinonaldehyde and nor-pinonaldehyde. The reaction products of betapinene with ozone were $CO_2(27\pm2\%)$, $HCHO(76\pm2\%)$, and 6,6dimethylbicyclo[3.1.1]heptan-2-one($40\pm2\%$). Aerosol yields in these reactions were relatively constant over the terpene concentration range 10 to 100 ppb at $18.3\pm1.1\%$ and $13.8\pm0.8\%$ 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 ($56\pm4\%$) and the major products for beta-pinene in the presence of NO were 6,6-dimethylbicyclo[3.1.1]heptan-2-one($79\pm8\%$) and HCHO ($54\pm5\%$). 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 SO_2/NO_2 and beta-pinene in the presence of SO_2 alone. In the latter case, oxidation rates of SO_2 were in the range 6 to 15% after four hours, and greater oxidation of SO_2 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 SO_2 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), eucalytptus 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 that 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 dominate 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 NOx 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 NOx, ozone was depleted, while emissions into an air mass with high NOx 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.

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 stateof-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

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.

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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).

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

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

* 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 oC 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 \circ 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 uE/m²/s light intensities. In the WSU inventory the curve for 400 uE/m²/s is used as the basis for normalization of the emission rate data, while in PC-BEIS the 800 uE/m²/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 uE/m²/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 uE/m²/s curve. Normalizing the raw emission rate data using either the 400 or 800 uE/m²/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 uE/m²/s light intensity. Assuming that the emission rate factors corresponded to conditions with 800 uE/m²/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 for 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 oC 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.

Chueng 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 CO_2 . Close control to maintain specific levels of moisture or CO_2 is not used. Guenther et al (1991) found weak dependence of isoprene emissions upon humidity and CO_2 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 fives 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/NOx 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 occuring 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 NOy 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 O₃, CO, NOy 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 SO₂, NO₂ and O₃. 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 H₂O and NO₂. Examination of the reaction kinetics and inorganic product yields appears to confirm that 1) NO₃ is a more reactive oxidant than O₃ and 2) water scavenges the initial O₃-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 SO₂ 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 SO₂-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, O₃ and NO₃ 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, NOx 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) <u>Emission Mechanism</u> -- 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) <u>Emission factors</u> -- 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 adsorbants may be required for collection and recovery of oxygenated hydrocarbons.

3) <u>Flux Estimates</u> -- 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) <u>Atmospheric chemistry</u> -- 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 workship 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.

Before the research tasks can be prioritized for the most efficient use of available resources, the accuracy of ambient measurements, emission inventories, and chemical oxidation models needed to achieve the overall research goal must be specified. For example, in an emission inventory, will uncertainties as large as a factor of two or three be acceptable in determining the relative role of biogenic versus anthropogenic hydrocarbon emissions in ozone control scenarios? If this level of uncertainty is unacceptable, then what type of measurements and how many measurements are required to reduce the uncertainty? What target accuracy in the emission inventory is required to achieve the research goal? In order to reach this level of accuracy in an emission inventory, how accurate must emission rate measurements, land use areas, climatological data, and other inventory variables be? What is the current level of accuracy in each of these variables and what is required to improve the accuracy? These

An integral part of addressing the target accuracy and existing uncertainties in each aspect of the analysis is to evaluate measurement and model uncertainties. The measurement strategies developed for this work should include the use of independent methods to obtain data for intercomparison of results and the approach should also include measurements needed to evaluate model performance. This is true for testing emission models at various scales (leaf, canopy, landscape, or regional scales) and for testing chemical oxidation models.

questions need to be answered at each stage in the research before the research steps outlined

3.3 EMISSION MEASUREMENTS

in this document can be prioritized and implemented.

There is a general lack of detailed hydrocarbon emission rate data for the dominant ecosystems in the U.S. In particular, there is a lack of diurnal and seasonal emission rate measurements and there is a need for supporting measurements of vegetation and environmental parameters coupled to emission rate data sets. There is a critical need to identify all of the compounds (including oxygenated species) emitted from the dominant vegetation so that the chemical reactivity of biogenic hydrocarbons can be correctly assigned. The lack of emission rate data from primary U.S. agricultural crops must also be addressed. These types of measurements are needed in order to develop more accurate emission inventory models which address a range of vegetation types and a range of environmental conditions. Finally, the accuracy of all of these types of measurements must be determined so that the corresponding uncertainty in models developed from these types of measurements can be defined. This need implies that a strong quality assurance program must be employed for all vegetation enclosure measurements and that to the extent possible, results from enclosure sampling should be verified using other independent methods.

The specific tasks recommended in this area include the following:

1. Compile a list of the dominant vegetation in each region of the U.S. including natural and agricultural species, and classify these vegetation types by ecosystem type and total land area or biomass.

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.

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- 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, additonal 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

correlated with emissions and the effects of changes in environmental conditions upon volatilization should be measured.

- 3. Laboratory identification of other compounds besides isoprene and terpenes released from dominant vegetation and crops and relative emission rates during different conditions or from different aged species.
- 4. Further measurements of leaf-to-leaf, branch-to-branch, tree-to-tree variablity in emission rate as a means of assigning achievable uncertainty limits to laboratory and field measurements.
- 5. Analysis of these data to develop appropriate models of emission mechanisms which reflect fundamental leaf activity. These models should be tested versus laboratory data and versus field data collected from the national survey. The model development efforts and field survey work must be closely coordinated so that the correct model parameters are measured in all of the field survey studies.

These laboratory studies are aimed at hydrocarbon emission mechanisms and do not address the fact that the environment surrounding a leaf must be described with an accuracy which matches that in the emission mechanism models. Recent results have shown that including canopy effects upon leaf temperature and PAR have a significant impact upon predicted isoprene emissions. An additional task to improve canopy and landscape models must be included as follows:

6. Perform forest canopy measurements to evaluate canopy leaf temperature and solar radiation models and to evaluate the combined emission mechanism and canopy model. These model evaluation studies should be completed in dominant deciduous and coniferous forest types. The measurements should include emission rate and ambient concentration measurements as a function of height through the canopy as well as other canopy variables including photosynthesis, transpiration, leaf temperature, solar radiation (PAR), humidity, wind speed, and leaf area or biomass. It should be noted that this type of experiment is being planned under EPA sponsorship for a deciduous southeast forest during 1992.

The laboratory and canopy studies combined with the national survey will provide an extensive base for the development and testing of emission mechanism and canopy models. Inherent in this development and testing of models will be the determination of the uncertainty in emission rate predictions at the leaf scale and at the canopy scale.

3.5 EMISSION INVENTORIES

Current emission inventories for biogenic hydrocarbons employ emission rate algorithms with biomass density factors to predict emission fluxes for either specific meteorological conditions or for climatological average conditions. In some cases these fluxes include canopy effects. Vegetation coverage and land use data derived from historical data

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 satelletite 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, peroxymethacryl 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, hydroxacetaldehyde, 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%),

			ISOPRENE -					
		FORMALDEHYDE	METHYLVINYLKETONE	METHACROLEIN			Ι	
			¥				1 	-
METHACRYLIC ACID	CARBON MONOXIDE	MPAN	METHYLGLYOXYL	HYDROXYACETALDEHY	HYDROXYACETONE	FORMALDEHYDE	IJ	DXIDATION STAGE
			¥	(DE				
	CO_2	CO	PYRUVIC ACID	FORMIC ACID	ACETIC ACID	PAN	III	ı

Not for Resale

Figure 3.1. Isoprene Oxidation Products

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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 that 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 (O3P). 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).

 $CH_2 = C(CH_3) - CH - O - O + H_2O \gg CH_2 = C(CH_3) - CHO + 2OH$ (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-NO₃ reaction is fast; however, it may not serve as a major atmospheric sink for isoprene. NO₃ 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 NO₃ in forested regions to judge whether or not it serves to remove isoprene from the atmosphere. Simultaneous measurements of isoprene and NO₃, 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 CO₂. 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 (Cg - C9) 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. Alphapinene 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 alphapinene 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.

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Alphabetical by author.

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AN CA101(15):126902t ΤI Application of atmospheric tracer techniques for determining biogenic hydrocarbon fluxes from an oak forest AU Allwine, G.; Lamb, B.; Westberg, H. Coll. Eng., Washington State Univ. CS LO Pullman, WA, USA Report, EPA-600/D-84-082; Order No. PB84-168624, 35 pp. Avail. NTIS SO From: Gov. Rep. Announce. Index (U. S.) 1984, 84(11), 12 11-1 (Plant Biochemistry) SC SX 9 DT T PY 1984 LA Eng AB The results of an SF6 tracer release procedure to quant. det. the isoprene emission flux for an isolated oak forest in Goldendale, Washington, are presented. The paper presents exptl. design development to effectively deploy tracer release sites within the forested area to simulate the natural vegetation release. The downwind sample collection program was designed to evaluate several math. approaches to calc. isoprene emission flux. The results presented indicate good comparability between the math. models and a bag enclosure technique which was also used for isoprene emission flux measurement.

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AN INITIAL GLOBAL INVENTORY OF BIOGENIC VOC

EMISSIONS FROM TERRESTRIAL SOURCES

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Submitted to Journal of Global Biogeochemical Cycles

March 14, 1991

Abstract

The elements needed to construct a global emission inventory of hydrocarbons released from vegetation are available in the form of gridded climatic temperatures, gridded land use classifications, a range of biomass density data from various literature sources, emission rate factors for some broad classes of vegetation, and emission rate algorithms for the same broad classes of vegetation. In this work, we are developing procedures for calculating a gridded. monthly emission inventory of biogenic isoprene and terpenes for global terrestrial sources.

In the initial inventory estimates, the global total emissions of isoprene are estimated to be more than 400 Tg/yr. Global emissions of alpha-pinene are estimated to be 38 Tg/yr and emissions of other identified mono-terpenes are estimated to equal 89 Tg/yr. Other organic emissions are estimated to be 279 Tg/yr. The total emissions of biogenic hydrocarbons are comparable to previous estimates which do not account for the gridded differences treated in the present work. Approximately 75% of the emissions are predicted to occur in the tropics; the need for better emission estimates in tropical forests is clearly important.



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AN CA109(4):26891k TI Enhanced biogenic emissions of nitric oxide and nitrous oxide following surface biomass burning AU Anderson, Iris C.; Levine, Joel S.; Poth, Mark A.; Riggan, Philip J. CS Langley Res. Cent., NASA LO Hampton, VA, USA SO J. Geophys. Res., D: Atmos., 93(D4), 3893-8 SC 59-2 (Air Pollution and Industrial Hygiene) DT J CO JGRDE3 1988 PY Eng LA AB Recent measurements indicate significantly enhanced biogenic soil emissions of NO and N2O following surface burning. These enhanced fluxes persisted for at least 6 mo following the burn. Simultaneous measurements indicate enhanced levels of exchangeable NH4+ in the soil following the burn. Biomass burning is known to be an instantaneous source of NO and N2O resulting from high-temp. combustion. Biomass burning also results in significantly enhanced biogenic emissions of these gases, which persist for months following the burn.



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JOURNAL OF GEOPHYNICAL RENEARCH AOU 95 NO D9 FAGES 14.02 (14.03) AUGENED (2000)

The Effects of Biogenic Hydrocarbons on the Transformation of Nitrogen Oxides in the Troposphere

CYNTHIA S. ATHERTON AND JOYCE E. PENNER

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The reactive odd nitrogen chemistry is examined for environments both typical of the urban troposphere and in which biogenic hydrocarbon emissions are appreciable. Results are presented in terms of a nitrogen shortfall, $X NO_x$, the fraction of reactive nitrogen present as species other than NO, NO₂, HNO₃, NO₇, and peroxyacetyl nitrate. In urban environments, the calculated nitrogen shortfall is 0.02–0.33. Both higher initial hydrocarbon concentrations and higher initial hydrocarbon-to-NO₄ ratios lead to greater shortfalls, with the latter effect being more important. Products of biogenic hydrocarbon emissions greatly increase the nitrogen shortfall in urban air that has aged for 48 hours. The nitrogen shortfall increases from 0.25 for a simulation, two sensitivity studies which examine the stability of nitrate species formed from the biogenic hydrocarbons are also presented. These show that for our scenarios, the stability of ISON, a species formed during isoprene oxidation can change the calculated nitrogen shortfall by 0.15. However, the stability of nitrates from the reactions of isoprene and pinene with NO₃ changes the calculated nitrogen shortfall by only 0.05.

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Atmospheric Environment Vol. 23, No. 5, pp. 903-909, 1989. Printed in Great Britain 0004-6981/89 \$3.00+0.00 Pergamon Press ple

, INDIVIDUAL VERSUS AVERAGED ESTIMATES OF PARAMETERS USED IN LARGE SCALE EMISSIONS INVENTORIES

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(First received 19 October 1987 and in final form 12 September 1988)

Abstract—Development of emissions inventories for large geographic areas is currently based on the use of 'mass balance' equations to estimate the emissions from each source. The general equation used states that the emissions from a particular source for a specific pollutant in a specified time frame are equal to the product of the activity rate of the source in the selected time frame, an emission factor, which estimates the amount of pollutant emitted per unit activity, and additional parameters which vary according to the type of source whose emissions are being estimated. Values of the parameters used to estimate emissions are estimated in two different ways. 'Individual' estimates (an estimate for each source considered) are used for certain parameters; for other parameters, such as the emission factor, 'averaged' estimates (average values obtained by sampling a subset of the sources in a category) are used. The statistics resulting from the use of these two different methodologies are quite different. Derivation of the equations needed to calculate the mean square error in each case show that when the sources included in a category are homogeneous, then the averaged estimator may be better than individual estimates for estimating emissions from a particular source, but is worse for estimating sums. A numerical simulation was conducted to demonstrate these results. An example showing how to account for the effect of averaged estimators in a simple assessment is also included.

Key word index: Emissions inventory, uncertainty, averaged parameters.











. . 1 NATURAL HYDROCARBONS, URBANIZATION, AND URBAN OZONE C. A. Cardelino and W. L. Chameides School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta abstract. Using the Atlanta metropolitan area as a case study. examine the effects of urbanization and its associated heat sland on urban ozone concentrations. Air quality data from Atlanta suggest that urban ozone concentrations are enhanced m increases in ambient temperature. Model calculations suggest that this enhancement is caused by the effect of emperature on the atmospheric chemistry of peroxyacenyl sitrate (PAN), as well as the temperature dependence of atural and anthropogenic hydrocarbon emissions. A omparison of summertime temperatures in Atlanta and a searby rural station, suggests that Atlanta's temperature over the past 15 years has increased by about 2°C due to arbanization and its concomitant intensification of the urban heat island. Numerical simulations using conditions of a apical summertime day in Atlanta suggest that this rise in imperature could have, (1.) resulted in a significant increase m the net emissions of natural hydrocarbons in the area in wite of the loss of about 20% of the area's forests over the same period, and (2.) negated the beneficial effects on summertime ozone concentrations that would have been obtained from a 50% reduction in anthropogenic hydrocarbon emissions. Because a NO_x-based ozone abatement strategy uppears to be less sensitive to temperature increases than does a hydrocarbon-based strategy, a NOx strategy may prove to be more effective in the future if temperatures continue to rise as a result of urbanization and the "greenhouse effect".

JOURNAL OF GEOPHYSICAL RESEARCH. VOL. 92, NO. D2, PAGES 2211-2220, FEBRUARY 20, 1987

Theoretical Study of the Initial Products of the Atmospheric Oxidation of Hydrocarbons

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The initial products of the tropospheric oxidation of a representative mixture of hydrocarbons have been studied theoretically, using a detailed chemical mechanism involving 26 alkanes (C_1 - C_8), alkenes (ethylene, propylene), aromatic hydrocarbons (benzene, toluene, o-, m-, and p-xylenes), and two terpenes (isoprene, a-pinene). For an NO_x-rich atmosphere the oxidation of the alkanes in the mixture leads to three main classes of initial products: aldehydes (34%), ketones (45%), and alkyl nitrates (21%). Both the 7-hydroxy-aldehydes (19%) and the 7-hydroxy-ketones (19% of all alkane initial products) are major products. For NO,-free conditions the major products of the alkane oxidation are expected to be the alkyl hydroperoxides. For NO₂-rich conditions the aldehydes dominate the alkene oxidation products (80" \circ), with smaller amounts of α -hydroxy-carbonyl compounds (9%) and organic acids (4%). The major products of the aromatic hydrocarbons in the mixture are z-dicarbonyls (24%), unsaturated ydicarbonyls (22%), phenols (<49%), aromatic aldehydes (3%), and aromatic nitrates (2%). The expected product distribution and lifetime data suggest that each class of hydrocarbon has certain unique products which should serve as useful indicators of the history of an aged air mass. It is concluded that the alkyl nitrates and the p-hydroxy-alkyl nitrates may contribute to the large, and as yet unidentified. fraction of the active nitrogen species noted in NO, determinations in the troposphere by Fahey et al. (1986).







