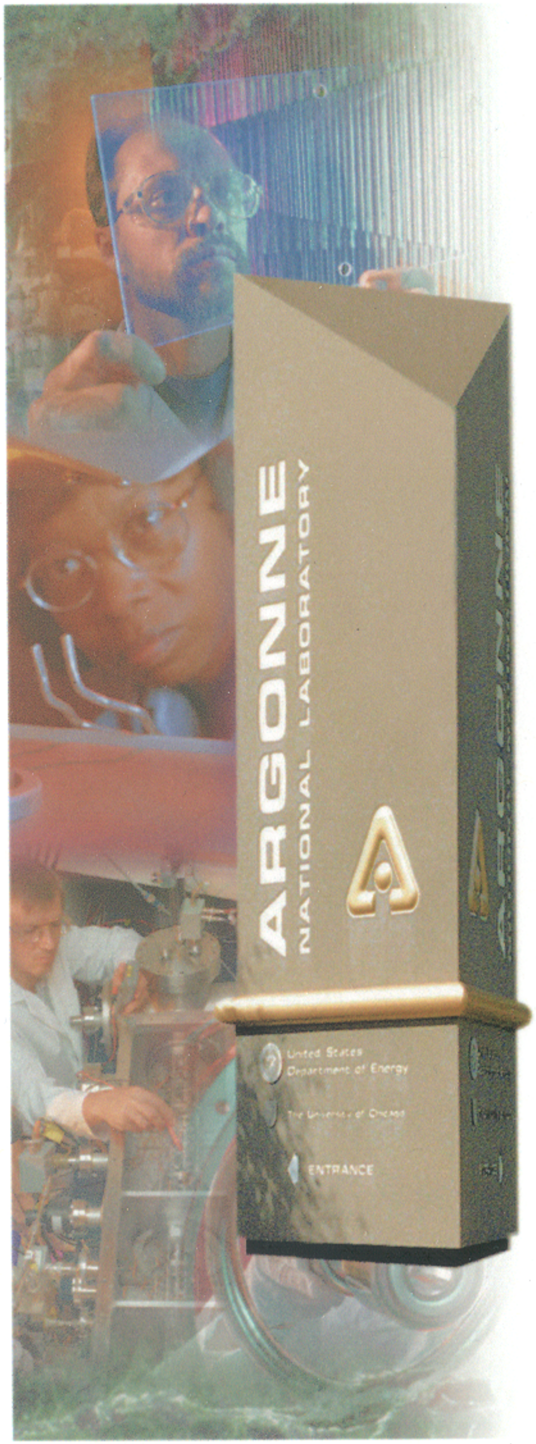

Measuring Trace Gas Fluxes from an Aircraft Platform

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U.S. Department of Energy

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Office of Science Laboratory
Operated by The University of Chicago

Outline

- Objectives and Motivation
- Aerosol Precursors and Yields
- Eddy Sampling Techniques
- Chemical Sensors and Samplers
- preCTEF I and CTEF I
- Fast Chemistry Effects on Emission Profiles
- Aerosol Field Studies

Objectives

- To develop aircraft-based methodologies for measuring the rate of exchange of oxidant and aerosol precursor gases with environmental surfaces.

- To make observations of the vertical flux and concentration profiles of trace gases and their oxidation products above urban and rural landscapes in order to evaluate meteorological chemical transport models and emission inventories.

Rural Emission Inventories

"For example, recent estimates of isoprene emission rates differed with measurements by 30-200% (Baldocchi et al. 1995; Lamb et al. 1996; Fuentes et al. 1996). One major source of modeling uncertainty involves the relatively small pool of data that has been used to test isoprene emission models. Before 1992, few direct measurements of canopy-scale isoprene flux studies were conducted or reported in the literature. At present, fewer than a dozen independent field campaigns exist in the literature."

Baldocchi et al., *J. Appl. Meteor. 38*, 885-898, 1999.

Urban Emission Inventories

"A significant question is whether our VOC observations are consistent with emission inventory estimates [Henry et al., 1997]. As was the case 15 years ago when the importance of biogenic emissions was being debated [Trainer et al., 1987; Chameides et al., 1988] a necessary prelude to formulating an O_3 control strategy for Houston, and possibly for other areas with similar industrial facilities, will be to obtain an accurate emission inventory consistent with ambient atmospheric measurements."

