

Estimating Biogenic VOC Emissions in California

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Ground-Level Ozone

- Formed by reaction of VOC with NO_x in presence of sunlight
- 100-140 ppb in the San Joaquin Valley
- Example of yield reductions (percent) for agricultural crops due to ozone
 - alfalfa (9)
 - cotton (16)
 - grapes (28)
 - oranges (32)

Background to the Problem

- The difference between effectiveness of NO_x and VOC emission controls may depend on contribution of hydrocarbons from vegetation.
- Biogenic VOC (BVOC) are highly reactive.
- However, biogenic emissions data are uncertain in key California airsheds.

General Equation for BVOC Inventory Development

$$Q = \sum_{(i = 1 \dots n)} [E_i * L_i * A_i * F_i]$$

where for each plant species:

E is a BVOC emission factor

L is leaf mass

A is areal coverage

F is an adjustment factor for light,
temperature, or both

Statement of the Problem

To produce an accurate BVOC inventory for California, data are needed for:

- Biogenic emission factors
- Quantitative leaf mass description
- Spatially-resolved plant identities

And questions of scaling need to be resolved at several levels, including within-canopy models for plants

Estimating Future Biogenic Emissions

- How will population increase affect ozone and PM concentrations?
- How will plant species changes affect ozone and PM levels?

California's Vegetation is Unusually Diverse



Richness of California's Native Flora

Location	Area (1000 km ²)	Species (No.)	Density (No./1000 km ²)	Endemic (%)
California	411	4839	11.8	29
Texas	751	4196	5.6	9
Alaska	1479	1366	0.9	6
NE US + Canada	3238	4425	1.4	14
Great Britain	308	1443	4.7	17

California's Naturalized Vegetation and BVOC

- 173 families, 1222 genera, 5862 species found in California's natural plant communities (*The Jepson Manual*)
- Hundreds of additional urban species
- Varied topography and climate zones
- BVOC factors span three orders of magnitude

BVOC Compound Classes

- Isoprene
 - The VOC emitted in greatest quantity by plants
- Monoterpenes
 - May form secondary aerosols
- Sesquiterpenes
 - Very reactive
- Oxygenates
 - Alcohols, aldehydes, ketones, esters, carboxylic acids
 - Methyl butenol a major emission of some pines
- Others?

BVOC Emission Rates

- Leaf Mass Basis
 - $\mu\text{g BVOC g}^{-1} \text{h}^{-1}$
 - $\mu\text{g C g}^{-1} \text{h}^{-1}$
- Leaf Area Basis
 - $\mu\text{g BVOC m}^{-2} \text{h}^{-1}$
 - $\mu\text{g C m}^{-2} \text{h}^{-1}$

Assigning BVOC Emission Factors



- Isoprene emissions from more than 75 plant species common in California have been measured in ARB projects.
- More than 250 plant species have been semi-quantitatively measured for BVOC.

Assigning BVOC Emission Factors

- A phylogenetic (taxonomic) approach has been used to assign isoprene and monoterpene emission factors
- Isoprene data are most complete
- Data for other compounds are needed

Emission Factor Type

- Branch-level factors
 - Have been used in ARB models
 - Integrate light and temperature conditions
- Leaf-level factors
 - Represent the emission of sun leaves
 - Must be coupled with a canopy model

Isoprene Emission Factors ($\mu\text{g g}^{-1} \text{h}^{-1}$)

	B96 (branch)	KW00 (branch)	G01 (leaf)
Blue Oak	8	27	63
Coast Live Oak	35	-	68
Valley Oak	3	23	76
Sweetgum	19	26	60

Adjusting Emissions for Environmental Conditions

- Adjustments for light and temperature
 - Guenther algorithm works well
 - Leaf developmental effects may be significant
- Canopy models
 - Closed canopy vs savanna conditions
 - May be empirical and species-specific

Leaf Mass or Leaf Area Estimation

Leaf Mass Density

- Sum of leaf mass above unit ground area
- g m^{-2}
- leaf column density

Leaf Area Index (LAI)

- Ratio of sum of areas of leaves to ground area beneath
- $\text{m}^2 \text{ m}^{-2}$

Leaf Mass to Area Conversion

- Mass and area of leaves in a plant crown may be calculated if the ratio of mass to area for leaves is known
- Specific leaf mass, g m^{-2}
- Specific leaf area, $\text{m}^2 \text{g}^{-1}$

Approaches for Leaf Mass Estimation

- Direct Measurement Methods
- Indirect Measurement Methods
- Allometric Measurement Methods

Campbell and Norman 1989

Direct Measurement Methods

- Volumetric method
 - Urban trees
 - Shrubs
- Dispersed individual plant method
- Whole-tree harvest