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 Terpenes discharged from plant leaves into atmosphere Chikamoto, Takeji; Yamakawa, Kazuhiko; Sakoda, Kichinosuke Eisei Kogai Kenkyusho Kyoto-fu Eisei Kogai Kenkyusho Nompo, Volume Date 1977, 22, 111-13 C 11-1 (Plant Biochemistry) X 4, 59 Y J X KEKNDS Y 1978 A Japan B Volatile materials discharged from needles of Japanese red pinc. Japanese cedar, and Himalayan cedar were mainly alphapinene, .betapinene, and 1,8-cineole. 	2
 C. Hikamoto, Fakeji, Famakawa, Kazunko, Sakoda, Kichnosuke Eisei Kogai Kenkyusho O Kyoto-fu Eisei Kogai Kenkyusho Nompo, Volume Date 1977, 22, 111-13 C. 11-1 (Plant Biochemistry) X 4, 59 Y J Y KEKNDS Y 1978 A Japan B Volatile materials discharged from needles of Japanese red pine. Japanese cedar, and Himalayan cedar were mainly .alphapinene, .beta-pinene, and 1,8-cineole. 	
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Atmospheric Environment Vol. 24A, No. 1, pp. 185-193, 1990. Printed in Great Britain. 0004-6981/90 \$3.00 + 0.00 () 1990 Pergamon Press pic

CALCULATION OF LONG TERM AVERAGED GROUND LEVEL OZONE CONCENTRATIONS

FRANK A. A. M. DE LEEUW, H. JETSKE VAN RHEINECK LEYSSIUS and PETER J. H. BUILTJES*

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(First received 22 December 1988 and received for publication 12 June 1989)

Abstract—Seasonal averaged ground level concentrations for O_3 have been calculated for The Netherlands by means of a two-layer Lagrangian long-range transport (LRT) model. The model includes emissions, nonlinear atmospheric chemistry, dry deposition, exchange between boundary layer (BL) and free troposphere (FT) and fumigation between a mixed layer and an aged smog layer. Concentrations of primary and secondary pollutants in the FT are obtained from a two-dimensional global model developed by Isaksen.

In the reference calculation the modelled concentrations of Ox (sum of O_3 and NO_2) and O_3 are in fair agreement with measurements. The NO_x (sum of NO and NO_2) and NO_2 concentrations are underestimated by the model but there is a good temporal correlation between calculated and measured concentrations. Validation of other components involved in the chemical scheme is hardly possible due to the paucity of measured data. It can only be stated that the results presented in this paper are not in disagreement with measured or modelled data presented in the literature.

In a number of sensitivity runs the influence of European anthropogenic emissions of NO_x and volatile organic compounds (VOC) has been investigated. The calculations indicate that the influence of European emissions on the growing season, daytime averaged (May-September, 10-17 h) O₃ concentrations in The Netherlands is small. For European reductions in the order of tens of per cents a VOC emission reduction is more effective than a NO_x emission reduction in lowering the O₃ concentrations. For strong reductions (about 70%) VOC and NO_x are equally effective. The effects of the modelled underprediction of NO_x concentrations on the production of O₃ on a European scale are probably small. On a local scale the effects are more pronounced due to the NO/O₃ titration (photostationary equilibrium). Therefore, an empirical correction is applied on the modelled O₃ concentrations. After this correction, it is shown that daytime O₃ levels during the growing season increase when European NO_x emissions are reduced (2.0-7.7% increase at S0% NO_x emission reduction). A reduction for 70% VOC emission reduction). For a combined reduction of 40% VOC emission reduction, 16% reduction for 70% VOC emission reduction). For a combined reduction of both VOC and NO_x slightly decreasing ground level O₃ concentrations are expected.

Key word index: Ozone, photochemistry, transport models, emission scenarios, nitrogen oxides.

Atmospheric Environment Vol. 23, No. 6, pp. 1361, 1371, 1989 0004 6981/89 \$3:00 + 0:00 Printed in Great Britain 1º 1989 Pergamon Press pic A COMPARISON OF MODEL PHOTOCHEMICAL OZONE FORMATION POTENTIAL WITH OBSERVED REGIONAL SCALE OZONE FORMATION DURING A PHOTOCHEMICAL EPISODE OVER THE UNITED **KINGDOM IN APRIL 1987** R. G. DERWENT Modelling and Assessments Group, Environmental and Medical Sciences Division, Harwell Laboratory, Oxfordshire, U.K. (First received 1 June 1988 and received for publication 2 November 1988) Abstract -- A photochemical trajectory model has been employed to calculate the maximum potential for ozone generation in air parcels passing over the U.K. during a photochemical pollution episode in April 1987. In all, 11 trajectories have been studied and the model results compared against an objective analysis of the integrated ozone generation based on the observations reported from the U.K. Department of the Environment ground level O_3 network. There is apparently good correlation between the observed O_3 formation and the model O₃ formation potential although the latter overestimates the former by a factor of about 2.8. The solar illumination conditions employed in the photochemical trajectory model may have

about 2.8. The solar illumination conditions employed in the photochemical trajectory model may have caused this overestimation, since the model is formulated for O_3 control strategy assessment and simulates the 'worst case' situation likely to give the maximum potential for secondary pollutant formation. In addition to the model results for O_3 , a wide range of primary and secondary pollutant concentrations from the model were examined, together with the influence of precursor pollutant emissions.

Key word index: Photochemical ozone, photochemical model, ozone network, ground level ozone concentrations.

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JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 95, NO. D4, PAGES 3635-3648, MARCH 20, 1990

Formaldehyde Production in Photochemical Smog as Predicted by Three State-of-the-Science Chemical Oxidant Mechanisms

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Atmospheric Resourch and Exposure Assessment Laboratory, U.S. Environmental Protection Agency Research Triangle Park, North Carolina

A moving box model was used to compare formaldehyde (HCHO) predictions obtained with three photochemical oxidant mechanisms. In simulations using a typical urban mix of organic pollutants, the mechanisms were found to yield HCHO predictions that agreed to within 10% of each other provided the same reaction rates were used in all three mechanisms to describe the photolysis of HCHO. The agreement for simulations using pollutant mixtures containing only one organic species showed more variability. Formaldehyde predictions obtained for ethene, propene, and acetaldehyde were in excellent agreement under most conditions; significant differences, however, were noted for the 2-alkenes and aromatic hydrocarbons. Predictions of ozone and hydrogen peroxide obtained with the urban mixture were very sensitive to the initial concentration of HCHO included in the simulations. Depending on whether HCHO was assumed to constitute 0% or 2% of the initial mix of organic pollutants, resulting ozone yields varied by as much as 15-30%; hydrogen peroxide yields differed by factors of 4-10 depending on the mechanism used. To estimate the effectiveness of various control measures for limiting HCHO production, simulations were also conducted where individual organic species within the urban mix were reduced and the resulting decreases in HCHO yields were noted. The largest decreases in HCHO occurred for reductions in ethene and the other 1-alkenes; the smallest decreases were obtained when the monoalkylbenzenes or the alkanes were reduced.



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NATURAL ORGANIC EMISSIONS AND THEIR IMPACT ON AIR QUALITY

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Not for Resale

For Presentation at the 73rd Annual Meeting of the

Air Pollution Control Association

Montreal, Quebec

June 22-27, 1980

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In recent years several investigators¹.² have reported that vegetaric emits substantial amounts of isoprene (GsHg) and terpenoid compounds (C $_{0}H_{15}$) to the troposphere. The magnitude of this natural hydrocarbon emission has been estimated to be between 0.5 and 20 times the hydrocarbon fie impact of this natural hydrocarbon enissions from antirropogenic sources when compared on a global basis³. The impact of this natural hydrocarbon is unknown. However, laboratory studies have shown that the annoterpenes are capable of reacting with oxides of nitrogen in the presence of souligh to produce ozone and other oxidants⁴.

Results from studies designed to measure isoprene and monoterpene cor centrations in urban and rural areas show jow levels of these compounds relative to the anthropogenic hydrocarbons². Therefore, there appears to be a conflict between what seems to be very large emissions and very low ambient concentrations. The possible explanations for this disagreement include: inaccurate natural hydrocarbon emission estimates; inaccurate anthropogenic hydrocarbon emission estimates; inaccurate being removed from the atmosphere much fister than the anthropogenic nydro carbons. These questions surrounding the atmospheric significance of natural hydrocarbons must be answered before state and local control agencies can develop effective oxidant control strategies. As part of an EPA effort to develop and validate a regional photochemical oxidant model. Washington State University initiated a sampling program aimed at establishing a natural hydrocarbon inventory for the state of Pennsylvania. The specific goal of the program was to determine the character and magnitude of natural hydrocarbons from the state's forest and agricultural lands. The purpose of this paper is to describe the inventory process and report emission factors for various types of natural vegetation.

Experimental

A bag enclosure method previously described by Zimmerman⁶ was used to sample the volatile hydrocarbon emissions from the major vegetation specie in Pennsylvania. This procedure involves enclosing a portion of the plant in a Teflon bag, and after a short period of time withdrawing an air sample. Samples were collected in stainless-steel canisters and inalyzed within 24-hours for individual $\zeta_4 - \gamma_2$ hydrocarbons. Details of the analyzed lytical procedure have been described elsewhere?

All emission samples were collected from a forested site in Hallem-Township. York county, Pennsylvania or near the city of Lancaster, PA. A sampling program was designed that would neasure emission variations due to changes in ambient conditions, sample location, date and time. In addition, a comparison was made between the hydrocarbon composition of the volatile emissions and the hydrocarbon composition of the leaf (needle) and wood tissues of each species sampled. This comparison was made by collecting a specimen of the leaf and wood tissue of each species sampled. The hydrocarbon composition of the samples was determined by excracting with carbon fisulfide and analyzing the extract on a gaschromatograph/mass-spectrometer (GC/MS) system. The samples were extracte in Lancaster, PA jowever, the analysis was performed in Pullman, WA using a GC/MS procedure

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Vol. 99, No. 4, 1981 April 30, 1981	BIOCHEMICAL AND BIOPHYSICAL RESEARCH COMMUNICATION: Pages 1456-146
IS	OPRENE - THE MAIN HYDROCARBON IN HUMAN BREATH
Da	vid Gelmont, Robert A. Stein and James F. Mead
Labor Un ive "Dep	ratory of Nuclear Medicine and Radiation Biology ersity of California, Los Angeles, CA 90024, and artment of Biological Chemistry, UCLA School of Medicine, Los Angeles, CA 90024
Received March 23,	1981
SUMMARY	
Isoprene was It was also identi as for a short-tin source of isoprene of isoprene produc	found to be the main endogenous hydrocarbon of human breath. ified in nursing Long-Evans and Sprague Dawley rats, as well ne post weaning. Several preliminary data, regarding the e are also available. We have been able to find small amount ction by rat's liver and kidney tissue slices.

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JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 94, NO. DIO, PAGES 12,925-12,956, SEPTEMBER 20, 1989 A PHOTOCHEMICAL KINETICS MECHANISM FOR URBAN AND REGIONAL SCALE COMPUTER MODELING Michael W. Gery,¹ Gary Z. Whitten,² James P. Killus,³ and Marcia C. Dodge⁴ A new chemical kinetics mechanism for simulating urban and regional photochemistry has been developed and evaluated. The mechanism, called the Carbon Bond Mechanism IV (CBM-IV), was derived by condensing a detailed mechanism that included the most recent kinetic, mechanistic, and photolytic information. The CBM-IV contains extensive improvements to earlier carbon bond mechanisms in the chemical representations of aromatics, biogenic hydrocarbons, peroxyacetyl nitrates, and formaldehyde. The performance of the CBM-IV was evaluated against data from 170 experiments conducted in three different smog chambers. These experiments included NO,-air irradiations of individual organic compounds as well as a number of simple and complex organic mixtures. The results of the evaluation indicate substantial improvement in the ability of the CBM-IV to simulate aromatic and isoprene systems with average overcalculation of ozone concentrations of 1% for the aromatic simulations and 6% for the isoprene simulations. The machanism also performed well in simulating organic mixture experiments. Maximum ozone concentrations calculated for 68 of these experiments were approximately 2% greater than the observed values while formaldehyde values were low by 9%.

	 LO Murray Hill, NJ 07974, USA SO Rev. Geophys. Space Phys., 17(5), 937-47 SC 53-0 (Mineralogical and Geological Chemistry) DT J CO RGPSBL IS 0034-6853 PY 1979 LA Eng AB A review with 63 refs. on the chem. structure, phys. property, and source information for 45 terpenoids known to be emitted into the atm. 	rre 17(5), 937-47 eological Chemistry) a the chem. structure, phys. property, and erpenoids known to be emitted into the	 AN CA91(26):213854x TI Terpenoids in the atmosphere AU Graedel, T. E. CS Bell Lab. LO Murray Hill, NJ 07974, USA SQ Rev. Geophys. Space Phys., 17(5), 937-47 SC 53-0 (Mineralogical and Geological Chemistry) DT J CO RGPSBL IS 0034-6853 PY 1979 LA Eng AB A review with 63 refs. on the chem. structure, phys. property, and source information for 45 terpenoids known to be emitted into the atm.
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- AN CA88(18):125612z
- TI The kinetic ozone photochemistry of natural and perturbed nonurban tropospheres
- AU Graedel, T. E.; Allara, D. L.
- CS Bell Lab.
- LO Murray Hill, N. J., USA
- SO U. S. Environ. Prot. Agency, Off. Res. Dev., [Rep.] EPA, Volume Date 1976, EPA-600/3-77-001a, Int. Conf. Photochem. Oxid. Pollut. Control Proc.: Vol. 1; PB-264 232, 467-73
- SC 59-2 (Air Pollution and Industrial Hygiene)
- DT T
- CO XPARD6
- PY 1977
- LA Eng
- AB Study of the emissions and reactions of terpenes, NH3, H2S, and other org. and inorg. compds shows that substantial amts. of O3 (.apprx. 32 ppb peak) occur naturally in the nonurban troposphere. Injections of addnl. NO have only minor effects on the O2 contain, whose peak decreases to .apprx.29 ppb, but there is increased formation of org. and inorg. nitrates.






- AN CA83(26):209153k
- TI Atmospheric reactivity of monoterpene hydrocarbons, NOx photooxidation, and ozonolysis
- AU Grimsrud, E. P.; Westberg, H. H.; Rasmussen, R. A.
- CS Coll. Eng. Res. Div., Washington State Univ.
- LO Puliman, Wash., USA
- SO Int. J. Chem. Kinet., Volume Date 1974, 7(Symp. 1), 183-95
- SC 59-2 (Air Pollution and Industrial Hygiene)
- SX 74
- DT J

AB

- CO UCKBO
- PY 1975
- LA Eng

An investigation of the atm. reactivity of selected volatile monoterpenes by measurements of their removal by the photolysis of added NOx [11104-93-1] and their rates of reaction with O3 [10028-15-6] in air is reported. Application of these results to rural atm. conditions indicates that terpenes are very reactive and their residence times in the atm. are very short. The relative importance of NOx photooxidn. and ozonolysis in the initial breakdown of each monoterpene is semiguant. described. Unlike most simpler hydrocarbons generally assocd. with urban pollution, reaction with O3 is of primary importance in the atm. breakdown of many terpenic hydrocarbons. The O3-monoterpene reactions generally exhibit good 2nd-order rates, with stoichiometries dependent on hydrocarbon type and relative concn. The effect of terpene structure on reactivity is discussed; terpenes with endocyclic conjugated diene systems are extraordinarily reactive due to reaction with O3.