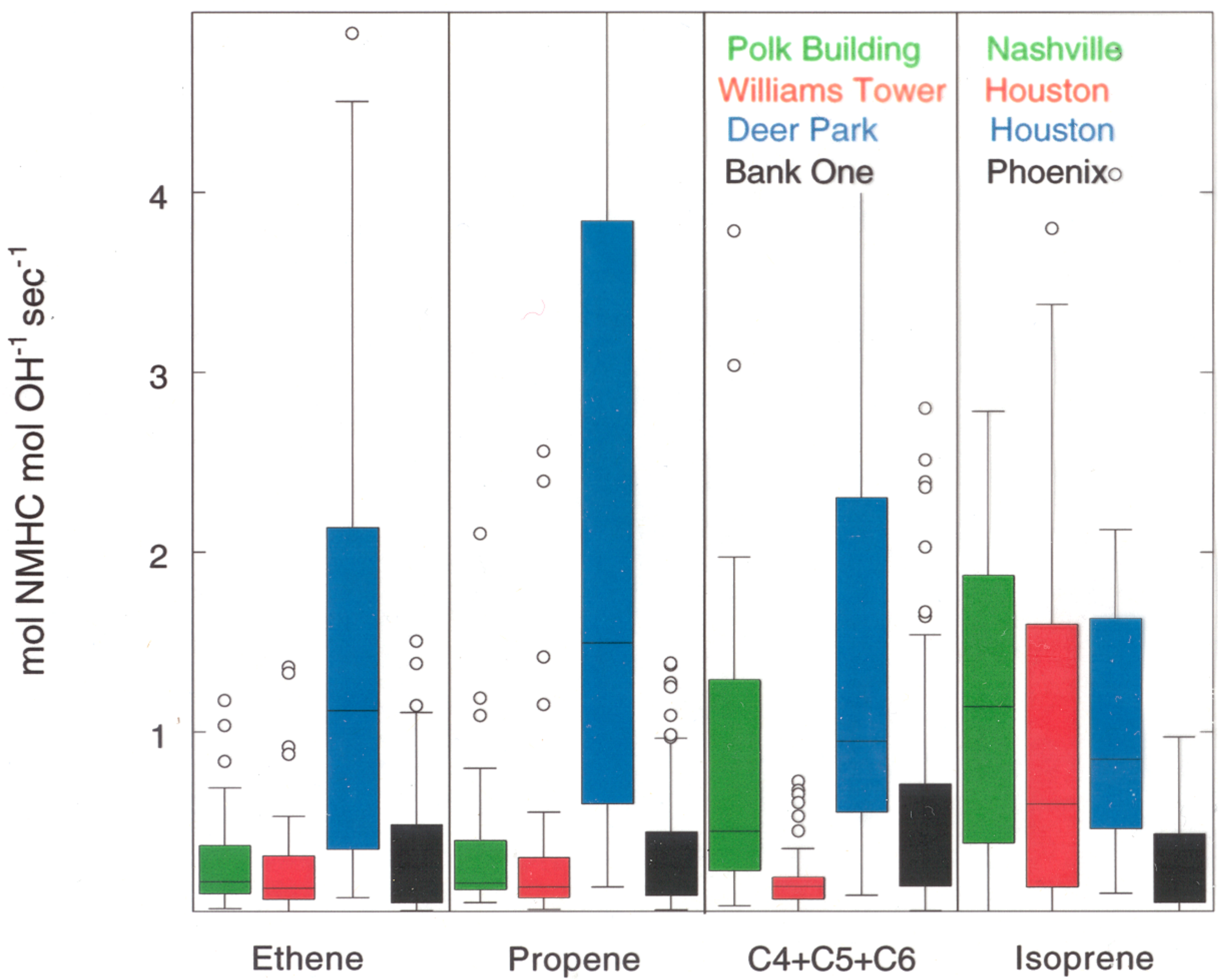
Kleinman et al., *Geophys. Res. Lett. 29*, 105-1 – 105-4, 2002.

