Estimating Biogenic VOC Emissions in California

John Karlik

University of California
Cooperative Extension
Ground-Level Ozone

- Formed by reaction of VOC with NOx 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 NOx 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

\[ Q = \sum_{(i = 1 \ldots n)} [E_i \times L_i \times A_i \times F_i] \]

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

<table>
<thead>
<tr>
<th>Location</th>
<th>Area (1000 km²)</th>
<th>Species (No.)</th>
<th>Density (No./1000 km²)</th>
<th>Endemic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>California</td>
<td>411</td>
<td>4839</td>
<td>11.8</td>
<td>29</td>
</tr>
<tr>
<td>Texas</td>
<td>751</td>
<td>4196</td>
<td>5.6</td>
<td>9</td>
</tr>
<tr>
<td>Alaska</td>
<td>1479</td>
<td>1366</td>
<td>0.9</td>
<td>6</td>
</tr>
<tr>
<td>NE US + Canada</td>
<td>3238</td>
<td>4425</td>
<td>1.4</td>
<td>14</td>
</tr>
<tr>
<td>Great Britain</td>
<td>308</td>
<td>1443</td>
<td>4.7</td>
<td>17</td>
</tr>
</tbody>
</table>
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
  - ug BVOC g \(^{-1}\) h\(^{-1}\)
  - ug C g \(^{-1}\) h \(^{-1}\)

- Leaf Area Basis
  - ug BVOC m \(^{-2}\) h \(^{-1}\)
  - ug C m \(^{-2}\) 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
<table>
<thead>
<tr>
<th>Plant Type</th>
<th>B96 (branch)</th>
<th>KW00 (branch)</th>
<th>G01 (leaf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue Oak</td>
<td>8</td>
<td>27</td>
<td>63</td>
</tr>
<tr>
<td>Coast Live Oak</td>
<td>35</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>Valley Oak</td>
<td>3</td>
<td>23</td>
<td>76</td>
</tr>
<tr>
<td>Sweetgum</td>
<td>19</td>
<td>26</td>
<td>60</td>
</tr>
</tbody>
</table>
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
- $g \text{ m}^{-2}$
- leaf column density
Leaf Area Index (LAI)

- Ratio of sum of areas of leaves to ground area beneath
- $m^2/m^2$
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, $m^2 \, g^{-1}$
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

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Feature</th>
<th>Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>electron transition</td>
<td>Chlorophyll a</td>
</tr>
<tr>
<td>460</td>
<td>electron transition</td>
<td>Chlorophyll b</td>
</tr>
<tr>
<td>640</td>
<td>electron transition</td>
<td>Chlorophyll b</td>
</tr>
<tr>
<td>660</td>
<td>electron transition</td>
<td>Chlorophyll a</td>
</tr>
<tr>
<td>910</td>
<td>C-H stretch</td>
<td>Protein</td>
</tr>
<tr>
<td>1020</td>
<td>N-H stretch</td>
<td>Protein</td>
</tr>
</tbody>
</table>

(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

\[ Q = \sum_{i=1}^{n} \left[ E_i \times L_i \times A_i \times F_i \right] \]

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

Wide Distribution

High isoprene emission rates
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

<table>
<thead>
<tr>
<th>Plant</th>
<th>GAP Percent</th>
<th>Field Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Lithocarpus densiflora</em></td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td><em>Ceanothus integerrimus</em></td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td><em>Arctostaphylos sp.</em></td>
<td>&gt;=11 &amp; &gt;=7</td>
<td>17</td>
</tr>
<tr>
<td><em>Quercus berberidifolia</em></td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td><em>Adenostoma fasciculatum</em></td>
<td>&gt;=7</td>
<td>9</td>
</tr>
<tr>
<td><em>Quercus chrysolepis</em></td>
<td>&gt;=11</td>
<td>7</td>
</tr>
<tr>
<td><em>Umbellularia californica</em></td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>
## GAP Data Revisited: Folsom Lake

<table>
<thead>
<tr>
<th>Plant</th>
<th>GAP Percent</th>
<th>Field Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Quercus douglasii</em></td>
<td>&gt;=13</td>
<td>33</td>
</tr>
<tr>
<td><em>Quercus chrysolepis</em></td>
<td>–</td>
<td>9</td>
</tr>
<tr>
<td><em>Quercus wislizenii</em></td>
<td>&gt;=13</td>
<td>6</td>
</tr>
<tr>
<td><em>Aesculus californica</em></td>
<td>–</td>
<td>2</td>
</tr>
<tr>
<td><em>Pinus sabiniana</em></td>
<td>&gt;=13</td>
<td>0</td>
</tr>
<tr>
<td><em>Avena spp.</em> and <em>Bromus spp.</em></td>
<td>&gt;=7</td>
<td>N.D.</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Plant</th>
<th>Est. Leaf Mass (kg ha(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinus radiata</td>
<td>2100</td>
</tr>
<tr>
<td>Pittosporum undulatum</td>
<td>1900</td>
</tr>
<tr>
<td>Ficus macrophylla</td>
<td>1400</td>
</tr>
<tr>
<td>Cupressus sempervirens</td>
<td>910</td>
</tr>
<tr>
<td>Eucalyptus viminalis</td>
<td>710</td>
</tr>
<tr>
<td>Plant</td>
<td>Est. Leaf Mass (kg ha(^{-1}))</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Pittosporum rhombifolium</td>
<td>2800</td>
</tr>
<tr>
<td>Pittosporum undulatum</td>
<td>1400</td>
</tr>
<tr>
<td>Cupressus sempervirens</td>
<td>660</td>
</tr>
<tr>
<td>Jacaranda acutifolia</td>
<td>360</td>
</tr>
<tr>
<td>Juniperus chinensis</td>
<td>270</td>
</tr>
</tbody>
</table>
## Urban Plant Dominance

<table>
<thead>
<tr>
<th>Location</th>
<th>Species (No.)</th>
<th>Top Five Volume (%)</th>
<th>Top Five Leaf Mass (%)</th>
<th>Top Five Isoprene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Santa Barbara</td>
<td>93</td>
<td>62</td>
<td>64</td>
<td>89</td>
</tr>
<tr>
<td>Thousand Oaks</td>
<td>51</td>
<td>68</td>
<td>74</td>
<td>96</td>
</tr>
<tr>
<td>Ventura</td>
<td>94</td>
<td>66</td>
<td>73</td>
<td>90</td>
</tr>
</tbody>
</table>
Comparison of Isoprene Emission of Sweetgum to Spilled Gasoline

- Isoprene emission rate of 26 ug g\(^{-1}\) 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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  • Rick Ramirez
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