Not for Resale

Environ. Sci. Technol 1985, 19, 151-155

Hydroxyl Radical Oxidation of Isoprene

Chee-liang Gu, Carolyn M. Rynard, Dale G. Hendry," and Theodore Mill*

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■ We have used the low total pressure (10 torr) flowing gas system and the high total pressure (760 torr) CH_3ON -O-NO photolysis system to study the reaction of OH with isoprene. Both systems give methyl vinyl ketone, methacrolein, and 3-methylfuran as the major products; 1,2addition is favored over 1,4-addition by a factor of 7. From the proposed mechanism and reaction pathways. we conclude that more than 2 mol of NO will be oxidized to NO₂ for each mole of isoprene oxidized by OH. Direct reaction of isoprene with NO₂ was also measured.

0004-6981/90 \$3.00 + 0.00 Atmospheric Environment Vol. 24A, No. 7, pp. 1673-1684, 1990. Printed in Great Britain Pergamon Press plc FIELD INVESTIGATIONS ON THE SNOW CHEMISTRY IN CENTRAL AND SOUTHERN CALIFORNIA-II. CARBONYLS AND CARBOXYLIC ACIDS DIETER W. GUNZ and MICHAEL R. HOFFMANN* California Institute of Technology, Environmental Engineering Science, W. M. Keck Laboratories 138-78, Pasadena, CA 91125, U.S.A. (First received 14 December 1988 and in final form 17 July 1989) Abstract-Snow samples from central and southern California were collected during the winter of 1987-1988 from three storms and analyzed for carbonyl compounds and carboxylic acids. Approximately 90% of the samples contained total aldehyde concentrations up to 40 μ M. Formaldehyde and acetaldehyde were the dominant aldehydes observed; secondary aldehydes included glyoxal, methylglyoxal, and benzaldehyde. The highest aldehyde concentrations were observed in snow collected in areas where deciduous and coniferous forests are widespread. However, these aldehydes can be attributed also in part to primary and secondary products of anthropogenic activities. Formic and acetic acid were analyzed in all measured samples with concentrations ranging from 0.5 to 4.9 μ M for HCOOH and from <0.3 to 13.4 μ M for CH₃COOH. Maximum contribution of organic acids to precipitation-free acidity, calculated by

assuming that the only sources of the measured formate and acetate were their respective acid forms, averaged 43.1% for samples with a pH \leq S. A consistent correlation between NH^{*} and acetate was found. [CH₃COOH] exceeded [HCOOH] in about 50% of the samples with the highest levels for CH₃COOH measured in cores collected from lower elevated locations adjacent to the Los Angeles basin. Results presented in this paper suggest that dry deposition and/or scavenging of carbonyl compounds and organic acids to snow-may be important sinks for these compounds.

Key word index: Organic snow chemistry, carbonyls, carboxylic acids and free acidity.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 94, NO. D10, PAGES 13.013-13.024, SEPTEMBER 20, 1989

REACTIONS OF OZONE WITH α -pinene and β -pinene in Air: yields of gaseous and particulate products

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> Abstract. Reactions of ozone with a-pinene and β -pinene were studied for the purpose of obtaining the quantitative yields of gaseous and particulate products. Major gaseous products from *a*-pinene were CO, CO₂, HCHO, and aldehydes mainly composed of pinonaldehyde and nor-pinonaldehyde, while those from β -pinene were CO₂, HCHO, and 6,6-dimethylbicyclo[3.1.1]heptan-2-one. Average molar yields from g-pinene were CO; 9 ± 1%, CO2; 30 ± 2%, HCHO; 22 ± 1%, and aldehydes; 51 ± 6%. Average molar yields from β -pinene were CO2; 27 ± 2%, HCHO; 76 ± 2%, and 6,6-dimethylbicyclo[3.1.1]heptan=2=one; 40 ± 2%. Particulate products were found to include pinonaldehyde, nor-pinonaldehyde, pinonic acid, and nor-pinonic acid from a-pinene. The yields of the particulate aldehydes decreased with the reaction time, whereas the yields of the acids increased. This observation suggests the sequential oxidation of aldehydes to carboxylic acids. From S-pinene, only 6,6-dimethylbicyclo[3.1.1]heptan-2-one was identified as a particulate product. For $\alpha\text{-}$ pinene, most of the products are explainable in terms of the reaction mechanism similar to that for the cyclohexene/ozone reaction, whereas for B-pinene the principal reaction path is that of the doubly substituted Criegee intermediate. The total yields of organic aerosols from both α - and β-pinene were measured with their concentrations at a lower ppb level. The yields were found almost constant in a pinene concentration range from 10 up to 100 ppb, being 18.3 ± 1.1 and 13.8 \pm 0.8 % for $\alpha-$ and $\beta-\text{pinene},$ respectively, which are much lower than the previously reported values.

API PUBL*309 92 🖿 0732290 0529758 778 🛲



Phytochemistry 1978, Vol 17, pp. 869-872 C Pergamon Press Ltd. Printed in England

0031-9422 78 0501-0869 \$02.0010

DISTRIBUTION OF AN ENZYME SYSTEM PRODUCING cis-3-HEXENAL AND n-HEXANAL FROM LINOLENIC AND LINOLEIC ACIDS IN SOME PLANTS

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(Received 10 October 1977)

Key Word Index—Distribution in 40 plants; enzyme system producing C_0 -aldehydes. cis-3-hexenal; cis-3-hexenal; trans-2-hexenal; n-hexanal.

Abstract—The activity of the enzyme system (E_2-I) producing C_6 -aldehydes from C_{18} -unsaturated fatty acids was investigated using about 40 plants. Green leaves of dicotyledonous plants belonging to the Sphenopsida. Pteropsida Theaceae and Leguminosae showed a high enzyme (E_2-I) activity but edible leafy vegetables and fuits and monocotyledonous plants showed a low activity. Seasonal changes in the enzyme (E_2-I) activities were observed. The concentrations of *cis*-3-hexenol (leaf alcohol) and *trans*-2-hexenal (leaf aldehyde) and the enzyme (E_2-I) activities showed a correlation; high concentrations were observed in the summer but they were low in the winter.





0004-6981/89 \$3.00+0.00 Atmospheric Environment Vol. 23, No. 3, pp. 661-669, 1989. C 1989 Pergamon Press pic Printed in Great Britain. SIMULATION OF PHOTOCHEMICAL SMOG IN THE MELBOURNE AIRSHED: WORST CASE STUDIES G. D. HESS BMRC, Bureau of Meteorology, Melbourne, Victoria 3001, Australia (First received 18 September 1987 and received for publication 21 September 1988) Abstract-The impact of a large NO, point source on photochemical smog in Melbourne is examined through the use of a numerical model described by Hess. Over most of the Melbourne Airshed the NMHC/NO_x ratio is found to be less than 10, in agreement with the results of Evans et al. For these cases trajectories passing through the Newport Power Station exhibit a decrease in ozone (compared to background values) of about 0.02 ppm and an increase in nitrogen dioxide of about the same amount due to Newport's emissions. This result confirms a preliminary finding by Form and Substance (1982). However, worst case scenarios have not been previously studied. Measurements indicate that any trajectory that links the high NO, from Newport and the high NMHC from Pt Cook will result in a worst case. The windfield observations reported here show the existence of a topographically generated mesoscale eddy in the airshed, as proposed by Spillane (1978, Clean Air 12, 50-56.), and its location tends to link Newport and Pt Cook. Simulation of two cases indicates that under worst case conditions Newport's emissions increase the ozone concentration by 0.01-0.04 ppm. These conditions are estimated to occur on one day in four to one day in three of high oxidant days in Melbourne.

Key word index: Photochemical smog, Eulerian-Lagrangian transport model, Spillane eddy, large point source, worst cases, Dodge plot.



۱ Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere eds. M.O. Andreac and D.S. Schimel, pp. 119-118 John Wiley & Suns Ltd © S. Bernhard, Dahlem Konferenzen, 1989 **Regional Extrapolation:** Vegetation–Atmosphere Approach **B.B.** Hicks NOAA/ATDD 456 South Illinois Avenue Oak Ridge, TN 37831, U.S.A. Abstract. Available data on the exchange of trace gases from the surface into the atmosphere is generated primarily by methods that yield locally representative flux information over short time intervals. On the other hand, regional-scale and global models require exchange data averaged over grid cells that are typically 100 km × 100 km, or larger. The extension from local data to grid-cell averages is far from trivial. Micrometeorological formulations of atmosphere-surface exchange are potentially well suited for use in such extrapolation, because they describe area averages at the outset (usually several hectares) and include descriptions of the terrain and vegetation properties that influence the exchange. However, these formulations lack the biological and chemical detail provided by models developed as a consequence of laboratory studies of soils and vegetation, and of field studies using cuvettes and chambers. Methods are required, therefore, to include the detail of these biological and chemical models in the micrometeorological routines, and then to use the modified micrometeorological methods to produce area averages. Here, methods are proposed for both purposes, based on the techniques developed to describe fundamental characteristics of vegetation in atmospheric models. This, then, constitutes the "Vegetation-Atmosphere Approach" of the title of this chapter. Micrometeorological relationships are presented in a format that offers an opportunity to include the results of detailed point-bypoint emission models in their specification of appropriate zero plane displacements, roughness lengths, and average surface-air concentrations. Extension to larger areas is then proposed to make use of a replicated application of the modified micrometeorological relations that are derived.

AN CA92(2):9267z TI Analysis of monoterpene hydrocarbons in rural atmospheres Holdren, M. W.; Westberg, H. H.; Zimmerman, P. R. AU CS Chem. Eng. Dep., Washington State Univ. Pullman, WA 99164, USA LO SO JGR, J. Geophys. Res., 84(C8), 5083-8 SC 53-10 (Mineralogical and Geological Chemistry) DT J CO JJGRDA IS 0148-0227 PY 1979 LA Eng AB Gas chromatog./mass spectrometric anal. of monoterpenes from a rural forested site in the northwestern United States is described. Use of a glass capillary column provided excellent resoln. of the hydrocarbons. Increased sensitivity and specificity of the mass spectrometer detector over the flame ionization detector were demonstrated for trace (parts per trillion) atm. hydrocarbons. As little as 10 parts per trillion of compd. was detectable in 100 cm3 air samples. Two anal. methods (cryogenic and solid adsorbent-Tenax-GC) were used in the collection of ambient air. Anal. results from the 2 techniques compared very well. Rural concns. of the monoterpenes varied considerably depending upon location within the forest canopy. The concn. of individual species never exceeded 1 ppb of compd. during a 10-mo sampling period. The monoterpene total for all samples fell in the range of 0.5- to 16-ppb compd. for C10 terpene.



AN CA100(10):71702z ΤI Measurement and modeling of the concentrations of terpenes in coniferous forest air AU Hov, Oeystein; Schjoldager, Joergen; Wathne, Bente M. CS Norwegian Inst. Air Res. LO Lillestroem N-2001, Norway SO JGR, J. Geophys. Res., [Sect.] C, 88(C15), 10679-88 SC 53-10 (Mineralogical and Geological Chemistry) DT J CO JJGADR IS 0196-2256 PY 1983 LA Eng AB In a coniferous forest area northeast of Oslo, Norway, air samples were collected by adsorption on activated C and analyzed by gas chromatog. with a high-resoln. glass capillary column and flame ionization detection. In samples collected during June and August, 1980, 7 terpenes were identified and had a total concn. range of 8.8-70.7 ppbC (ppb, as C), with .alpha.-pinene, terpinene, and p-cymene occurring in the highest concns. A one-dimensional vertical grid model of the atm. boundary layer with a detailed mechanism for inorg. and org. gas phase chem. turnover was applied to assess the vertical variability of the terpene concns. as a function of the O3 concn., the source strength of the terpenes, the time of the day, the upwind air compn., etc. The calcus. showed that very little of the terpene emissions remained airborne after 4-8 h, in contrast to the anthropogenic hydrocarbons. The anthropogenic fraction of the hydrocarbons may dominate in concn., even though the natural part of the source is the larger one. Emission of 2000 .mu.g/m2.h of terpenes was calcd., giving ground level concns. of total terpenes of .ltoreq.25 ppbC, comparable to or less than the measured concns. As a result of chem, degrdn, of the terpenes their emission at this rate suppresses the OH concn. but the impact on O3 during daytime was negligible.

API PUBL*309 92 🖿 0732290 0529768 617 📟





AN CA101(16):136079u

- TI Compilation of a biogenic hydrocarbon emissions inventory for evaluating ozone control strategies in the San Francisco Bay area
- AU Hunsaker, Donald B., Jr.; Moreland, Roberta M.
- CS Assoc. Bay Area Gov.
- LO Berkeley, CA, USA
- SO Proc., Annu. Meet. Air Pollut. Control Assoc., 75th(3), 82-51.5, 16 pp.
- SC 59-2 (Air Pollution and Industrial Hygiene)

SX 74

DT J

- CO PRAPAP
- IS 0099-4081
- PY 1982

LA Eng

AB A regional, disaggregated, and gridded biogenic hydrocarbon emissions inventory was prepd. for the San Francisco Bay area (California) using remote sensing data and biogenic hydrocarbon emission factors. Nonattainment of the std. is a complex problem involving chem., meteorol., and topog. Major efforts should be directed towards detg. the extent to which biogenic hydrocarbon compds. combine with anthropogenic emissions of NOx and hydrocarbons to form O3 so that effective control programs can be designed and implemented to protect the public from unhealthy O3 levels in urban areas.



API PUBL*309 92 📖 0732290 0529772 048 📟

- AN CA102(23):201125t
- TI Volatile organic compounds in the atmosphere of forests
- AU Isidorov, V. A.; Zenkevich, I. G.; Ioffe, B. V.
- CS Dep. Chem., Leningrad State Univ.
- LO Leningrad 199164, USSR
- SO Atmos. Environ., 19(1), 1-8
- SC 11-1 (Plant Biochemistry)
- SX 59
- DT J
- CO ATENBP
- IS 0004-6981
- PY 1985
- LA Eng

AB The procedure of sampling and gas chromatog.-mass spectrometric anal. of air contg. volatile emissions from living plants is described. The qual. compn. of volatile org. compds. (VOC) produced by 22 species of plants which are characteristic for Northern hemisphere forests was studied. The emission rates of isoprene and terpenes for some of them were detd. Terpene concns. in coniferous forests of different regions of the U.S.S.R were also detd. The list of compds. identified includes >70 substances of different classes. Total terpene concns. in the coniferous forests air usually vary from 3.5 to 35 .mu.g/m3. Strong influence of meteorol. conditions on the emission rate and terpene concns. in the air under the forest canopy was obsd.

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JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 93, NO. D2, PAGES 1477-1486, FEBRUARY 20, 1988

Photochemistry of Biogenic Emissions Over the Amazon Forest

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The boundary layer chemistry over the Amazon forest during the dry season is simulated with a photochemical model. Results are in good agreement with measurements of isoprene. NO, ozone, and organic acids. Photochemical reactions of biogenic isoprene and NO_x can supply most of the ozone observed in the boundary layer. Production of ozone is very sensitive to the availability of NO_x , but is insensitive to the isoprene source strength. High concentrations of total odd nitrogen (NO_y) are predicted for the planetary boundary layer, about 1 ppb in the mixed layer and 0.75 ppb in the convective cloud layer. Most of the odd nitrogen $(\approx 70\%)$ is present as PAN-type species, which are removed by dry deposition to the forest. The observed daytime variations of isoprene are explained by a strong dependence of the isoprene emission flux on sun angle. Nighttime losses of isoprene exceed rates of reaction with NO₃ and O₃ and appear to reflect dry-deposition processes. The 24-hour averaged isoprene emission flux is calculated to be 38 mg m⁻² d⁻¹. Photooxidation of isoprene could account for a large fraction of the CO enrichment observed in the boundary layer under unpolluted conditions and could constitute an important atmospheric source of formic acid, methacrylic acid, and pyruvic acid.