NMOC Sources

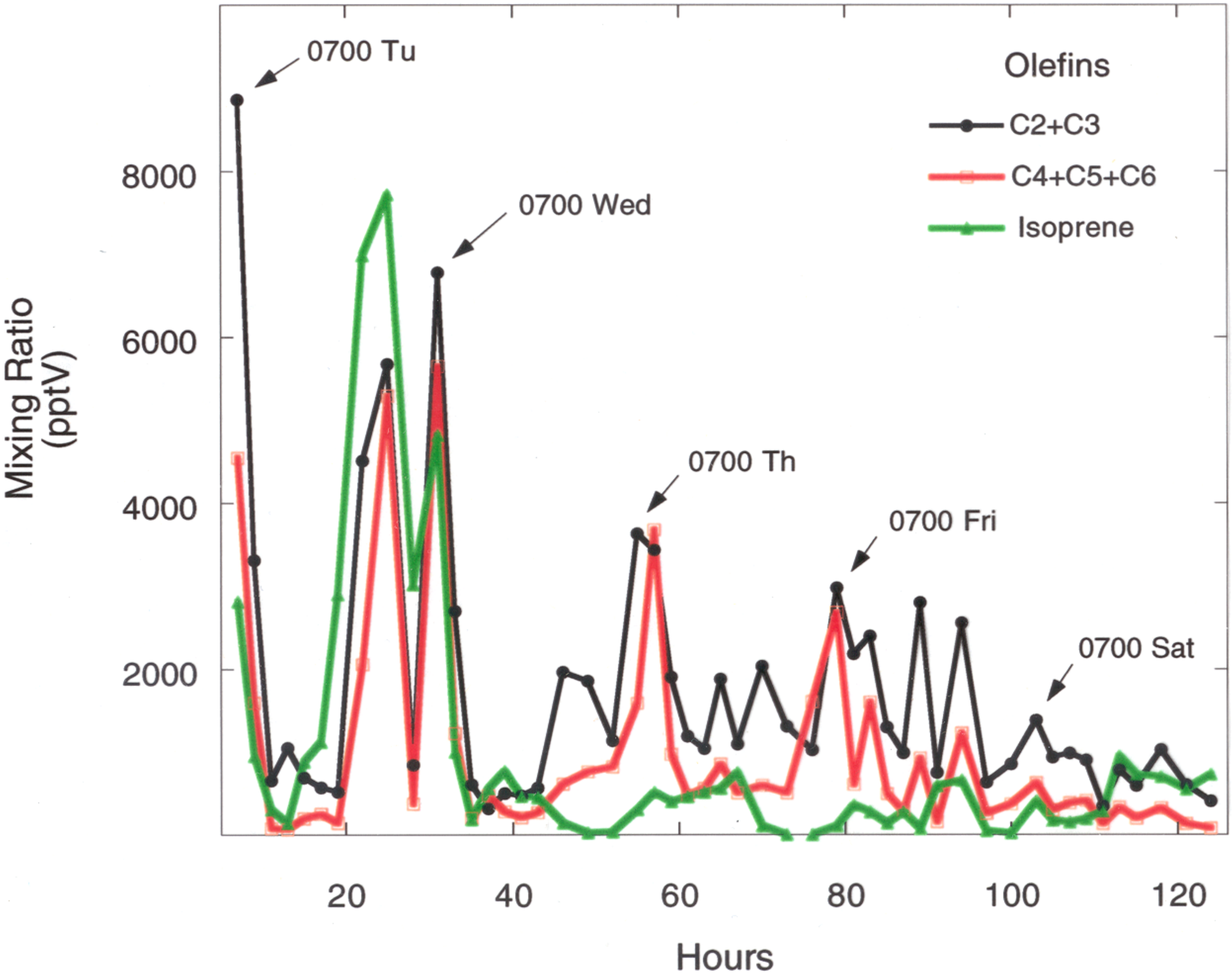
Source	Global Emission Rate (Tg C a^{-1})	
	NMOCs	Aerosol Precursors
Biogenic (vegetation, including agricultural crops)	1150	130
Anthropogenic (petroleum fuels — use, distribution, refining)	125	50

