



Review of Biogenic Volatile Organic Compounds and Their Products

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Biogenic Day
9-10 December 1999

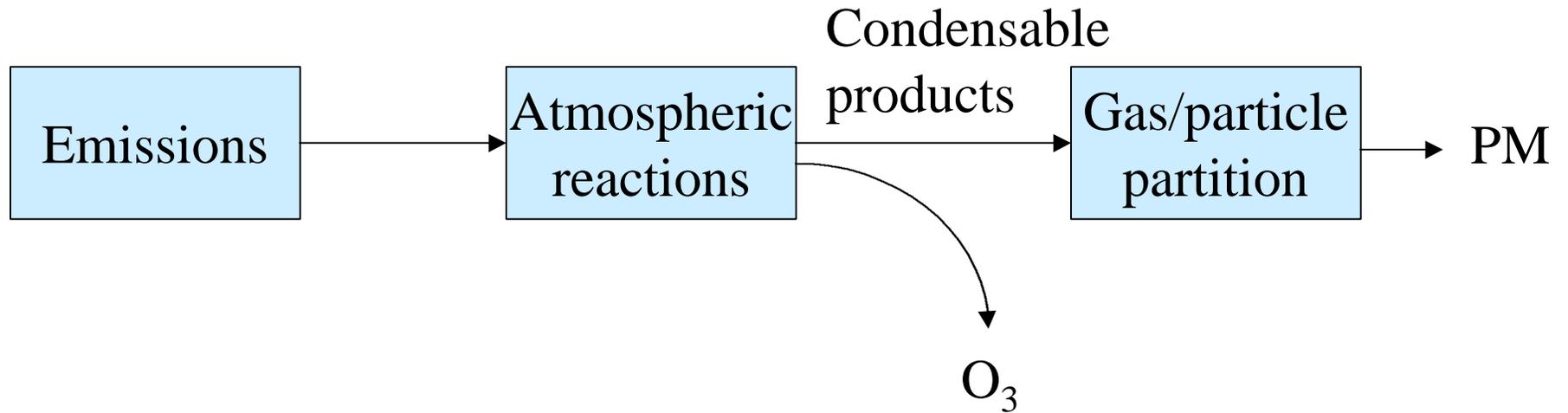
(1) Washington State University, Pullman, WA

(2) DGA, Inc., Ventura, CA

(3) AER, San Ramon, CA

Introduction

Biogenic compounds are precursors to ozone (O_3) and particulate matter (PM)



Biogenic Volatile Organic Compounds

Emission %
in North America

- Isoprene 31%
- Methylbutenol (MBO) 5%
- Monoterpenes + sesquiterpenes 22%
- Reactive oxygenates 16%
- Less reactive oxygenates 26%

Isoprene

- Sampling, analytical, eddy covariance flux methods are well-developed

Emission Characteristics

- Dominant VOC
- From deciduous species and spruce
- During day-light hours only
- Depends on leaf temperature and PAR

Isoprene Data Needs

- Vegetation types other than oaks, poplars, aspen, and spruce
- Effects of temperature history and season
- Landcover data

Monoterpenes

- Predominant compounds: α -, β -pinene, limonene, and Δ^3 -carene

Emission Characteristics

- From conifers and some deciduous species
- Depends on temperature
 - Some Mediterranean oaks emit terpenes with isoprene-like light, temperature dependence

Monoterpene Data Needs

- Emission capacities of individual monoterpene compounds
- Characterization of emission response to
 - rainfall / humidity
 - herbivory
- Canopy-scale measurements
- Comparison of measurements and inventory models

Sesquiterpenes

- Semivolatile, low emission capacities
- May contribute up to 16% of total BVOC landscape-scale flux

Data Needs

- Identification of individual sesquiterpenes and their emission capacities
- Canopy-scale measurements
- Regional emissions estimates

Oxygenated VOC

- Methylbutenol, emitted via the light-dependent chloroplast mechanism
- Other oxygenates emitted by defense mechanisms or cut and drying vegetation
- Regional emissions difficult to quantify due to intermittent emissions
- No canopy-scale information
- No evaluation at landscape scale