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JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 91, NO. D12, PAGES 13,239-13,256, NOVEMBER 20, 1986

Nonmethane Hydrocarbons in the Troposphere: Impact on the Odd Hydrogen and Odd Nitrogen Chemistry

JAMES F. KASTING AND HANWANT B. SINGH

Space Science Division, NASA Ames Research Center, Moffett Field, California

The chemistry of light nonmethane hydrocarbons (NMHCs), including C₂H₆, C₃H₈, n-C₄H₁₀, C₂H₄, and C₃H₆, was incorporated into a seasonally varying, one-dimensional model of the mid-latitude troposphere (45 N). Simulations were performed for both marine and continental atmospheres. Where possible, these simulations have been compared with surface and aircraft measurements of test molecules, such as C₂H₆, C₃H₈, CO, peroxyacetyl nitrate (PAN), and peroxypropionyl nitrate (PPN). Model calculations predict that NMHC oxidation produces acetaldehyde and acetone in concentrations that can exceed that of formaldehyde. Organic peroxides were found to be present in concentrations that, considered collectively, are comparable to that of hydrogen peroxide. Peroxyacetyl nitrate is the dominant odd nitrogen (NO.) compound in wintertime and is surpassed only by HNO3 during the summer. The inclusion of NMHC-PAN chemistry has little effect on summertime odd hydrogen/odd nitrogen photochemistry, but is shown to have a substantial impact in wintertime, particularly over the continents, where NO_x concentrations are high and temperatures are low. Under these circumstances, oxidation of NMHC compounds can enhance ground-level OH and HO, concentrations by factors of 5-50. respectively. Formation of PAN during the wintertime can reduce upper tropospheric NO, concentrations by a factor of 2-3 over the oceans and a factor of 20-30 over the continents. Significant changes also occur in the predicted concentrations of HNO₃ and HO₂NO₂. The effects of NMHCs on wintertime photochemistry might be moderated by seasonal variations in NMHC source strengths or by horizontal transport of trace gases from the continents to the oceans and from high latitudes toward the equator. Nonetheless, it seems likely that models of the troposphere must include NMHC-PAN chemistry in order to correctly predict the seasonal behavior of trace chemicals.



JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 91, NO. D12, PAGES 13,239-13,256, NOVEMBER 20, 1986

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The chemistry of light nonmethane hydrocarbons (NMHCs), including C₂H₆, C₃H₈, n-C₄H₁₀, C₂H₄, and C₃H₆, was incorporated into a seasonally varying, one-dimensional model of the mid-latitude troposphere (45 N). Simulations were performed for both marine and continental atmospheres. Where possible, these simulations have been compared with surface and aircraft measurements of test molecules, such as C₂H₆, C₃H₆, CO, peroxyacetyl nitrate (PAN), and peroxypropionyl nitrate (PPN). Model calculations predict that NMHC oxidation produces acetaldehyde and acetone in concentrations that can exceed that of formaldehyde. Organic peroxides were found to be present in concentrations that, considered collectively, are comparable to that of hydrogen peroxide. Peroxyacetyl nitrate is the dominant odd nitrogen (NO.) compound in wintertime and is surpassed only by HNO3 during the summer. The inclusion of NMHC-PAN chemistry has little effect on summertime odd hydrogen odd nitrogen photochemistry, but is shown to have a substantial impact in wintertime, particularly over the continents, where NO_x concentrations are high and temperatures are low. Under these circumstances, oxidation of NMHC compounds can enhance ground-level OH and HO, concentrations by factors of 5-50, respectively. Formation of PAN during the wintertime can reduce upper tropospheric NO, concentrations by a factor of 2-3 over the oceans and a factor of 20-30 over the continents. Significant changes also occur in the predicted concentrations of HNO3 and HO2NO2. The effects of NMHCs on wintertime photochemistry might be moderated by seasonal variations in NMHC source strengths or by horizontal transport of trace gases from the continents to the oceans and from high latitudes toward the equator. Nonetheless, it seems likely that models of the troposphere must include NMHC-PAN chemistry in order to correctly predict the seasonal behavior of trace chemicals.

Atmospheric Ensironment Vol. 24A, No. 8, pp. 2127-2132, 1990. Printed in Great Britain. 0004-6981/90 \$3.00+0.00 Pergamon Press pic

REACTION OF MONOTERPENES WITH OZONE, SULPHUR DIOXIDE AND NITROGEN DIOXIDE—GAS-PHASE OXIDATION OF SO₂ AND FORMATION OF SULPHURIC ACID

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Commission of the European Communities, Joint Research Centre, Ispra (VA), Italy

(First received 15 December 1988 and in final form 29 September 1989)

Abstract—Teflon bag experiments were carried out in the dark in order to study the gas-phase reactions of selected monoterpenes with O₃ in the presence of SO₂ (β -pinene) as well as in the presence of SO₂/NO₂ (α -pinene, β -pinene, limonene). Emphasis was given in identifying the main reaction products and in quantifying the H₂SO₄ aerosol formed. Apart from the H₂SO₄ aerosol no other S containing compounds could be detected.

It was found that the reaction of β -pinene with O₃, SO₂ and NO₂ leads mainly to 6,6-dimethyl-bicyclo [3.1.1] heptan-2-one (nopinone), the α -pinene-O₃-SO₂-NO₂-reaction produced 2',2'-dimethyl-3-acetyl cyclobutyl ethanal (pinonaldehyde). The reaction of limonene with O₃-SO₂-NO₂ leads mainly to an unidentified product with a molecular weight M⁺ 134. In addition to the above-mentioned volatile products, the formation of organic nitrates could be established by means of gas chromatography-mass spectrometry.

The yield of H_2SO_4 in the system β -pinene/ O_3/SO_2 varies between 0.13 and 0.44 depending on the initial conditions, e.g. humidity. In the system terpene/ $O_3/SO_2/NO_2$ the yield of H_2SO_4 for α -pinene (after 1 h reaction time) was 0.01-0.03, for β -pinene (2 or 4 h reaction time) 0.07-0.13 and for limonene (1 h reaction time) 0.02-0.09.

Key word index: Monoterpenes, ozone, sulphur dioxide, nitrogen oxides, pinonaldehyde, organic nitrates.

DEVELOPMENT OF A NATIONAL INVENTORY FOR NATURAL HYDROCARBON EMISSIONS

Brian Lamb, David Gay, Hal Westberg, and Eugene Allwine Department of Civil & Environmental Engineering Washington State University Pullman, WA 99164-2910

A Contributed Paper for presentation at the NAPAP 1990 International Conference on "Acidic Deposition: State of Science and Technology" 11-16 February 1990, Hilton Head Island, USA

This paper has not been subjected to external peer review

SUMMARY AND CONCLUSIONS

The objective of this research was to develop methods for estimating the emission fluxes of biogenic hydrocarbons as a basis for compiling emission inventories for use in the Regional Acid Deposition Model (RADM) and other air quality applications. A first generation biogenic emissions inventory was developed at the outset of the NAPAP program (Lamb et al., 1987). In this initial step, arithmetic mean emission rates from Zimmerman's (1979) extensive sampling program in Tampa Bay, FL were used with temperature-lightemissions algorithms from Tingey's (1981) environmental chamber studies. The emission algorithms were combined with biomass factors from the literature, and land use and climatic data from the Geoecology Data Base (Olson, 1980) to predict isoprene, alpha-pinene, and other volatile organic emissions with a monthly time scale and a U.S. county spatial scale.

In a second emission inventory, hydrocarbon emissions data from a number of field and laboratory studies were used in a simple temperature-emission regression approach to develop new emission rate algorithms for isoprene, the sum of mono-terpenes, and other volatile organic emissions. Furthermore, a simple forest canopy model was also developed to provide a better simulation of the forest environment. These methods were applied by Gay (1987) for the second inventory using the same land use and biomass factors as in the initial effort. Mean minimum and maximum monthly temperatures for state climatic divisions given in the Geoecology Data Base were used in this step to generate diurnal temperature profiles. Solar radiation input for use in the canopy model was calculated on a seasonal basis for each climatic zone.

For the latest inventory, efforts were made to determine the fraction of unidentified emissions and to specify emission algorithms for isoprene, identified

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API PUBL*309 92 🛲 0732290 0529784 86T 🎟

- AN CA104(11):84646s
- TI Isoprene emission fluxes determined by an atmospheric tracer technique
- AU Lamb, B.; Westberg, H.; Allwine, G.
- CS Lab. Atmos. Res., Washington State Univ.
- LO Pullman, WA 99164, USA
- SO Atmos. Environ., 20(1), 1-8
- SC 9-3 (Biochemical Methods)
- SX 11
- DT J

CO ATENBP

- IS 0004-6981
- PY 1986
- LA Eng

AB SF6 tracer was used in a series of expts. to simulate isoprene emissions from an isolated oak grove. The measured tracer release rate and ambient concns. of isoprene and SFI obsd. along downwind sample lines were combined to det. the mass flux of isoprene from the forest. The fluxes detd. from the tracer data increased exponentially with temp. and were in close agreement with ests. detd. from emission rate measured in a series of branch enclosure samples. The results of this field study demonstrate the feasibility and usefulness of simulating forest emission as a tool for investigating turbulent transport in forested areas. Isoprene emission fluxes that can be applied in regional models are reported.



Atmosphere Instrument Vol. 25A, No. 2, pp. 491-501, 1991 Printed in Creat Britain traid word of Strate little Pergamon Press pic

OZONE, SULFUR DIOXIDE, AND NITROGEN DIOXIDE TRENDS AT RURAL SITES LOCATED IN THE UNITED STATES

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and

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(First received 11 June 1990 and in final form 13 August 1990)

Abstract-We have investigated the existence of trends for ozone, sulfur dioxide, and nitrogen dioxide at rural sites in the U.S. For the ozone analysis, at 54 of the 77 sites (70%) for the 10-year analysis (1979-1988) and at 118 of 147 sites (80%), with at least 4 years of data for the 5-year analysis (1984-1988), there was no indication of trends, either positive or negative. For the 10-year analysis, ozone sites in the Southern and Midwest forestry regions showed more positive than negative significant slope estimates. For the 5-year analysis, similar results were obtained, except that the mid-Atlantic region also experienced more positive than negative significant slope estimates. In most of the agricultural regions, there were not many significant trends in either the 10- or 5-year analysis. However, for the agricultural Appalachian region, 50% and 34% of the trends, respectively, were significant and there were more positive than negative significant ozone trends for both the 10- and 5-year periods. For sulfur dioxide, there was an indication of trends at 37 of 64 sites (58%) for the 10-year analysis (1978-1987). For the 5-year analysis (1983-1987), with at least 4 years of data, there was no indication of trends at 115 of 137 sites (84%). For sites in some regions of the U.S., there is an indication that sulfur dioxide concentrations have declined for both the 5- and 10-year periods, but the rate of decline on an aggregate basis has slowed in the 5-year period. There is a strong indication that the sulfur dioxide level decreased at many sites in the Midwest forestry and the Corn Belt agricultural regions for the 10-year period. In the Southern forestry and Appalachian agricultural regions, many sites showed a decrease in the index for the 10-year, but not the 5-year, period. The lack of monitoring data for nitrogen dioxide made any conclusion extremely tenuous.

Key word index: Trends, ozone, sulfur dioxide, nitrogen dioxide, cumulative exposure, agriculture, forestry.










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PRESENTATION DE L'EXPERIENCE ATILA (ACTION DES TERPENES ET ISOPRENE DANS L'ATMOSPHERE) EFFECTUEE EN FORET TEMPERE AU SUD OUEST DE LA FRANCE (FORET DES LANDES)

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Laboratoire d'Aérologie, Laboratoire associé au CNRS no 354, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France

(First received 11 June 1987 and in final form 5 February 1988)

Résumé--Nous présentons dans le cadre de ce travail, les objectifs, le disposif expérimental mis en place et les premiers résultats obtenus lors d'une campagne de mesure effectuée en zone de forêt tempérée du Sud-Ouest de la France: forêt des Landes (Expérience ATILA).

L'action des hydrocarbures biogéniques sur la chimie de l'atmosphère est étudiée à partir de la mesure de concentrations de constituants traces effectuées sous le couvert végétal, à l'interface couvert atmosphère et dans la couche limite (ozone, CO, aérosols, hydrocarbures biogéniques). Les premiers resultats font apparaître un bilan d'ozone légérement négatif au dessus de la forêt qui confirme les résultats obtenus par simulation lors d'une émission de NO, faible. La formation de particules et de monooxyde de carbone par réactions physicochimiques sur les hydrocarbures naturels est restée faible durant la période de l'expérience.

Abstract—We present, with this work, the aims, the experimental set-up and the first results obtained during a campaign in atmospheric chemistry undertaken in a temperate forest area in southwestern France, the forest of Landes (experiment ATILA).

To study the action of biogenic hydrocarbons in atmospheric chemistry, measurements of trace constituent concentrations were made under plant cover, at the interface between the cover and the atmosphere and in the boundary layer (ozone, CO, particles, biogenic hydrocarbons). The first results show a slightly negative ozone balance over the forest, which supports the results obtained by simulations with a low NO_x source. Particles and CO formation through photochemical reaction on natural hydrocarbons remained low during the period of the experiment

Key word index: Tropospheric chemistry, ozone, aerosols, CO, biogenic hydrocarbons.



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Not for Resale

Journal of Natural Products Vol. 50. No. 5, pp. 950-952, Sep-Oct 1987

VOLATILES OF SORGHUM BICOLOR SEEDLINGS

W. LWANDE

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Sorghum bicolor (L.) Moench, grain sorghum, is one of the world's most important cereal crops, ranking fifth in world acreage and production after wheat, rice, corn, and barley (1). In Africa and Asia where about 3/4 of the world's acreage produces only 1/3 of the sorghum grain crop, insect pests take an immense toll. Nearly 150 insect species are known to be pests of S. bicolor, the most important being the sorghum shootfly (Atherigona soccata) and the spotted stalk borer, Chilo partellus, which attack 3- to 5-week-old sorghum seedlings (1-3).

Odors emanating from S. bicolor plants may play a role in the orientation of its insect pests towards the plant and in ultimate recognition of the host plant for feeding and oviposition (4). Thus, knowledge of the volatile compounds of S. bicolor may be useful in the study of insect pest-sorghum plant relationships. No report in the literature on the volatiles of S. bicolor has been found by the authors.

In the present study, air-borne volatiles of 4-week-old S. bicolor (Serena cultivar) seedlings were trapped on Tenax TA adsorbent. The trapped volatiles were released directly into a capillary gas chromatograph mass spectrometer (gc/ ms) by heating the Tenax trap. Identification of the volatiles by ms was confirmed by comparison of their mass spectra and retention times with those of authentic samples. A list of the identified volatiles is shown in Table 1.

Traditional techniques such as solvent extraction, steam distillation, and distillation under reduced pressure lead to destruction of the plant tissue. This may

Compound										Relative %
Toluene				•						3.9
Hexanal										5.2
(Z)-3-He	en	i- 1	-0	d						14.0
m-Xylene										4.7
o-Xylene										2.0
(Z)-3-Hex	en	- 1	-0	l.						
acetate										65.0
Nonanal		•								3.8
Decanal										1.4

TABLE 1. Air-borne Volatiles Trapped from

4-Week-Old Seedlings of Sorghum bicolor

(Serena cultivar)

*Based on integration of peaks in the gc-ms total ion current chromatogram without use of internal standards.

products that are normally not present in the intact plant and that may mask the original volatiles (5,6). Enzyme action may also degrade some of the plant volatile compounds. The collection technique for volatiles used in this study may yield a better understanding of what insects perceive in the environment around the sorghum plant. In the present study, the sorghum seedlings were cut near the base of their stems to eliminate soil that would otherwise introduce other volatiles into the system. Although cutting the plant like this may also lead to formation of some metabolic artifacts, the damage is much less severe as compared to steam and reduced-pressure distillation, where the whole plant is macerated and subjected to high temperatures.