NMOCs - Nonmethane organic compounds

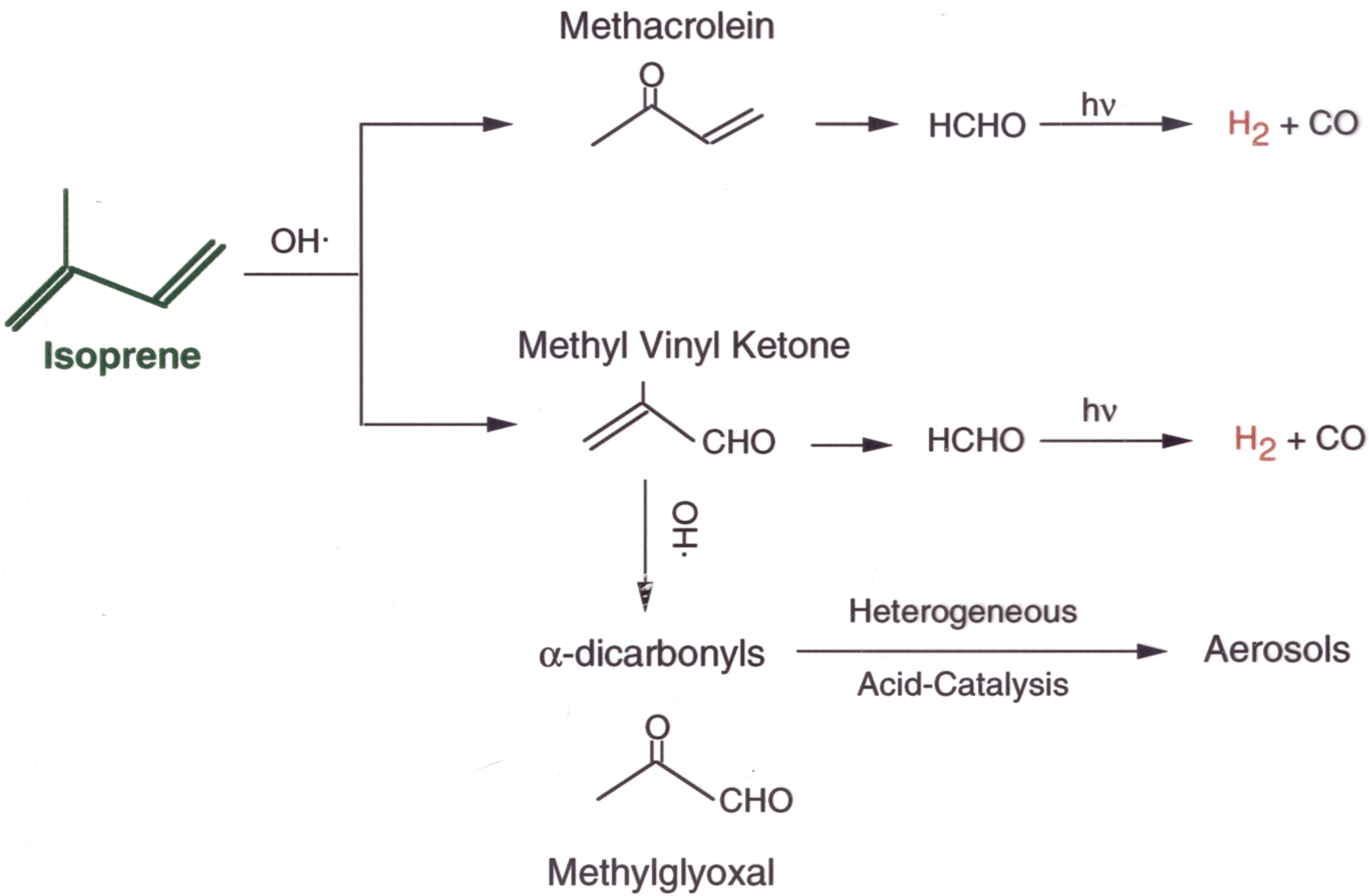
C_2-C_{12} aliphatic, aromatic, and oxygenated hydrocarbons.