Biogenic Emissions Modeling

$$F = eDgdr$$

ε = area-average emission capacity

D = foliar density

γ = activity factor for light, temperature, leaf age

δ = activity factor for other factors

ρ = canopy escape efficiency

Canopy Modeling



- Microclimate within a forest canopy as a function of height
 - temperature (heat flux)
 - PAR

Measurements and Modeling (Isoprene)

- Measurement scale-up studies



- 40% difference between leaf and canopy scales
- Reconciliation of measurements with models
 - 30% difference between flux measurement and model for site specific applications
 - factor of 1.2 to 2 using inverse modeling of ambient concentrations

Chemical Functionality

- Saturated aliphatics
 - Alkanes, alcohols, aldehydes, ketones, acids, esters, ethers
- Aromatics
- Unsaturated Aliphatics
 - Alkenes, dienes, terpenes (1 to 3 C=C), sesquiterpenes (1 to 3 C=C)
- Unsaturated Oxygenates
 - alcohols, esters, aldehydes, ketones

Kinetics of Saturated Aliphatics and Aromatics

- Saturated aliphatics react only with OH
- Aromatics react mainly with OH, NO₃ may be a minor pathway
- Missing kinetic data for hexanal, camphor, cineole, and p-cymene can be estimated by structure-reactivity relationships
- Acetone has the maximum $\tau_{1/2}^{(1)} = 36$ days
- Hexanal has the minimum $\tau_{1/2}^{(1)} = 6$ hours

(1) OH = 10⁶ molec/cm³

Kinetics of Unsaturated Compounds

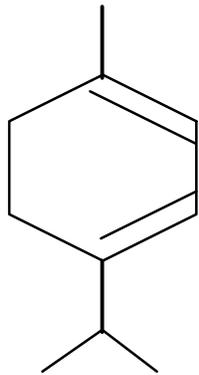
Unsaturated VOC react with OH, O₃, and NO₃

	<u>$\tau_{1/2,OH}^{(1)}$ (hours)</u>	<u>$\tau_{1/2, O_3}^{(2)}$ (hours)</u>
alkenes	3.0 - 23	1.3 - 160
isoprene	1.9	20
terpenes	0.53 - 3.6	0.01 - 280
sesquiterpenes	0.65 - 4.1	0.02 - >500
oxygenates	1.2 - 6.6	0.60 - 130

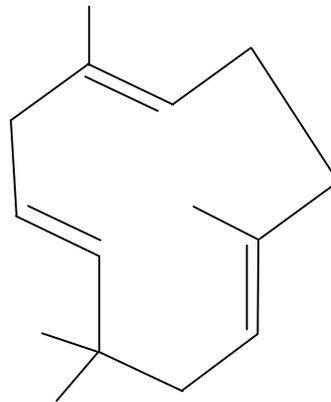
(1) OH = 10⁶ molec/cm³; (2) O₃ = 30 ppb

Highly Reactive Compounds

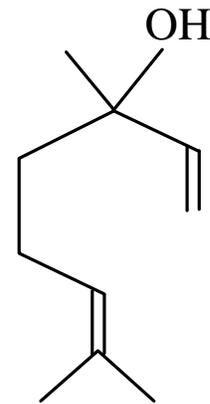
α -terpinene



α -humulene

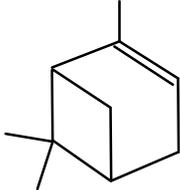


Linalool



Reaction with O_3 may be the dominant removal process for the more reactive BVOC

First-Generation Products

- Example: OH + α -pinene 
 - Pinonaldehyde, acetone, formaldehyde
 - Organic nitrates, hydroxy nitrates, dihydroxy nitrates, dihydroxycarbonyls
- For O₃ and OH reactions
 - Detailed information for alkenes, α -, and β -pinene, and unsaturated alcohols
 - Limited or no information for >20 BVOC
- Less information on NO₃ reaction

SOA Formation

- 14 BVOC known to form SOA
 - 10 terpenes (α -pinene most studied)
 - 2 sesquiterpenes
 - 2 unsaturated alcohols
- Isoprene does not form SOA
- SOA composition studied for 5 BVOC (reactions with O_3 and OH only): α -, β -pinene, d-limonene, terpinolene, Δ^3 -carene