(Z)-3-Hexen-1-ol acetate was the major volatile trapped from the seedlings of S. bicolor (Table 1). It has also been found to be the major volatile compound in the leaves of the cereal grain Provided by IHS under license with API No reproduction or networking permitted without license from IHS in enzyme-catalyzed oxidation Not for Resale nts of oat and wheat (6,7). (Z)-3-

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THE ROLE OF BIOGENIC HYDROCARBONS IN THE PRODUCTION OF OZONE IN URBAN PLUMES IN SOUTHEAST ENGLAND

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(First received 18 February 1990 and in final form 22 July 1990)

Abstract—First-order approximations of the rates of emission of isoprene and α -pinene are made for the region around London. Isoprene is found to be the dominant biogenic non-methane hydrocarbon species by mass in the region. Chemical degradation schemes for isoprene and α -pinene are added to an existing urban plume model which has previously been applied to London. The influence of each hydrocarbon is investigated by comparing model runs which include biogenic chemistry to a base case scenario. Overall, the effect is small: ozone levels in the plume are increased by the addition of the new schemes by up to 8 ppb. A model run with biogenic hydrocarbon and NO_x emissions only, demonstrates the VOC-limited behaviour of the urban plume. Conversely, removal of anthropogenic VOC emissions from the rural/suburban model results in a decrease of only 5 ppb in ozone production over one day. The reason for this difference in behaviour is the difference NMHC/NO_x ratios within and outside the urban plume. The inclusion of biogenic NMHC chemistry in the model results in a negligible change to the calculated "urban ozone effect" defined as the difference between ozone concentrations within and outside of the plume. Substantial chancement to present biogenic NMHC databases are required if our understanding of urban plume chemistry is to be made more accurate.

Key word index: Urban plume model, biogenic hydrocarbons, emissions, ozone.







Atmospheric Environment Vol. 24A, No. 5, pp. 1107-1133, 1990. 0004-6981/90 \$3.00 + 0.00 Printed in Great Britain. Pergamon Press pic / AGGREGATION AND ANALYSIS OF VOLATILE ORGANIC COMPOUND EMISSIONS FOR REGIONAL MODELING PAULETTE MIDDLETON* and WILLIAM R. STOCKWELL Atmospheric Sciences Research Center, State University of New York at Albany, Albany, New York, U.S.A. and WILLIAM P. L. CARTER Statewide Air Pollution Research Center, University of California, Riverside, California, U.S.A. (First received 18 May 1989 and in final form 18 October 1989) Abstract-A general two-step procedure for aggregating the hundreds of reported volatile organic compounds (VOCs) into a much smaller set of lumped classes appropriate for regional airshed modeling is described. In the first step, the compounds are condensed into a manageable number of emission categories which could be adapted to a variety of molecularly-based lumped chemical mechanisms. In the second step, the emissions are further aggregated into a smaller set of VOC classes which directly correspond to those in a particular model's mechanism. The application of this procedure is illustrated by aggregating the National Acid Precipitation Assessment Program (NAPAP) anthropogenic VOC emissions inventory the U.S. first into the 32-class system, and then into the groups of model species used in the latest version of the Regional Acid Deposition Model (RADM2.0). The importance of different VOC categories and source types on regional pollution production is explored by comparing the contributions of each of the emissions groupings, RADM model species, and major emissions sources, to total moles carbon VOC reacted in model simulations. For this particular anthropogenic inventory and chemical mechanism, it is found that over 50% of the moles carbon reacted is associated with mobile sources. Such analysis can help indicate which uncertainties in anthropogenic emissions inventories may have the greatest impact on results of regional simulations. Key word index: Volatile organic compounds, emissions, emissions aggregation, regional airshed models, acid deposition, RADM, atmospheric reactivity, emissions source analysis.

Performent Vol 22 No 3, pp 511-536 1988 (894-698) 85 \$3 (8) + 12 (8 and in Great Britain Pergamon Press pk ATMOSPHERIC DEPOSITION OF POLYCYCLIC AROMATIC HYDROCARBONS TO WATER SURFACES: A MASS **BALANCE APPROACH** BRUCE D. MCVEETY* and RONALD A. HITES* School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, IN 47405, U.S.A (First received 16 April 1987 and in final form 31 August 1987) Abstract-A mass balance model was developed to explain the movement of polycyclic aromatic hydrocarbons (PAH) into and out of Siskiwit Lake, which is located on a wilderness island in northern Lake Superior. Because of its location, the PAH found in this lake must have originated exclusively from atmospheric sources. Using gas chromatographic mass spectrometry, 11 PAH were quantified in rain, snow. air, lake water, sediment core and sediment trap samples. From the dry deposition fluxes, an aerosol deposition velocity of 0.99 ± 0.15 cm s⁻¹ was calculated for indeno[1,2,3-cd]pyrene and benzo[ghi]perylene, two high molecular weight PAH which are not found in the gas phase. The dry aerosol deposition was found to dominate the wet removal mechanism by an average ratio of 9:1. The dry gas flux was negative, indicating that surface volatilization was taking place; it accounted for 10-80", of the total output flux depending on the volatility of the PAH. The remaining PAH were lost to sedimentation From the dry gas flux, an overall mass transfer coefficient for PAH was calculated to be 0.18 ± 0.06 m d⁻¹ In this case, the overall mass transfer is dominated by the liquid phase resistance.

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Key word index: Deposition to water, PAH, mass balance.

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Isoprene Emission from Aspen Leaves¹

Influence of Environment and Relation to Photosynthesis and Photorespiration

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ABSTRACT

teoprene emission rates from quaking aspen (Populus tremufoldes Michx.) leaves were measured simultaneously with photosynthesis rate, stomatal conductance, and intercellular CO₂ partial pressure, isoprene emission required the presence of CO₂ or/ O2, but not both. The light response of isoprene emission mission rate paralleled that of photosynthesis. Isoprene emission was inhibited by decreasing ambient O2 from 21% to 2%, only when there was oxygen insensitive photosynthesis. Mannose (10 millimolar) fed through cut stems resulted in strong inhibition of isoprene emission rate and is interpreted as evidence that isoprene biosynthesis requires either the export of triose phosphates from the chloroplast, or the continued synthesis of ATP. Light response experiments suggest that photosynthetically generated reductant or ATP is required for isoprene biosynthesis. Isoprene biosynthesis and emission are not directly linked to glycolate production through photorespiration, contrary to previous reports. isoprene emission rate was inhibited by above-ambient CO2 partial pressures (640 microbar outside and 425 microbar inside the leaf). The inhibition was not due to stomatsi closure. This was established by varying ambient humidity at normal and elevated CO₂ partial pressures to measure isoprene emission rates over # range of stomatal conductances. Isoprene emission rates were inhibited at elevated CO₂ despite no change in stomatal conductance. Addition of abscisic acid to the transpiration stream dramatically inhibited stomatal conductance and photosynthesis rate, with a slight increase in isoprene emission rate. Thus, isoprene emission is independent of stomatal conductance, and may occur through the cuticle. Temperature had an influence on Isoprene emission rate, with the Q_w being 1.8 to 2.4 between 35 and 45°C. At these high temperatures the amount of carbon lost through isoprene emission was between 2.5 and 8% of that assimilated through photosynthesis. This represents a significant carbon cost that should be taken into account in determining midsummer carbon budgets for plants that are isoprene emitters.



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A Comparison of Natural and Man-made Hydrocarbon Emission Inventories Necessary for Regional Acid Deposition and Oxidant Modeling

by

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For Oral Presentation at:

The 79th Air Pollution Control Association Annual Meeting

June 22-27, 1986

Minneapolis, Minnesota

*On assignment from the National Oceanic and Atmospheric Administration, U. S. Department of Commerce A Comparison of Natural and Man-made Hydrocarbon Emission Inventories Necessary for Regional Acid Deposition and Oxidant Modeling

Abstract

The effect of natural hydrocarbon emissions on ozone formation has been a topic of interest for several years and is now receiving additional attention because of the potential influence of ozone in the production of acid species. Because the atmospheric chemistry of sulfur dioxide, nitrogen oxides, and reactive organics is so intricately coupled, natural hydrocarbon emissions have become an important input requirement for both regional acid deposition and oxidant models. A greater emphasis has been placed on treating key chemical components individually in the chemical mechanisms of the models. Applying this concept to emission requirements, there is a greater need for more resolved natural and man-made hydrocarbon emissions estimates.

This paper focuses on natural sources by presenting a method of estimating natural hydrocarbon emissions which is detailed enough to provide quantitive estimates of isoprene and monoterpene emissions from individual vegetation species. This finely gridded natural hydrocarbon emissions inventory was prepared for the northeastern United States and is compared with man-made hydrocarbon emissions over the same area. Natural hydrocarbon emissions represent 60% of the regional hydrocarbon emissions, completely dominating in the non-industrial states. The influence of these natural emissions on the spatial variation of NO_X to HC ratios is presented. The initial concentration ratios of these two species have a significant impact on model predictions of sulfuric and nitric acids, ozone, and hydrogen peroxide. A thorough understanding of the magnitude and distribution of natural hydrocarbon emissions is essential for proper interpretation of regional model predictions. Atmospheric Environment Vol. 24A, No. 3, pp. 449-456, 1990. Printed in Great Britain.

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STATISTICAL IMPLICATIONS OF THE DEPENDENCE BETWEEN THE PARAMETERS USED FOR CALCULATIONS OF LARGE SCALE EMISSIONS INVENTORIES

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(First received 19 October 1987 and in final form 7 September 1989)

Abstract—Development of emissions inventories for large geographic areas is currently based on the use of "mass balance" equations to estimate the emissions from each source. The general equation used states that the instantaneous emission factor, control efficiency, etc. The emission total over a time period T is thus $E = T\Pi U_i$, but is approximated as $\vec{E} = T\Pi U_i$. This gives rise to an error of approximation distinct from and logically prior to the usual errors of estimation found in statistical applications. The time series aspect of the emission parameters has very little effect on the bias of \vec{E} , but the covariance between contemporaneous values of the emission parameters has a large effect. With two emission parameters X and Y, the bias is bounded by $(0, -T\sigma_{XY})$ for a wide variety of time series in X and Y. To date, studies have been unable to detect any dependence between currently used emission parameters; thus values of \vec{E} are approximately unbiased. However, for a roughly realistic time series model, the mean squared error of \vec{E} depends on the correlation between emission parameters one day apart. A conservative approach involves using $\sqrt{MSE} \approx 100\sigma_X\sigma_Y$.

Key word index: Emissions inventory, uncertainty, averaged parameters.



AN CA99(20):161897g Seasonal variation of monoterpenes in the atmosphere of a pine ΤI forest Okouchi, Y.; Okaniwa, M.; Ambe, Y.; Fuwa, K. AU CS Div. Chem. Phys., Natl. Inst. Environ. Stud. LO Ibaraki 305, Japan SO Atmos. Environ., 17(4), 743-50 53-10 (Mineralogical and Geological Chemistry) SC SX 30 DT J CO ATENBP IS 0004-6981 PY 1983 LA Eng AB Seasonal variation of monoterpene concn. in the atm. of a pine forest was measured and is discussed in relation to various environmental factors. The concn. of monoterpenes was low in winter, and higher and more variable in summer and autumn. Rough seasonal variation is explained by temp. differences, but changes from day to day are anticorrelated with O3 concn. The emission rate of monoterpenes from a pine forest was estd. on the basis of atm. concn., assuming that the disappearance of monoterpenes in the forest is governed by atm. reactions.

mal of Atmospheric Chemistry 4 (1986), 63–80.
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BACKGROUND OZONE AND ANTHROPOGENIC OZONE ENHANCEMENT AT NIWOT RIDGE, COLORADO

D. D. Parrish, D. W. Fahey, E. J. Williams, S. C. Liu, M. Trainer, P. C. Murphy, D. L. Albritton and F. C. Fehsenfeld Aeronomy Laboratory, NOAA/Environmental Research Laboratories 325 Broadway, Boulder, CO 80303 USA

 $_{\rm ABSTRACT}$. The mixing ratios for ozone and NO_X (NO \bullet NO₂) have been reasured at a rural site in the United States. From the seasonal and diurnal trends in the ozone mixing ratio over a wide range of NO_{x} levels, we have drawn certain conclusions concerning the ozone level expected at this site in the absence of local photochemical production of ozone associated with NO_x from anthropogenic sources. In the summer (June 1 to September 1), the daily photochemical production of ozone is r_{ound} to increase in a linear fashion with increasing NO_x mixing ratio. For NO_X mixing ratios less than 1 part per billion by volume (ppbv), the daily increase is found to be (17 ± 3) [NO_X]. In contrast, the winter data (December 1 to March 1) indicate no significant increase in the afternoon ozone level, suggesting that the photochemical production of ozone during the day in winter approximately balances the chemical titration of ozone by NO and other pollutants in the air. The extrapojated intercept corresponding to $[NO_x] = 0$ taken from the summer afternoon data is 13% less than that observed from the summer morning data, suggesting a daytime removal mechanism for 03 in summer that is attributed to the effects of both chemistry and surface deposition. No significant difference is observed in the intercepts inferred from the morning and afternoon data taken during the winter.

The results contained herein are used to deduce the background ozone level at the measurement site as a function of season. This background is equated with the natural ozone background during winter. However, the summer data suggest that the background ozone level at our site is elevated relative to expected natural ozone levels during the summer even at low NO_X levels. Finally, the monthly daytime ozone mixing ratios are reported for $0 \leq [NO_X] \leq 0.2$ ppbv, 0.3 ppbv $\leq [NO_X] \leq 0.7$ ppbv and 1 ppbv $\leq [NO_X]$. These monthly ozone averages reflect the seasonal ozone dependence on the NO_X level.

Key words. Tropospheric ozone, photochemistry, nitrogen oxides.

Atmospheric Environment Vol. 14, pp. 79-81. © Pergamon Press Ltd. 1980. Printed in Great Britain. 0004-6981/80 0101-0079 \$02 00 0

AN ESTIMATE OF THE POSSIBLE CONTRIBUTION OF BIOGENIC SOURCES TO AIRBORNE HYDROCARBON CONCENTRATIONS

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(First received 21 December 1978 and in final form 17 July 1979)

The importance of plants as sources of photoreactive hydrocarbons, oxidant precursors, is widely discussed (Coffey and Westberg, 1977). The two main questions appear to be: (1) are natural hydrocarbons emissions large enough to result in significant atmospheric concentrations and (2) do naturally emitted hydrocarbons contribute significantly to ozone formation? This note addresses the first question.

Emission rates for specific hydrocarbon species and total nonmethane hydrocarbons have been measured for several vegetation types (e.g. Table 1). Also, the influence of environmental factors such as light intensity and temperature on emission rates has been studied (Kamiyama *et al.*, 1978; Tingey *et al.*, 1978a, b).

Ordinarily the movement of air in the atmosphere dilutes pollutants emitted into it to concentrations below levels considered dangerous, however let us consider those occasions when weather is dominated

• On assignment from the National Oceanic and Atmospheric Administration.

by a slowly moving anticyclone, when wind speeds are small and when vertical mixing is inhibited by the stability of the overlying air. Under these conditions, in order to make a rough estimate of concentrations of biogenically-produced hydrocarbons which could occur we can use a simple box model (e.g., Peterson 1978):

$$\frac{1}{x}\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{Q}{xh}-k,$$

where

x is the spatial average concentration,

Q is the spatial average source strength,

h is the mixing height,

k is the rate constant for the transformation or decay (ozonolysis or photoxidation) of the material under consideration, and

t is time.

This model is appropriate for sources distributed over a large area or when the wind speed is small.



Not for Resale



JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 95, NO. D9, PAGES 14,049-14,062, AUGUST 20, 1990

Model Calculations of Tropospheric Ozone Production Potential Following Observed Convective Events

KENNETH E. PICKERING,¹ ANNE M. THOMPSON,² RUSSELL R. DICKERSON,³ WINSTON T. LUKE,⁴ DONNA P. MCNAMARA,^{3,5} JAMES P. GREENBERG,⁶ AND PATRICK R. ZIMMERMAN⁶

Photochemical modeling and analysis of field data have been used to evaluate the effects of convective clouds on tropospheric trace gas chemistry. Observations were made during a 1985 field campaign over the rural south-central United States. Meteorological data and measurements of CO. NO, NO, O₃, and hydrocarbons were collected in air surrounding and inside clouds during and immediately following cloud convection. A one-dimensional photochemical model has been used to calculate O₃ production potential before and after cloud redistribution of O₃ precursor gases. Four distinct types of convective events have been analyzed. Fair weather cumulus clouds increase O₃ production in a layer immediately above the boundary layer (to 4 km in the case studied). Outflow from deeper convection can cause enhanced O₃ production in the upper troposphere hundreds of kilometers downstream from the clouds. A comparison of trace gas profiles measured in and around a large cumulonimbus during dissipation shows O3 production in the upper troposphere may be increased fourfold by convection relative to undisturbed air. Convective enhancement of O₃ production for the entire tropospheric column is about 50%. Compared to nonurban continental regions with no convection, the rate of O_3 production potential in air processed by convection is up to 3-4 times greater. Catalysis of O₃ production becomes more efficient when NO becomes more dilute after being transported from the boundary layer to the free troposphere. Free tropospheric NO may also be enhanced by lightning, adding to O3 production, particularly when sufficient hydrocarbons are transported to such locations.