mol NMHC mol OH^{-1} sec^{-1}
4
3
2
1
Polk Building
Williams Tower
Deer Park
Bank One
Nashville
Houston
Houston
Phoenix
Ethene
Propene
C4+C5+C6
Isoprene

Polk Building, Nashville

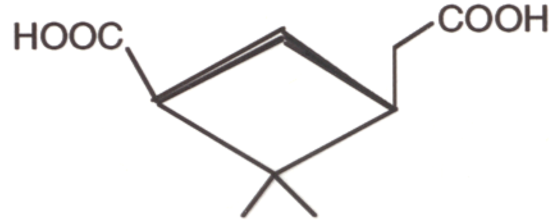


Isoprene Chemistry

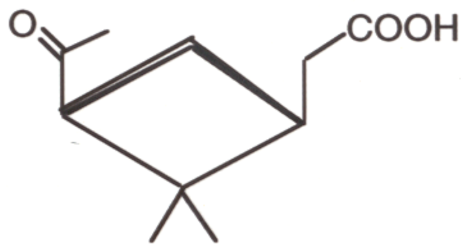


Monoterpene Photooxidation Products Identified in Forest Aerosol

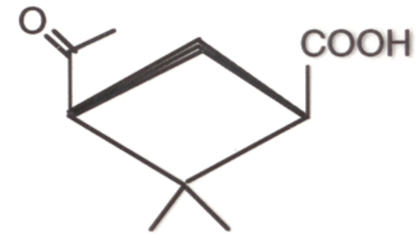
(Kavouras et al., *Environ. Sci. Technol. 33*, 1028-1037, 1999)