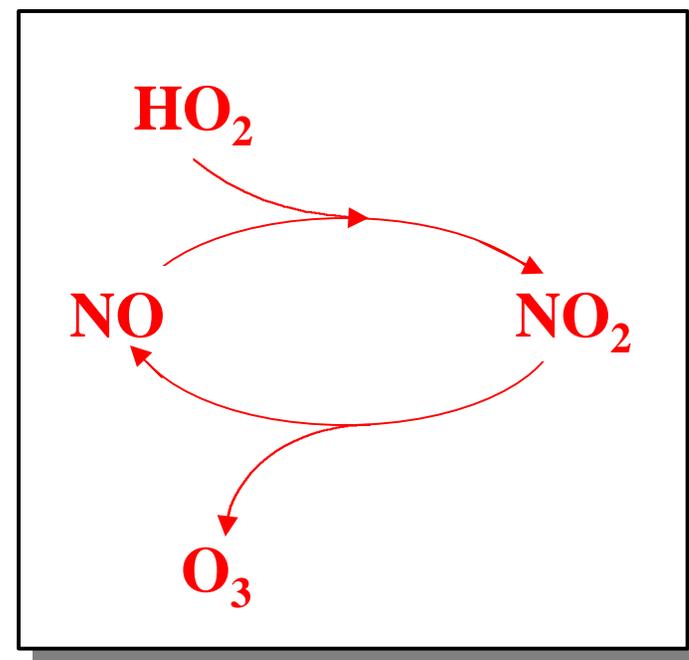
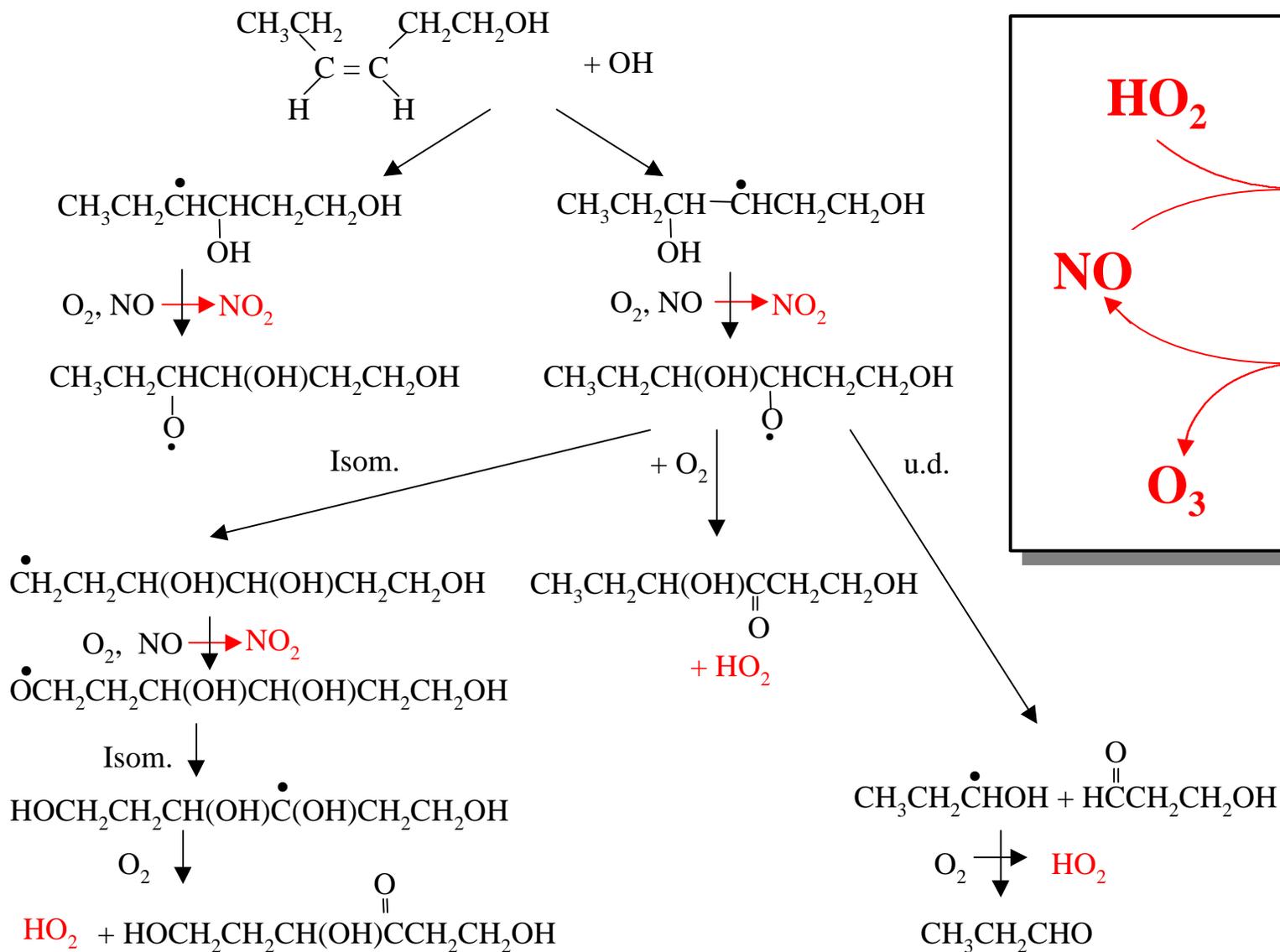
Reactions of First-Generation Products