JOURNAL OF GEOPHYSICAL RESEARCH, VOE 95, NO, DS, PAGES 11, 57, 10, 175, 10, 17, 29, 1990

A Physical Model of the Bidirectional Reflectance of Vegetation Canopies 2. Inversion and Validation

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Office for Interdisciplinary Earth Studies, University Corporation for Atmospheric R. search, Boulder, Colorado

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A physically based, analytical model of the bidirectional reflectance of porous media was derived in a companion paper (Verstraete et al., this issue). This model is validated against laboratory and ground-based measurements taken over two vegetation covers, both in the visible and near-infrared spectral regions. An inversion procedure, based on a nonlinear optimization technique, is used to infer the intrinsic optical properties of the leaves, as well as information on the morphology of the canopies, that is, on the geometrical arrangements of these scatterers in space. The model is then used to generate theoretical bidirectional reflectances, using the values of the relevant parameters retrieved from the inversion procedure, and these values compare favorably with the actual observations over the entire range of illumination and observation angles. The values of the parameters retrieved from the inversion procedure are discussed, validated against actual independent measurements, and interpreted in terms of the physical and morphological properties of the vegetation covers.





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AN CA110(18):159578f TI Preconcentration and analysis of atmospheric isoprene and monoterpenes: system automation Riba, Mariel Louise; Tsiropoulos, Nicolas; Clement, Bruno; Golfier, AU Andre; Torres, Liberto CS Ec. Natl. Super. Chim., Inst. Natl. Polytech. LO Toulouse 31077, Fr. J. Chromatogr., 456(1), 165-73 SO SC 59-1 (Air Pollution and Industrial Hygienc) SX 80 DT J CO JOCRAM IS 0021-9673 PY 1988 LA Eng AB As part of a study on terpene hydrocarbons in the biosphere-atm. exchange processes, an entirely automatic device was elaborated for sampling, preconcn., and anal. of isoprene and the principal atm. monoterpenes. This device comprises mainly a gas chromatograph for anal. and a programmable controller for the management of the operations. It permits measurement of the concn. and flux rate of terpenes. Automatic and continuous cycles (sampling-anal.) were carried out over several days. They were characterized by a reproducibility better than 1%.

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	TI	An estimate of the possible contribution of biogenic sources to
		airborne hydrocarbon concentrations
	AU	Peterson, Ernest W.; Tingey, David T.
	CS	Corvallis Environ. Res. Lab., US Environ. Prot. Agency
	LO	Corvallis, OR 97330, USA
l	SO	Atmos. Environ., 14(1), 79-81
	SC	59-5 (Air Pollution and Industrial Hygiene)
l	SX 1	1
	DIJ	
		JUU-0981 1090
	ΤΔ	Fng
l	AR	Using a simple box model and previously reported hydrocarbon
I		emission rates from various vegetation types possible diumal
l		variations of concus, of monoterpenes and isoprene [78-79-5] were
l		estd. under conditions simulating meteorol, situations where weather
I		is dominated by a slowmoving anticyclone. Calcns. indicated that,
I		under certain conditions of atm. stagnation in warm environments.
I		such as during the summer in south eastern United States, biogenic
I		emissions of hydrocarbons may contribute to total airborne
I		hydrocarbon concn.
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API PUBL*309 92 🖿 0732290 0529826 049 1

AN CA103(16):128224p ΤI A simple, efficient device for determining terpenes present as traces in the atmosphere AU Riba, M. L.; Tathy, J. P.; Mathieu, J.; Torres, L. CS Ec. Natl. Super. Chim., Inst. Natl. Polytech. LO Toulouse 31077, Fr. SO Int. J. Environ. Anal. Chem., 20(3-4), 255-63 SC 59-1 (Air Pollution and Industrial Hygiene) SX 80 DT J CO IJEAA3 IS 0306-7319 PY 1985 LA Eng AB Natural hydrocarbons, such as isoprene [78-79-5] and the monoterpenes, play an important role in the phys. chem. of the atm. because of their high reactivity; however, their true contribution to the natural chem. system has not yet been clearly defined as the seasonal variations in their concns. are not sufficiently accurately known due to their low content in the atm. (a few hundredths of a ppb to a few ppb). An anal. procedure which enables quant. trapping to be carried out together with excellent chromatog. sepn. consists of enrichment on adsorbents followed by very rapid thermal desorption and instantaneous chromatog, injection without further cryogenic trapping. The adsorption-desorption cycle does not reduce the efficiency of the chromatog. scpn. and does not bring about any decompn. of these highly reactive plant oils.

AN CA102(4):31056b Sampling and analysis of monoterpene hydrocarbons in the atmosphere TI with Tenax gas chromatographic porous polymer Roberts, J. M.; Fehsenfeld, F. C.; Albritton, D. L.; Sievers, R. E. AU CS Dep. Chem., Univ. Colorado LO Boulder, CO 80303, USA Identif. Anal. Org. Pollut. Air, 371-87. Edited by: Keith, Lawrence SO H. Butterworth: Boston, Mass. SC 59-1 (Air Pollution and Industrial Hygiene) SX 80 DT C CO 52MKAX PY 1984 LA Eng AB The sampling of monoterpenes (A) with Tenax GC porous polymer in air anal. is discussed. Destruction of A by O3 during sampling was .ltoreq.6% (as worst case, for d-limonene [5989-27-5]) for sample vol. <1.5 L and O3 concn. 40 ppb. The storage of ambient air samples for ltoreq.1 mo showed no loss of A with time. Anal. of the std. contg. 1-2 ng of each of the A species yielded relative std. deviations of 1.3-3.2%. Replicate samples collected within 20 min of one another at the same locations under the same meteorol. conditions yielded an overall precision for A anal. of .+-.10% at .gtoreq.30 parts per trillion for the individual compds.

- AN CA100(14):107018x
- TI Measurement of monoterpene hydrocarbons at Niwot Ridge, Colorado
- AU Roberts, J. M.; Fehsenfeld, F. C.; Albritton, D. L.; Sievers, R. E.
- CS Aeron. Lab., NOAA
- LO Boulder, CO 80303, USA
- SO JGR, J. Geophys. Res., [Sect.] C, 88(C15), 10667-78
- SC 53-10 (Mineralogical and Geological Chemistry)
- DT J
- CO JJGADR
- IS 0196-2256
- PY 1983
- LA Eng
- AB Mr

B Measurements of atm. monoterpene hydrocarbons were made at a site in the Colorado mountains. The research was undertaken to examine the influence of the compds. on the photochem. of the troposphere. A sampling technique was developed using Tenax GC porous polymer traps with anal. by capillary gas chromatog. and detection by flame ionization and mass spectrometry. Pos. identification of 6

monoterpene hydrocarbons (.alpha.-pinene, camphene, .beta.-pinene, myrcene, .DELTA.-3-carene, and d-limonene) was obtained, as well as tentative identification of .alpha.-thujene and .beta.-phellandrene.

A definite seasonal trend was evident in the av. monoterpene mixing ratios. The summertime av. was 0.30 ppb by vol. for the sum of the

5 major identified monoterpenes (.bcta.-pinene, .alpha.-pinene, .DELTA.-3-carene, camphene, and d-limonene), with a high degree of constancy in relative ratios of each throughout the summer months. Wintertime measurements gave mixing ratios below the detection limits (0.001 ppb by vol. of an individual compd.). Simultaneous measurements of O3, NO, NO2, and monoterpene hydrocarbons allowed examn. of the contribution of monoterpene photooxidn. to O3 prodn. Based on reported modeling studies, monoterpenes were estd. to be a small source of O3, insufficient to account for the relatively high

O3 mixing ratios (>80 ppb by vol) sometimes obsd. at this sampling site.



- TI Monoterpene hydrocarbons in the nighttime troposphere
- AU Roberts, James M.; Hahn, Carole J.; Fehsenfeld, Fredrick C.; Warnock, James M.; Albritton, Daniel L.; Sievers, Robert E.
- CS Aeron. Lab., Natl. Ocean. Atmos. Adm.
- LO Boulder, CO 80303, USA
- SO Environ. Sci. Technol., 19(4), 364-9
- SC 59-2 (Air Pollution and Industrial Hygiene)
- SX 53
- DT J
- CO ESTHAG
- IS 0013-936X
- PY 1985
- LA Eng
- OS CJAČS
- AB Monoterpene hydrocarbons were measured during the night at a rural site in the Rocky Mountains. The compds. pos. identified and quantified were .alpha.-pinene [80-56-8], camphene [79-92-5], .beta.-pinene [127-91-3], .DELTA.3-carene [13466-78-9], and d-limonene [5989-27-5]. The av. sum of the mixing ratios of the 5 compds. measured during the nighttime between July and Oct. 1982, was 0.63 ppb (vol.), which was about twice the corresponding daytime av. sum. No significant difference was obsd. between day and night in the relative concns. of the individual monoterpenes. Increased atm. stability, with attendant reduced mixing and diln. during the night, was found to contribute to the larger nighttime vs. daytime monoterpene mixing ratios. Nighttime atm. stability was also responsible for the observation of O3 diminution and a corresponding inverse relationship between monoterpene and O3 mixing ratios. The results indicate that, at this site, transport rather than chem. dets. the concns. of the monoterpenes. The ultimate fate of the monoterpenes is chem. reaction with O3, OH, or NO3. Because of the differences in rate consts. of reactions between the various monoterpenes and the above species, chem. reactions should cause systematic changes in the relative concns. of monoterpenes, which are characteristic of the reactant species involved.





API PUBL*309 92 🖿 0732290 0529832 342 🎟



AN CA	11	13(1	12):	102530s
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- TI Organic matter of the troposphere V: Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations
- AU Simoneit, Bernd R. T.
- CS Coll. Oceanogr., Oregon State Univ.
- LO Corvallis, OR 97331, USA
- SO J. Atmos. Chcm., 8(3), 251-75
- SC 59-2 (Air Pollution and Industrial Hygicne)
- SX 53
- DT J
- CO JATCE2
- IS 0167-7764
- PY 1989
- LA Eng

Org. matter in tropospheric aerosols is derived from 2 major sources AB and is admixed depending on the geog. area. These sources are biogenic detritus and anthropogenic emissions. The biogenic materials in the solvent-extractable org. matter consist predominantly of higher plant waxes, with lesser amts. of resin, and microbial detritus, and the anthropogenic components are primarily vehicular emissions (e.g., oils, soot, etc.) and input from combustion (e.g., charcoal, thermally-altered biogenic matter, Both biogenic detritus and anthropogenic emissions contain etc.). org. compds. (C12-40+), which can be identified with unique and distinguishable distribution patterns. Mol. compn. anal. were applied to such exts. after suitable chem. sepn. into subfractions (i.e., hydrocarbons, ketones, aldehydes, carboxylic acids, alcs., and wax esters). Both homologous compd. series and specific natural products (e.g., phytosterols, terpenes, etc.) are identified as mol. Aerosols from rural and remote areas in the western US. markers. South America, Nigeria, and Australia were analyzed and all contained predominantly plant waxes. The loadings of hydrocarbons were .apprx.10-1400 nm/m3 of air, of fatty acids from 10-450 ng/m3 and of fatty alcs. from 10-1650 ng/m3. These higher mol. wt. lipids primarily from flora comprise a major component of the org. C in rural and remote aerosols. They are thus important indicators for regional biogenic sources in the global cycling of org. C.



JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 93, NO. D12, PAGES 15,861-15,878, DECEMBER 20, 1988

Measurements of Selected C_2 - C_5 Hydrocarbons in the Troposphere: Latitudinal, Vertical, and Temporal Variations

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WILLIAM VIEZEE AND LOUIS J. SALAS

Geoscience and Engineering Center, SRI International, Menlo Park, California

Results are presented on the tropospheric distribution of C_2 - C_3 hydrocarbons based on (1) shipboard measurements over the eastern Pacific Ocean from latitude 47 N to 47 S. (2) ground-based measurements at a remote coastal site in northern California (39 N), and (3) airborne studies of the troposphere over Colorado and over the eastern Pacific Ocean (38 N) during the summer and winter seasons. A total of 1077 hydrocarbon samples were processed during these comprehensive field programs. In agreement with previous studies, the shipboard measurements show large north-to-south gradients for virtually all nonmethane hydrocarbons (NMHCs) and clearly indicate their northern hemispheric sources. Ethane, the most abundant NMHC, is present at a concentration of 2 ppb in the northern hemisphere (NH) mid-latitudes, with southern hemisphere (SH) concentrations of about 0.3 ppb. All other NMHC concentrations are in the sub-ppb range. The measurements at the remote coastal site of Point Arena. California, show that NMHC concentrations can decrease by a factor of 2 or more during the passage of cold fronts in winter and spring. During these events the behavior of NMHCs is strongly correlated with primary anthropogenic species (e.g., CH₂Cl₂, CH₂ClCH₂Cl, and CH₃CCl₃) as well as secondary oxygenates (e.g., peroxyacetyl nitrate (PAN) and ozone) Aircraft measurements of NMHC concentrations made over Colorado and near the coastal zone of northern California were higher over land than over the ocean in the lower troposphere (< 5 km) Upper tropospheric concentrations were found to be lower and. in general, much less spatially variable than those present in the lower troposphere Because of the differences in NMHC concentrations between ocean and land and between lower and upper troposphere evident in the measurements, it is possible that weather systems associated with significant horizontal and vertical transport can cause large temporal and spatial variations in NMHC concentrations on local and regional scales

- AN CA104(5):31748v
- TI Secretion of volatile substances by coniferous plants and their flammability hazards
- AU Stepen, R.; Sukhinin, A.
- CS Inst. Lesa Drevesiny
- LO Krasnoyarsk, USSR
- SO Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Biol. Nauk, (2), 47-52
- SC 11-1 (Plant Biochemistry)
- DT J
- CO ISBNBN
- IS 0568-6547
- PY 1985
- LA Russ
- AB Amts. of volatile substances released by conifers were higher in young than old plantings, and they were low in May, increased to a max. at the end of June to the beginning of July, and decreased gradually to the end of Sept. when they reached a min. Temp, was the main abiotic factor affecting the content of the volatile substances. The order of volatile substance release by vegetative organs of conifer trees was cedar > pine > fir .apprxeq. larch > spruce. Increasing the temp. by 10.degree. (the Q10 factor) resulted in an .apprx.2-fold increase in release of terpene volatiles. A large increase in the concn. of the org. products in the atm. (1-4 g/m3) may greatly increase the flammability hazard. The peak assocd, with compds, released at 58-60, degree, resulted from the large amt. of monoterpene hydrocarbons among the released volatiles, the release of a mixt. of volatiles rich in O-contg. terpenes was assocd, with a max, at 70.degree., and a release of volatiles rich in other terpenes, including sesquiterpenes, was assocd. with a max. at 80.degree. When the needle moisture decreased, the max. sesquiterpene release was obsd. at 66-68.degree.. Terpenes constituted .gtoreq.90% of the volatiles released, and monoterpenes constituted 65-85% of all terpenes. Of the monoterpenes released 15 compds. were identified, with .alpha.-pinene being the main one; of the 28 substances of cedar volatiles 23 were identified. The volatile substances released are not self-combustible but may be ignited easily. Their accumulation in young plantings may greatly increase fire hazards in forests.