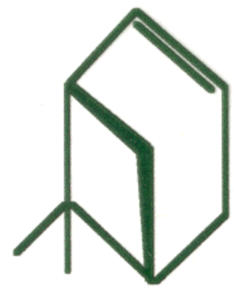
cis-Pinic Acid



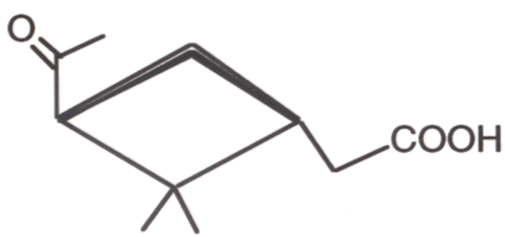
cis-Pinonic Acid



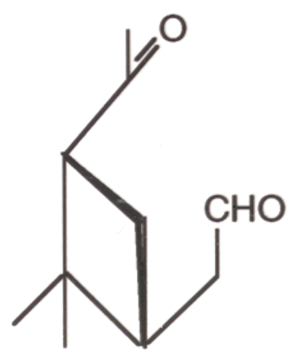
cis-nor-Pinonic Acid



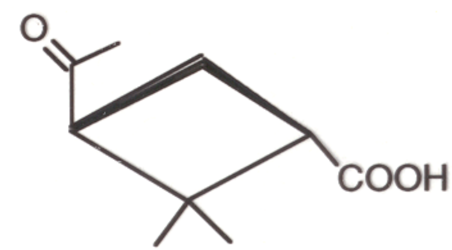
β-Pinene



trans-Pinonic Acid

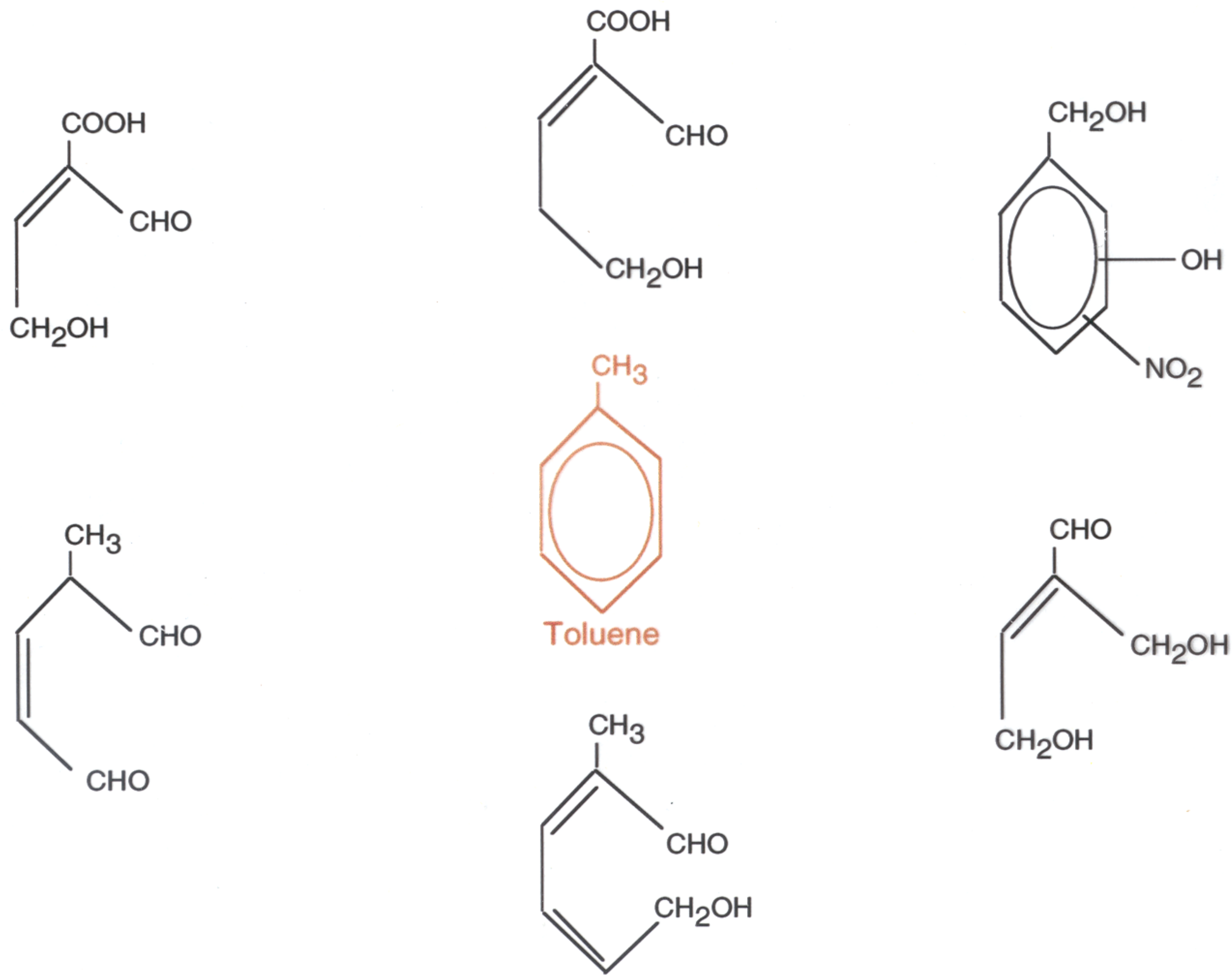


Pinonaldehyde



trans-nor-Pinonic Acid

Tentatively Identified Toluene Photooxidation Products in Aerosols



Aerosol Yields

Chemical	Aerosol Yield ($\mu g\ m^{-3}\ ppb^{-1}$)	Products
Isoprene (C_5H_{10})	?	
Monoaromatics (C_7-C_9)	0.140-0.580	Organic diacids,
Diaromatics	0.400-0.600	multifunctional carbonyls,
Monoterpenes ($C_{10}H_{16}$)	0.760	and organic nitrates
Sesquiterpenes ($C_{15}H_{24}$)	10	

"Additionally, biogenic and anthropogenic emissions of carbonyl species associated with photooxidation cycles are considerable. Processing these carbonyl compounds via particle-phase heterogeneous reactions constitutes a previously unstudied, and to date unquantified, source of global aerosol material."

Jang et al., *Science 298*, 814-817, 2002.