- Kinetic data for first-generation products are limited
 - Aldehydes removed rapidly by OH reaction
 - Unsaturated carbonyls react with O₃
- Product studies conducted for only 6 first-generation compounds
 - Very limited information on second-generation products

Detailed BVOC Mechanisms

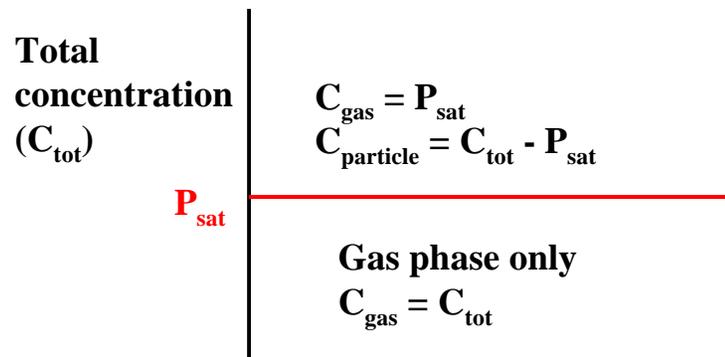
- With the exception of isoprene and α -pinene, detailed mechanisms cannot be constructed for BVOC

O₃ Formation from BVOC

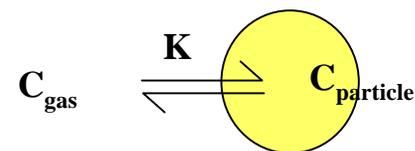


Organic Aerosol Partition Theories

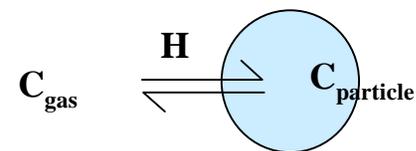
- Saturation
 - Fixed yield approach



- Absorption into an organic phase



- Aqueous dissolution



Existing SOA Modules

Models-3, DAQM2

1. Fixed yield
5 products
2. Absorption
6 products

SAQM-AERO

Fixed yield

UAM-AERO

Absorption (Raoult's law)
6 products

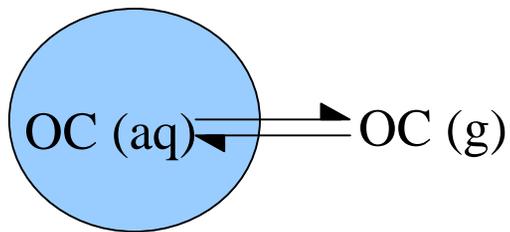
Models-3/EPRI

Absorption (Griffin/Odum)
34 products

Modules Under Development

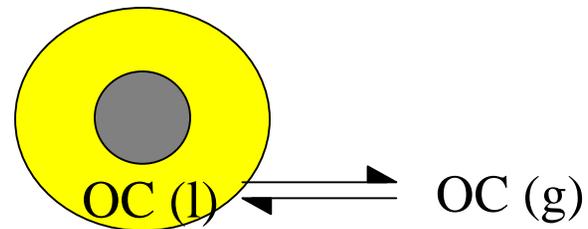
- Externally Mixed Aerosols
- Surrogate Species