Plant Physiol. (1971) 48, 50 52

Identification and Quantitative Analysis of the Volatile Substances Emitted by Maturing Cotton in the Field

Received for publication December 3

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ABSTRACT

When atmosphere from cotton plants (Gossypium hirsutum L., var. Deltapine Smoothleaf) was condensed by passing it over the expansion coil of an air conditioner and three 1-hour collections per day (early morning, noon, and late afternoon) were made, the total essential oils were found to consist of 50 to 60% β -bisabolol (I_k 1660) and γ -bisabolene (I_k 1550) and 30 to 40% geraniol (I_k 1250), myrtenal (I_k 1328), nerolidol (I_k 1520), and β -caryophyllene oxide (I_k 1590). As the plant matured, trans-2-hexanol was produced in concentrations of 7 to 27%. Before fruiting, β -bisabolol made up as much as 60% of the total essential oil transpired by the plants, and as the concentration of β -bisabolol increased, that of γ -bisabolene decreased. Planta (1981) 152:565-570



Effects of environmental conditions on isoprene emission from live oak

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Abstract. Live-oak plants (Quercus virginiana Mill.) were subjected to various levels of CO2, water stress or photosynthetic photon flux density to test the hypothesis that isoprene biosynthesis occurred only under conditions of restricted CO₂ availability. Isoprene emission increases as the ambient CO₂ concentration decreased, independent of the amount of time that plants had photosynthesized at ambient CO₂ levels. When plants were water-stressed over a 4-d period photosynthesis and leaf conductance decreased 98 and 94%, respectively, while isoprene emissions remained constant. Significant isoprene emissions occurred when plants were saturated with CO_2 , i.e., below the light compensation level for net photosynthesis (100 μ mol m⁻² s⁻¹). Isoprene emission rates increased with photosynthetic photon flux density and at 25 and 50 μ mol m⁻² s⁻¹ were 7 and 18 times greater than emissions in the dark. These data indicate that isoprene is a normal plant metabolite and not - as has been suggested - formed exclusively in response to restricted CO₂ or various stresses.

Key words: Carbon dioxide and isoprene emission – Isoprene – Light and isoprene emission – Quercus – Water stress. 112 DAVID T. TINGEY ET AL.

Physiol. Plant. 47: 112-118. 1979

The Influence of Light and Temperature on Isoprene Emission Rates from Live Oak

By

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(Received 12 March, 1979; revised 5 June, 1979)

Abstract

There is a growing awareness of the role of vegetation as a source of reactive hydrocarbons that may serve as photochemical oxidant precursors. A study was designed to assess independently the influence of variable light and temperature on isoprene emissions from live oak (Quercus virginiana Mill.). Plants were conditioned in a growth chamber and then transferred to an environmentally controlled gas-exchange chamber. Samples of the chamber atmosphere were collected; isoprene was concentrated cryogenically and measured by gas chromatography. A logistic function was used to model isoprene emission rates. Under regimes of low temperature (20°C) or darkness, isoprene emissions were lowest. With increasing temperature or light intensity, the rate of isoprene emission increased, reaching maxima at 800 μ E m⁻² s⁻¹ and 40-44°C, respectively. Higher temperatures caused a large decrease in emissions. Since the emissions of isoprene were light-saturated at moderate intensities, temperature appeared to be the main factor controlling emissions during most of the day. Carbon lost through isoprene emissions accounted for 0.1 to 2% of the carbon fixed during photosynthesis depending on light intensity and temperature.

Key words: Quercus virginiana — isoprene — hydrocarbon emission.

Plant Physiol. (1980) 65, 797-801 (1032-0889/80/65/0797/05/\$00.50/0

Influence of Light and Temperature on Monoterpene Emission Rates from Slash Pine

Received for publication September 17, 1979 and in revised form December 26, 1979

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ABSTRACT

There is a growing awareness of vegetation's role as a source of potentially reactive hydrocarbons that may serve as photochemical oxidant precursors. This study assessed the influence of light and temperature, independently, on monoterpene emissions from slash pine (Pinus elliottii Fugelm.). Plants were preconditioned in a growth chamber, then transferred to an environmentally controlled gas exchange chamber. Samples of the chamber atmosphere were collected; the monoterpenes were concenscated cryogenically and measured by gas chromatography. Five monoterpenes (a-pinene, B-pinene, myrcene, limonene, and B-phellandrene) were present in the vapor phase surrounding the plants in sufficient quantity for reliable measurement. Light did not directly influence monoterpene emission rates since the emissions were similar in both the dark and at various tight intensities. Monoterpene emission rates increased exponentially with temperature (i.e. emissions depend on temperature in a log-linear manner). the summed emissions of the five monoterpenes ranged from 3 to 21 micrograms C per gram dry weight per hour as temperature was increased from 20 to 46 C. Initially, emission rates from heat-stressed needles were similar to healthy needles, but rates decreased 11% per day. Daily carbon loss through monoterpene emissions accounted for approximately 0.4% of the carbon fixed during photosynthesis.



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JOURNAL OF GEOPHYSICAE RESEARCH, VOE, 95, NO, D8, PAGES 11, 755, 11, 765, JULY 20, 1886

A Physical Model of the Bidirectional Reflectance of Vegetation Canopies 1. Theory

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BERNARD PINTY² AND ROBERT E. DICKINSON

National Center for Atmospheric Research, Boulder, Colorado

An analytical expression for the bidirectional reflectance field of a vegetation canopy is derived from physical and geometrical considerations of the transfer of radiation through a porous medium. The reflectance pattern is shown to depend explicitly on the optical properties of the scatterers (for example, leaves), and on the structural parameters of the canopy, such as the statistical distribution of the orientation of these scatterers, the leaf area density, the size of the scatterers and their interspacing. This theory provides a simple and accurate way to understand the anisotropy of the radiation field over a vegetated surface. It can be useful for modeling applications (for example, the albedo is a by-product which can be numerically estimated), as well as for extracting some of the structural and physical properties of the surface. These applications are discussed in the accompanying paper (Pinty et al., this issue).

The Application of Forest Classification from Landsat Data as a Basis for Natural Hydrocarbon Emission Estimation and Photochemical Oxidant Model Simulations in Southeastern Virginia

John Salop Virginia State Air Pollution Control Board

N. T. Wakelyn Langley Research Center National Aeronautics and Space Administration Gerald F. Levy Old Dominion University

Elizabeth M. Middleton, Janette C. Gervin Eastern Regional Remote Sensing Applications Center National Aeronautics and Space Administration

The possible contribution by natural hydrocarbon emissions to the total ozone budget recorded in the Tidewater region of southeastern Virginia during the height of the summer period was examined. Natural sources investigated were limited to the primary HC emitters and most prevalent natural vegetation, the forests. Three forest types and their areal coverage were determined for Region VI of the Virginia State Air Pollution Control Board using remotely sensed data from Landsat, a NASA experimental earth resources satellite. Emission factors appropriate to the specific types (coniferous 0.24 imes 10¹³, mixed 0.63 \times 10¹³, deciduous 1.92 \times 10¹³ µg/h), derived from contemporary procedures, were applied to produce an overall regional emission rate of 2.79 \times 10¹³ µg/h for natural non-methane hydrocarbons (NMHC). This rate was used with estimates of the anthropogenic NO, and NMHC loading, as input into a photochemical box model. Additional HC loading on the order of that estimated to be produced by the natural forest communities was required in order to reach certain measured summer peak ozone levels as the computer simulation was unable to account for these measured episodic levels on the basis of the anthropogenic inventory alone.





API PUBL*309 92 📟 0732290 0529848 70T 📟

AN CA113(6):45504k Terpenes in the atmosphere TI Sasai, Haruo; Satsumabayashi, Hikaru; Ueda, Hiromasa AU CS Naganoken Eisei Kogai Kenkyusho LO Nagano, Japan Nagano-ken Eisei Kogai Kenkyusho Kenkyu Hokoku, 11, 12-15 SO 59-2 (Air Pollution and Industrial Hygiene) SC SX 11 DT J CO NKEHDL 0387-9070 IS PY 1988 LA Japan The atm. concns. of terpenes measured in the residential areas of AB Nagano City, Japan, in the summer of 1984 showed that the isoprene concn. was higher during the day and the monoterpene concn. was higher at night. From the relations between the terpene concn. ratios and atm. oxidant concn., the prodn. rate of .alpha.-pinene at night was detd. to be of the same order of magnitude as that of isoprene, but 6-fold that of .beta.-pinene. Based on the terpene-O3 reactions, the prodn. rate of terpenes was higher during the day than at night, with isoprene and .alpha.-pinene daytime prodn. rates of 2.39 and 0.56 .mu.g/m3-h, resp.

United States Environmental Protection Agency Environmental Sciences Research Laboratory Research Triangle Park NC 27711

Research and Development

EPA-600/S3-82-010 June 1982

Project Summary

Measurement of Loblolly Pine Terpene Emissions

R. L. Seila, R. R. Arnts, R. L. Kuntz, F. L. Mowry, K. R. Knoerr, and A. C. Dudgeon

A new method for quantifying biogenic hydrocarbon emission rates without disturbing the vegetation is presented. An energy balance/Bowen ratio approach was used to estimate fluxes of α -pinene from measurements of net radiation and vertical gradients of α -pinene, temperature, and water vapor above a loblolly pine forest canopy. The mean flux for 20 determinations ranging from 19 to 84 $\mu g/m^2/min$ was 41 $\mu g/m^2/min$. This method was compared to an enclosure method, in which foliage is enclosed with a Teflon bag for emission rate determinations. For this comparison, the energy balance/Bowen ratio flux values were converted to emission rate units of $\mu g \alpha$ -pinene/g dry needle mass/hr using site-specific biomass factors. Seventeen enclosure method determinations from mature loblolly pine trees yielded a median value of 4.7 μ g/g/hr over a range of 1.2 to $32 \mu g/g/hr$. While both methods displayed relatively high variances, the variance of the enclosure method was considerably higher than that of the energy balance/Bowen ratio method. There was no statistically significant difference between the results of the two methods.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering informa Not for Resale ack).

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AN CA99(6):42697g TI Ambient concentrations of hydrocarbons from conifers in atmospheric gases and aerosol particles measured in Soviet Georgia Shaw, Robert W., Jr.; Crittenden, Alden L.; Stevens, Robert K.; AU Cronn, Dagmar Rais; Titov, Vitali S. CS Environ. Sci. Res. Lab., US Environ. Protec. Agency LO Research Triangle Park, NC 27711, USA Environ. Sci. Technol., 17(7), 389-95 SO SC 59-2 (Air Pollution and Industrial Hygiene) DT J CO ESTHAG IS 0013-936X PY 1983 LA Eng OS CJACS AB A 1-mo field study was performed in the mountains of the Georgian USSR in July, 1979, to study the properties of aerosols in a relatively clean environment contg. naturally emitted hydrocarbons, in this case, terpenes from evergreen forests. Gas chromatog. anal. of gaseous hydrocarbons and mass spectrometric anal. of aerosol particles were performed. Terpenes were present in the gas phase at an estd. av. concn. of 40 ppb C. The estd. upper limits of terpenes and their reaction products found in aerosol particles were of the order of 1% of the corresponding gas-phase terpene concns. The amts. of natural org. materials were much smaller than amts. of sulfate in the aerosol particles and were relatively insignificant with respect to visibility.

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A COMPUTER SYSTEM TO CALCULATE BIOGENIC EMISSIONS

VOLUME I: TECHNICAL ASPECTS

by -

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ATMOSPHERIC SCIENCES RESEARCH LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY RESEARCH TRIANGLE PARK, NC 27711

ABSTRACT

To assess the contribution of anthropogenic (man-made) hydrocarbons to air pollution, the contribution of biogenic (naturally occurring) hydrocarbons must be known. The Biogenic Emissions Software System (BESS) was developed to generate biogenic emissions inventories for important plant species and emission species throughout large-scale gridded regions. A need exists for such a comprehensive system, because discrepancies have occurred between measured ambient levels of biogenic hydrocarbons and levels predicted by earlier models (Zimmerman, 1979a).

BESS was designed with two goals in mind: (a) produce a biogenic emissions inventory compatible with the anthropogenic hydrocarbon emissions inventory for the Regional Oxidant Model (ROM), thus providing a means for determining whether biogenic emissions are significantly contributing to ozone formation, and (b) provide a generalized framework for building gridded biogenic inventories of other types for a variety of applications.

The system performs the following functions.

- Generates hourly gridded emissions compatible with the ROM
 - (a) for a variable number of hydrocarbon emission species;(b) from a variable number of plant species, leaf litter,
 - and surface waters;
 - (c) for any latitude/longitude-based grid system.
- Applies temporal variations to emission factors on a diurnal and/or seasonal basis.
- Incorporates variations in temperature and solar radiation into emission factors.
- Provides spatial resolution compatible with the ROM
- Allows for future modification of emission factors to incorporate submodel calculations, including leaf temperature, foliar density, soil types, moisture availability, and disease prevalence.
- Provides summary reports of emissions by grid cell, county, U.S. Forest Service region, and state.

BESS is designed as a series of processor modules; each processor performs a separate calculation. The system's modular design will facilitate future changes in the software.

Volume I of this report describes the calculations on which the system is based and the preparation of data sources. Volume II contains the functional requirements of each software processor module.

This report was submitted in partial fulfillment of contract number GSA-IAG DW930026-01-01 (Task B64A) by Computer Sciences Corporation, under the sponsorship of the U.S. Environmental Protection Agency. This report describes work completed as of June, 1986.

AN CA108(22):190258j TI Measurements of atmospheric hydrocarbons and biogenic emission fluxes in the Amazon boundary layer AU Zimmerman, P. R.; Greenberg, J. P.; Westberg, C. E. CS Natl. Cent. Atmos. Res. LO Boulder, CO, USA SO J. Gcophys. Res., D: Atmos., 93(D2), 1407-16 SC 53-10 (Mineralogical and Geological Chemistry) DT J CO JGRDE3 PY 1988 LA Eng AB Tropospheric mixing ratios of CH4, C2-10 hydrocarbons, and CO were measured over the Amazon tropical forest near Manaus, Amazonas, Brazil, in July and August 1985. The measurements, consisting mostly of altitude profiles of these gases, were all made within the atm. boundary layer .ltoreq.1000 m above ground level. Data characterize the diurnal hydrocarbon compn. of the boundary layer in this tropical forest area. Biogenic emissions of isoprene control hydroxvl radical concns. over the forest. Biogenic emission fluxes of isoprene and terpenes are estd. to be 25,000 .mu.g/m2/day and 5600 .mu.m/m2/day, resp. This isoprene emission is equiv. to 2% of the net primary productivity of the tropical forest. Atm. oxidn. of biogenic isoprene and terpene emissions from the Amazon forest may account for daily increases of 8-13 ppb for CO in the planetary boundary layer.

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AN CA96(2):14807n TI Ouantitation of biogenic hydrocarbon emissions Zimmerman, Patrick; Moore, Barry AU CS Natl. Cent. Atmos. Res. LO Boulder, CO, USA CHON Photochem. Troposphere, Notes Colloq., Issue NCAR/CQ-7+1980-ASP SO , 88-90. Natl. Cent. Atmos. Res.; Boulder, Colo. SC 80-6 (Organic Analytical Chemistry) SX 9.53 DT C CO 46RKA7 PY 1980 LA Eng A sampling method is described for gas chromatog, quantitation of AB volatile hydrocarbon emission rate from all biol. sources. The area of soil, water, or vegetation of interest is enclosed in a small bag and samples are taken immediately (as background) and after a short interval (perhaps 5 min). Diln. of a known vol. of an appropriate std. gives the sampling vol. Samples are pumped into 4-L stainless steel vessels to approx. 15 psig, and are analyzed by gas chromatog. with flame ionization detection. Results are expressed as .mu.g m-2 h-1 or as .mu.g (leaf biomass)-1 h-1, as appropriate.

Chemosphere No. 4, pp 163 - 168, 1972. Pergamon Press. Printed in Great Britain.

ATMOSPHERIC PHOTOCHEMICAL REACTIVITY OF MONOTERPENE HYDROCARBONS

REPRINT

CONLEGATION

346

H. H. Westberg and R. A. Rasmussen

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(Received in USA 28 April 1972; received in UK for publication 14 July 1972)^{(TO.4 STATE} In recent years numerous studies have been conducted to define hydrocarbon reactivity under conditions of atmospheric photochemical oxidation¹⁻⁴. Generally, these studies have concentrated on the lower molecular weight hydrocarbons (<C₁₀) which arise primarily from sources associated with the internal combustion engine. In contrast to this area which has been extensively researched, a second, but little investigated group of hydrocarbons in the atmosphere are the volatile terpene emissions from plants. Several monoterpene hydrocarbons have been shown to exist in the atmosphere and published estimates of these emissions on a global basis indicate that this source is responsible for millions of tons annually^{5,6}. The fate of these natural hydrocarbons remains essentially undetermined and, except for a few individual compounds, the atmospheric photochemical reactivity of volatile terpenes has not been studied.