Aerosol Sources

Aerosol Type	Global Emission Rate ($Tg\ C\ a^{-1}$)
Secondary Organic	45-230
Carbonaceous Soot	5-20
Biogenic Sulfate	80-150
Anthropogenic Sulfate	170-250

Eddy Production Patterns of Turbulent Flow above a Forest Canopy

Approach

The instantaneous flux of a chemical (F_C) is determined as the product of the instantaneous fluctuations (deviations from the mean) of the vertical wind velocity (w´) and the chemical mixing ratio (c´).

$$F_c = \overline{w'c'} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} w'(t)\, c'(t)\, dt$$

For aircraft applications w´ is measured continuously with a gust probe and c´ can be measured with fast- and slow-response chemical sensors using a variety of eddy sampling techniques.

Eddy Covariance Techniques

Eddy Covariance (EC) - Continuous measurements of w' and c' are made with similar frequency. The technique requires sensors that operate at about 10-50 Hz (10-50 measurements s^{-1}).

Disjunct Eddy Covariance (DEC) - A set of disjunct samples are rapidly collected in a periodic manner essentially using a subset of the eddy covariance time series of data. Chemical sensors with response times on the order of 10 s or longer can be used with this technique.

Eddy Accumulation Techniques

Relaxed Eddy Accumulation (REA) - Ambient air is continuously passed through separate paths representing ascending and descending air. The flux of the chemical (F_C) is calculated as follows:

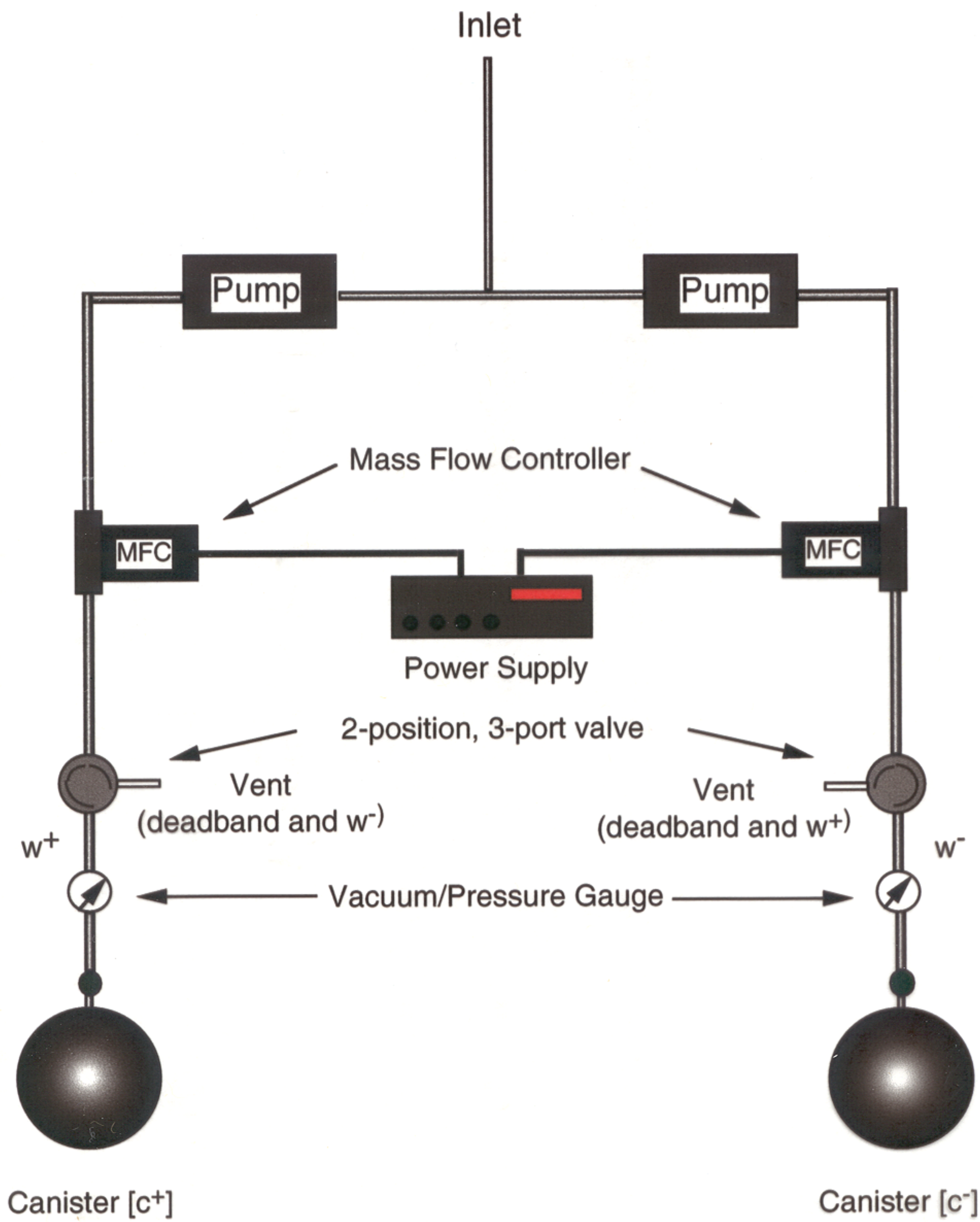
$$F_c = \overline{w'c'} \approx b\sigma_w \left(c^+ - c^-\right)$$