Type A (Aqueous)



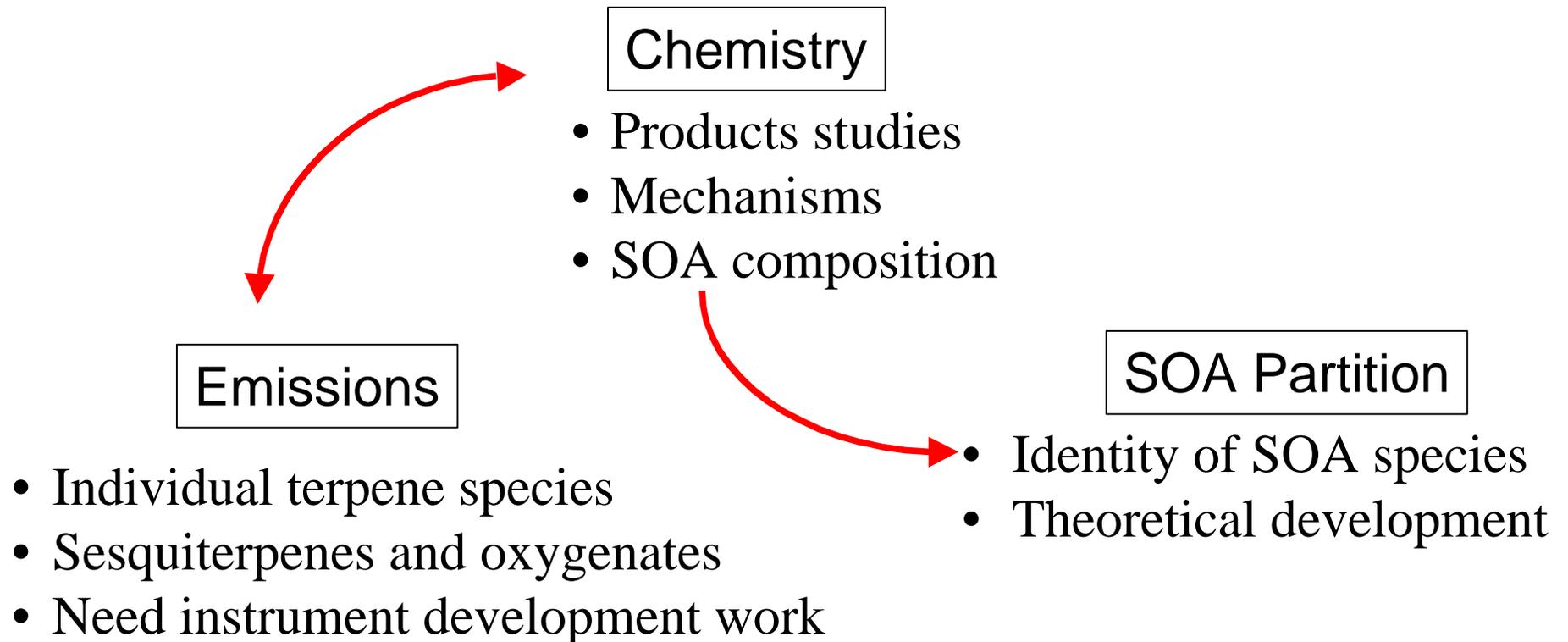
e.g., Malic acid,
Glyoxalic acid

Type B (Organic)



e.g., Octadecanoic acid

Data Needs



Acknowledgement

This work is funded by the Coordinating Research Council (CRC), Contract Number A-23