In conjunction with an overall program of identification and quantification of volatile organic compounds in non-urban environments we have examined the reactivity of a number of monoterpene hydrocarbons that are known or expected to be present in ambient forest air. The hemiterpene isoprene was also included since it has recently been shown to be emitted by several species of plants ⁷. Our study has focused on the reactivity of terpenes in the presence of nitrogen oxides and light consisting of wavelengths characteristic of natural sunlight. In terms of techniques and apparatus, the experimental procedure has been patterned after that employed for the determination of hydrocarbon reactivity in urban areas. A major experimental difference, of course, is the necessity of employing much lower concentrations of terpenic hydrocarbons and nitrogen oxides in order to simulate the atmospheric photochemical reactions in unpolluted non-urban air. Studies in this laboratory indicate that on an individual basis, monoterpene hydrocarbon concentrations of at most in the low ppb range⁸. Nitrogen oxides are believed to be present in concentrations of

AN CA89(6):46733g Measurement of terpenes and other organics in an Adirondack Mountain ΤI pine forest AU Whitby, Robert A.; Coffey, Peter E. New York State Dep. Environ. Conserv. CS LO Albany, N. Y., USA SO J. Geophys. Res., 82(37), 5928-34 SC 53-10 (Mineralogical and Geological Chemistry) DT J CO JGREA2 IS 0022-1406 PY 1977 Eng LA AB The total terpene concn. beneath the canopy of an eastern US coniferous forest was of the order of 50 .mu.g/m3. Similar measurements within the forest but outside the canopy was 3-32 .mu.g/m3. Two samples collected at a mountain summit above the tree line contained 7 and 27 .mu.g/m3 total terpenes. Downwind from the coniferous forest in an area of deciduous vegetation, the mean morning total terpene level was 4 and increased to 11 .mu.g/m3 during the afternoon. Unidentified species, primarily in the C5-C9 range, were obsd. in total concns. which averaged approx. twice the sample total terpene value. A concn. range of 8-130 .mu.g/m3 for C5-C10 ors. was found in rural atm. in the Adirondack Mountain region of New York State. The majority of obsd. orgs. are of natural origin.

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API PUBL*309 92 🗰 0732290 0529858 659 📟

INVESTIGATION OF THE HOLE OF NATURAL EVEROCARBONS IN FROTOCHERICAL SHOG FORMATION IN CALIFORNIA

Final Report

Contract No. A0-056-32

California Air Resources Board

February 1983

Principal Investigator Dr. Arthur M. Winer

Program Managers Mr. Dennis R. Fitz Dr. Faul R. Miller

Program Research Staff Dr. Roger Atkinson Mr. David E. Brown Dr. William P. L. Carter Ms. Margaret C. Dodd Mr. Claude W. Johnson Hr. Claude G. Jonson Ms. Harlyce A. Myers Mr. Kurt R. Heisess Ms. Hinn P. Poe Dr. Edgar R. Stephens

STATEWIDZ ATR POLLUTION RESEARCH CENTER UNIVERSITY OF CALIFORNIA RIVERSIDE, CALIFORNIA 92521

ABSTRACT

A asjor uncertainty in present emission inventories for California's urban airsheds is the lack of data concerning reactive organics (ROG) from vegetation; the contribution of such emissions to formation of photochemical air pollution has been the subject of considerable controversy. In particu-lar, an experimentally determined, "airshed-specific" estimate of such emis-sions has not been available for the California South Coase Air Basin (CSCAB) as an input to the Basin's Air Quality Hanagement Plan. In order to acquire the mecassary data for the CSCAB, we designed and implemented a three-tisred, stratified, random sampling approach, which could be applied to other airsheds as well. This approach involved: (a) quantita-tive assessments of the area coverage of vegetation in randomly selected sample areas within the CSCAB urban area, using a combination of high altitude (MASA 0-2) and low altitude, high resolution, color infrared imagery; (b) field determinations of the distribution and green leaf mass of the trees, shrubs and ground covers found in the selected sample areas; and (c) experi-sental measurments of emission rates of isoprens and monoterpenes from the most abundant natural and oransental species found in the CSCAB. From these coordinated studies several significant data bases were generated which were evon previously available. These include: • Experimentally determined rates of emission of isoprens and mono-terpense for wort than 60 plant species indigenous to Southern California. • The first detailed survey of wegetation species composition and dis-tribution in the urban portion of the Los Angeles Basin. • Development of last mass constants for -50 of the species identified in the study area.

in the study area.

 bewadparet of leaf mass constants for ~50 of the species identified in the study area.
a Acquisition of low altitude, high resolution color infrared izagery for 20 rendoaly selected areas of the Esin.
Estimates of total green leaf mass and total percent cover by vegeta-tion in the study area.
Using these data, estimates of gmission strengths of isoprene and nono-terpenes were derived for a 2600 km urban area. These were combined with results for the native cossels asge and chaparral communities in the foothills surrounding Los Angelas. The total inventory for isoprene and monoterpenes emitted from vegetation in the 4500 km² study area during a summer day ranged from ~51 to ~60 tons day² depending upon the specific data analysis spoloy-ed. The higher value, and a "worst case" upper limit of 93 tons day⁻¹, were somoterpenes at levels corresponding to the detection limit of our chroma-tographic techniques. Since the study area encompassed 69.42 of the total anthropogenic ROC emitted from anthropogenic sources in the same to ~1200 tons day⁻¹ drocarbons emitted by vegetation may be compared to ~1200 tons day⁻¹ of ROC emitted from anthropogenic sources in the same

srea. So that detailed computer modeling of the impacts of ROG emissions from vegetation can be made, our emissions inventory is available in a format consistent with the grid system employed for the emission inventory assembled for anthropogenic sources in the 1962 AORD for the CSCMS. While detailed airshed modeling was beyond the scope of this program, we have carried out "EXM-type calculations. The results suggest that isopreme and monoterpose emissions in the CSCMS will contribute no more than, and probably much less than, a few tens of a part per billion (ppb) of O₃, under conditions which correspond to the production of several hundred ppb O₃ from anthropogenic ROG.

HYDROCARBON EXISSIONS FROM VEGETATION

FORMED IN CALIFORNIA'S CENTRAL VALLEY

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ABSTRACT

1.

An essential database for modeling photochemical air pollution in California's Central Valley is a reliable gridded emission inventory for reactive organic gases (ROG). To date, however, there has been a lack of quantitative information concerning the amounts of organic gases emitted from natural sources, particularly vegetation, in the Sacramento Valley and San Joaquin Valley Air Basins. To address this need, we have measured the rates of emission of speciated hydrocarbons from more than thirty of the most important (based on acreage) agricultural and natural plant types relevant to California's Central Valley.

These measurements employed flow-through Teflon chambers, solid adsorbent/thermal desorption sample collection, and the close coupling of gas chromatography (GC) and GC-mass spectrometry (GC/MS) for compound identification and quantitation. Emission rate protocols were conducted in the summers of 1988 and 1989 on plant specimens grown at UC Riverside according to standard agricultural practices. Some four dozen individual compounds were identified as emissions from the agricultural and natural plant species studied. In addition to isoprene and the monoterpenes, sesquiterpenes, alcohols, acetates, aldehydes, ketones, ethers, esters, alkanes, alkanes and aromatics were all observed. Data obtained in this study demonstrated again that there can be large variations in emission rates from a single specimen of a given plant species, as well as from multiple specimens of a cultivar.

Mean emission rates for total monoterpenes ranged from none detected in the case of beans, grapes, rice and wheat, to as high as 25-67 $\rm ug\ hr^{-1}$ gm⁻¹ for pistachio and tomato. Other agricultural species exhibiting substantial rates of emission of monotervenes included carrot, cotton. lemon, orange and walmut. All of the agricultural crops and natural plant species for which full sampling protocols were conducted showed total assigned plant emission (TAPE) rates above the detection limits in this study, with a range between 0.1 and 70 μ g hr⁻¹ gs⁻¹. Based on the measured TAPE rates and available acrease data. it appears that emissions from tomato, rice, grape, cotton, alfalfa, and irrigated pasture are likely to be important components of a Central Valley agricultural emissions inventory, and that aggregated emissions from nut and fruit trees may also be important.
API PUBL*309 92 🛲 0732290 0529860 207 🎟

- AN CA100(23):188758p
- TI Terpenes emitted from trees
- AU Yatagai, Mitsuyoshi
- CS Forest. For. Prod. Res. Inst.
- LO Ibaraki 305, Japan
- SO Mokuzai Gakkaishi, 30(2), 190-4
- SC 11-I (Plant Biochemistry)
- DT J
- CO MKZGA7
- IS 0021-4795
- PY 1984
- LA Eng
- AB Monoterpenes in the atm., emitted from 7 Eucalyptus species, were collected, and the followings were identified: .alpha.-pinene, .beta.-pinene, sabinene, myrcene, .alpha.-terpinene, limonene, 1,8-cineol, .gamma.-terpinene, ocimene, p-cymeme, and terpinolene. The concn. of each was in the low ppb range. The relative content of Eucalyptus monoterpenes obtained by 3 different methods, i.e., water distillate, headspace volatiles, and atm. collected near the trees, were compared. The relations between the concns. of monoterpenes in the atm. and the height above the ground were also studied. The air of a Pinus thumbergii forest near a well-traveled road was analyzed for volatiles from exhaust gas from automobiles and pine terpenes.

- AN CA108(23):201970p
- TI Terpenes emitted from trees. II. Terpenes in the atmospheres of forests
- AU Yatagai, Mitsuyoshi; Ohira, Tatsuro; Unrinin, Genji; Kadir, Azizol bin Abdul; Hayashi, Yoshioki; Ohara, Seiji
- CS For. For. Prod. Res. Inst.
- LO 305, Japan
- SO Mokuzai Gakkaishi, 34(1), 42-7
- SC 11-8 (Plant Biochemistry)
- SX 53
- DT J
- CO MKZGA7
- IS 0021-4795
- PY 1988
- LA Eng

AB Distribution of terpenes in the atmospheres of sugi (Cryptomeria japonica) and hinoki (Chamaecyparis obtusa) forests were studied. The largest concn. of .alpha.-pinene was obsd. on a hillside in the morning. The 2nd largest was obsd. at the top of a hill, and the lowest was at the foot of a hill. The concns. of terpenes in sugi forest covered with snow were 1/3 to 2/3 of those in the fall season. The terpene concn. in a sugi forest as well as that in a Japanese red pine (Pinus densiflora) forest were greater than that in a broadleaved forest. There were small differences in the terpene concns. between heavily-thinned and lightly-thinned forests. The distribution pattern of terpenes in the atm. of a hiba (Thujopsis dolabrata hondai) forest was very similar to those of sugi and hinoki forests. The concn. of terpenes in a mill sawing hiba logs was more than sixty times the greatest concn. in the hiba There were large differences in the relative concns. of forest. each component between samples from hiba forest and the mill sawing hiba logs. Terpenes in the atm. of Picea glehni, Abies sachalinensis, Picea jezoensis, and Betula platyphyla japonica forests were studied. The terpenes in the forest air were diffused by increasing temp. and wind, even a light breeze. The amts. of terpenes in the atm. of a Larix leptolepis forest were small in the early morning, and there was little difference in concns. among the components. In the late morning, the concns. of terpenes increased and the differences in the concns. of individual components were marked.

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API PUBL*309 92 📰 0732290 0529865 899 📰

ΤI The relationship of the monoterpene composition in the atmosphere, the foliar emission gas and the leaf oil of Pinus densiflora AU Yokouchi, Yoko; Ambe, Yoshinari; Fuwa, Keiichiro CS Div. Chem. Phys., Natl. Inst. Environ. Stud. LO Ibaraki 305, Japan SO Chemosphere, 10(2), 209-13 SC 11-13 (Plant Biochemistry) DT J CO CMSHAF IS 0045-6535 PY 1981 LA Eng AB The emission rate of individual monoterpenes from pine needles was proportional to the product of the amt. in the leaf oil and the approx. vapor pressure. The compn. of monoterpenes in the atm. was consistent with the foliar emission rates with the supposition that the terpenes emitted into the atm. react with O3 and photochem. with N oxides.

API PUBL*309 92 🖿 0732290 0529866 725 🎟





API PUBL*309 92 🖿 0732290 0529868 5T8 📟

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 AN CA98(7):50291q TI The atmospheric chemistry of volatile terpenoids of plant origin AU Yokouchi, Yoko; Ambe, Yoshinari CS Div. Chem. Phys., Natl. Inst. Environ. Stud. LO Yatabe 306, Japan SO Chikyu Kagaku (Nippon Chikyu Kagakkai), 16(1), 30-41 SC 11-0 (Plant Biochemistry) SX 59 DT J CO CKNKDM IS 0386-4073 PY 1982 LA Japan A review with 42 refs. discussing the emission rate, concn. in the atm., reactivities, and impact on air quality of volatile terpenoids of plant origin.

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API PUBL*309 92 🖿 0732290 0529869 434 📟

CA104(6):38927m AN ΤI Plant-origin organic matter in atmosphere Yokouchi, Yoko; Yasube, Yoshiya: Fujii, Toshihiro; Mukai, Hitoshi AU Natl. Inst. Environ. Stud. CS LO Yatabe, Japan Kokuritsu Kogai Kenkyusho Kenkyu Hokoku, 58, 30-8 SO 59-2 (Air Pollution and Industrial Hygiene) SC DT J CO KKOKDD PY 1984 LA Japan The background levels of monoterpene hydrocarbons (e.g., AB .alpha.-pinene [80-56-8]) and pinonic aldehyde [2704-78-1] in air in Japan were detd. by gas chromatog.-mass spectrometry. Sesquiterpenes, n-alkanes, and other common org. components of plant origin were also found.

API PUBL*309 92 🖿 0732290 0529870 156 🖿

AN CA94(10):70384t ΤI Can biogenic emissions of natural hydrocarbons affect urban ozone levels? US controversy on possible role of vegetation in photochemical smog formation AU Zannetti, Paolo CS Aero Vironment Inc. LO Pasadena, CA, USA SO Inquinamento, 22(10), 91-2 59-0 (Air Pollution and Industrial Hygienc) SC DT J CO IQAAAW 0001-4982 IS PY 1980 LA Ital AB A review with 5 refs.

NATURAL SOURCES OF OZONE IN HOUSTON: NATURAL ORGANICS Patrick Zimmerman National Center for Atmospheric Research P. O. Box 3000 Boulder, Colorado As part of the 1978 Houston study a concurrent experimental program was conducted in order to provide data which would allow estimates of the emission rates of biogenic hydrocarbons into the Houston air mass. The program included direct measurements of the emission rates of hydrocarbons from selected vegetation, soil and leaflitter and from fresh and saltwater surfaces. Ambient air grab samples were collected in the vicinity of many of the biogenic emission sources. Emission rates from the vegetation sampled were similar to those made previously in Tampa, Florida and in North Carolina. Although the emission rates measured indicate that vegetation in the Houston area emits a substantial amount of reactive hydrocarbons, the grab samples of ambient air indicate that ambient concentrations of biogenic ozone precursers are present at very low concentrations. Reasons for the low concentrations of biogenic hydrocarbons in ambient air and the oxidant potential of these biogenic hydrocarbons are discussed.

API PUBL*309 92 📰 0732290 0529872 T29 📟

AN CA98(18):148807n Testing of hydrocarbon emissions from vegetation and methodology for TI compiling biogenic emission inventories AU Zimmerman, Patrick R. CS Natl. Cent. Atmos. Res. LO Boulder, CO 80303, USA SO Atmos. Biog. Hydrocarbons, Volume 1, 15-33. Edited by: Bufalini, Joseph J.; Arnts, Robert R. Ann Arbor Sci.: Ann Arbor, Mich. SC 59-1 (Air Pollution and Industrial Hygiene) SX 80 DT C CO 49LLAZ PY 1981 LA Eng The results of several studies conducted to test a new sampling AB methodol. for biogenic hydrocarbons are discussed. Results obtained from the new sampling were similar to those obtained from enclosure and other type studies. Computer models were used to store the data obtained and develop biogenic hydrocarbon emission inventories for large areas. In addn., a characterization of future biogenic hydrocarbon research is presented.



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