Blue Oak Leaf Mass Density (g m^{-2})

- 410-1300, mean 730
- Site value based on grid area 310
- Overall value 155
- Comparisons:
 - Atlanta oak woodland 375 (Geron et al. 1995)
 - Contiguous US 375 (Lamb et al. 1987, 1993)
 - Castelporziano, Italy 300-600 (Seufert et al. 1997)

Allometric Measurement Methods

- Equations relate leaf mass or LAI to:
 - DBH
 - Crown Dimensions
- Equations for urban trees (Harris et al. 1973, Nowak 1996)
- Equations for blue oaks (Winer and Karlik 2001, Karlik 2002)

Indirect Measurement Methods

- Inclined Point Quadrant
- Gap Function Analysis
 - Light interception
 - Fisheye photography
- Spectral reflectance via remote sensing

Leaf Mass Estimation Using Remote Sensing Methods

- Spectral reflectance data can be used to generate vegetation indices
- LAI obtained from vegetation indices through
 - Empirical correlations
 - Analytical models
- Leaf mass density (g m^{-2}) then obtained from LAI and specific leaf mass

Data from Remote Sensing: Advantages

- Rapid and complete coverage of study area
- Change patterns can be seen
- Digital storage and manipulation allow accumulation of data layers
- Good for LAI

Data from Remote Sensing: Limitations

- LAI can become saturated
- Not as helpful for leaf mass
- Plants are similar to one another in chemical composition
 - For species ID, spectral data must be coupled with classification scheme
 - Phenology is helpful in separating among plant species

Spectral Reflectance of Plants

Shared Absorption Features

<u>Wavelength</u> (nm)	<u>Feature</u>	<u>Chemical</u>
430	electron transition	Chlorophyll a
460	electron transition	Chlorophyll b
640	electron transition	Chlorophyll b
660	electron transition	Chlorophyll a
910	C-H stretch	Protein
1020	N-H stretch	Protein

(Curran, 1989)

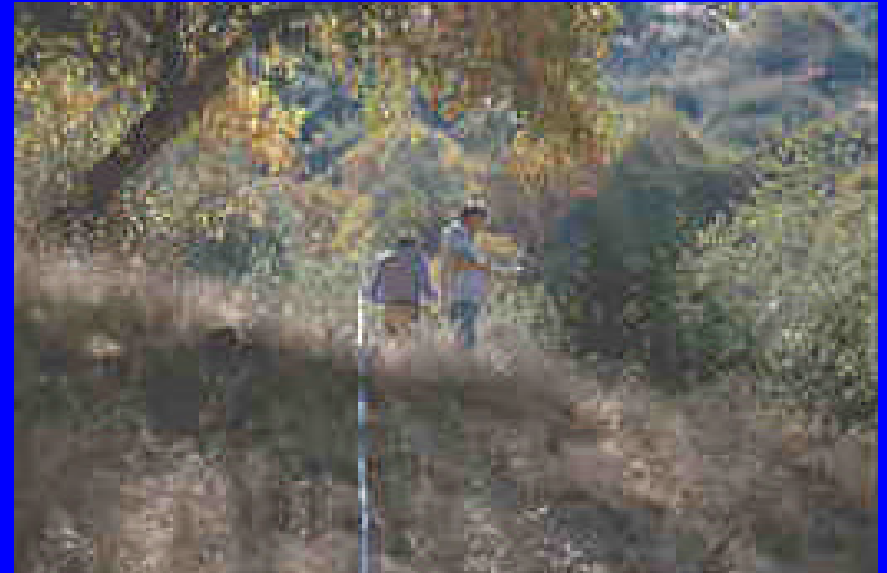
Field Measurements of LAI for Comparison to ARB Data

- 6 remote sites, 15 transects
- Measurement of LAI with LiCor LAI-2000 and CID CI-110 instruments
- Estimation of LAI via a volumetric approach
- Comparison to LAI values from Nikolov
- Nikolov values appear plausible

Blue Oak LAI

- California Hot Springs, 975 m elevation, data from harvest of 14 trees
- 2.5-7.7 for individual trees, mean 4.4
- Site LAI value based on grid area 1.8
- Overall LAI value ~0.9

Landcover Description



I dreamt of being a geographer
but I found the subject too
complex. So I switched to
physics.

A. Einstein

(as quoted in Utah Gap Analysis 1-1)

Landcover Description

- Advances in vegetation description and mapping may provide an opportunity for improvement in BVOC inventory assembly.

Landcover Databases

- Agricultural Commissioner data for crops
- GAP or similar for natural vegetation
 - Three ARB-funded studies in 1995-2001
 - 35 polygons evaluated from San Diego to Mendocino Co.
 - GAP was in good agreement with field data
- Urban vegetation problematic

Alternative Approaches for BVOC Emission Inventories

- Plant community rather than species basis
- What plants could dominate the inventory?
- Verification with canopy-scale and regional measurements

General Equation for BVOC Inventory Development

$$Q = \sum_{(i = 1 \dots n)} [E_i * L_i * A_i * F_i]$$

where

E is a BVOC emission factor

L is leaf mass

A is areal coverage

F is an adjustment factor for light,
temperature, or both

California's Oaks and BVOC

Large Areal Coverage



High isoprene emission rates

Wide Distribution



Estimated Isoprene Emissions, Blue Oaks

- 3.9 mg C m⁻² h⁻¹ based on branch-level emission data, whole-tree harvest, and 50% areal coverage
- Comparisons:
 - 2.2-11 mg C m⁻² h⁻¹ for mixed deciduous/coniferous woodlands (Guenther et al. 1994)
 - 0.8-4.3 mg C m⁻² h⁻¹ for scrub woodlands (Guenther et al. 1994)
 - 9 mg C m⁻² h⁻¹ for southern African savannas (Otter et al. 2002)
 - 2-3 mg C m⁻² h⁻¹ at midday for a *Q. pubescens* woodland in Mediterranean France (Serca et al. 1999)

GAP Data Revisited: Carmel Valley

<u>Plant</u>	<u>GAP Percent</u>	<u>Field Measurement</u>
<i>Lithocarpus densiflora</i>	-	27
<i>Ceanothus integerrimus</i>	-	22
<i>Arctostaphylos</i> sp.	≥ 11 & ≥ 7	17
<i>Quercus berberidifolia</i>	-	14
<i>Adenostoma fasciculatum</i>	≥ 7	9
<i>Quercus chrysolepis</i>	≥ 11	7
<i>Umbellularia californica</i>	-	2

GAP Data Revisited: Folsom Lake

<u>Plant</u>	<u>GAP Percent</u>	<u>Field Measurement</u>
<i>Quercus douglasii</i>	≥ 13	33
<i>Quercus chrysolepis</i>	–	9
<i>Quercus wislizenii</i>	≥ 13	6
<i>Aesculus californica</i>	–	2
<i>Pinus sabiniana</i>	≥ 13	0
<i>Avena spp. and Bromus spp.</i>	≥ 7	N.D.

GAP Data for Emitting Species

- 2000 GAP Study: 9 polygons
 - 12 listings for oak species
 - 7 correct, 1 incorrect, and 4 below co-dominant percentages. 4 additional primary, 2 secondary, 2 tertiary co-dominants
 - 11 listings for emitting plants such as *Salix* and *Populus*
 - 4 correct, 7 below co-dominants percentages. 5 additional primary, 1 secondary, and 8 tertiary co-dominants.
- 1998-1999 GAP Study: 18 polygons
 - 25 listings for oak species
 - 20 correct, 3 incorrect, and 2 below co-dominant percentages. 3 additional primary, 10 secondary co-dominants, and 9 tertiary co-dominants.
 - 14 listings for emitting plants such as *Salix* and *Populus*
 - 3 correct, 4 were incorrect, and 7 below co-dominant percentages. 1 additional primary, 6 secondary, and 4 tertiary co-dominants.

Santa Barbara Urban Survey

<u>Plant</u>	<u>Est. Leaf Mass</u> (kg ha ⁻¹)
Pinus radiata	2100
Pittosporum undulatum	1900
Ficus macrophylla	1400
Cupressus sempirvirens	910
Eucalyptus viminalis	710

Ventura Urban Survey

<u>Plant</u>	<u>Est. Leaf Mass</u> (kg ha ⁻¹)
Pittosporum rhombifolium	2800
Pittosporum undulatum	1400
Cupressus sempirvirens	660
Jacaranda acutifolia	360
Juniperus chinensis	270

Urban Plant Dominance

Location	Species (No.)	Top Five Volume (%)	Top Five Leaf Mass (%)	Top Five Isoprene (%)
Santa Barbara	93	62	64	89
Thousand Oaks	51	68	74	96
Ventura	94	66	73	90

Comparison of Isoprene Emission of Sweetgum to Spilled Gasoline

- Isoprene emission rate of $26 \text{ ug g}^{-1} \text{ h}^{-1}$ (at 30°C under sunny skies)
- Leaf mass of 40.5 kg (medium-sized tree)
- Resulting hourly emission of 1 g isoprene
- Approximately equivalent to 4.5 mL gasoline spilled per hour
- For 10,000 trees, isoprene emission approximately equivalent to 45 L gasoline spilled per hour

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