b = An empirical constant.

σ_w = The standard deviation of the vertical wind velocity.

The air can be collected in a container or the chemical trapped on a solid sorbent.

Relaxed Eddy Accumulation System



Eddy Accumulation Techniques

Disjunct Eddy Accumulation (DEA) - Separate samples of ambient air are rapidly collected ($t_s < 0.5$ s) in a reservoir and directed into a sample containers representing ascending or descending air at a rate proportional to w. The samples are collected in a periodic manner in a container or the chemicals are trapped on a solid sorbent or partitioned into a polydimethylsiloxane liquid phase.

$$F_c = \langle w'c' \rangle = \frac{1}{N} \sum_{i=1}^{N} w'(t_i)c'(t_i)$$

Sensors

Gust Probe - Dynamic differential pressure, sideslip differential pressure, attack-angle differential pressure.

TANS - Platform position, velocity, attitude.

IRGA - Open path infrared absorption analyzer for measurement of CO_2 and H_20.

Ozone Sensor (O_3) - Chemiluminescence and uv absorption.

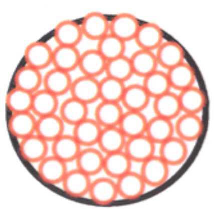
Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) - Organic trace gases are ionized by a proton transfer reaction with H_3O^+ ions in an ion drift-tube reactor. Reagent and product ions are analyzed with a quadrupole mass spectrometer.

Fast Isoprene Sensor (FIS) - O_3 Chemiluminescence and photon counting.

Container - Summa® passivated canister, Silcosteel® treated canister, Teflon® sphere.

Solid Sorbents - Chemical adsorption onto carbon-based solids.

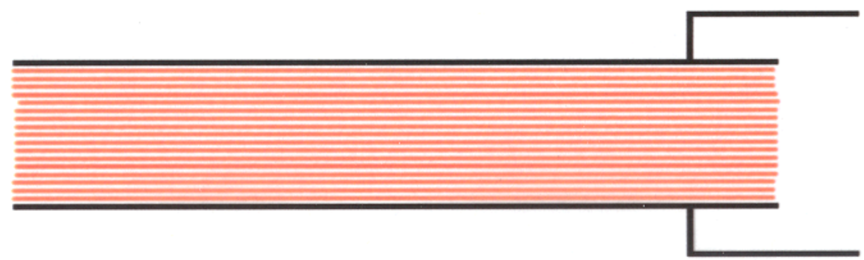
Multicapillary Collection Device (MCCD) - Partitioning of chemicals into a polydimethylsiloxane liquid phase coated on the inner walls of a bundle of fused silica capillary columns.



289 Fused Silica Capillaries

0.254 m x 0.53 mm ID

5 µm Film Thickness - Polydimethylsiloxane



0.254 m x 1.6 cm OD

Silcosteel Coated Stainless Steel

Sampling Rates and Eddy Sampling Techniques for Chemical Sensors

Chemical Sensor or Sampling Device	Analyte(s)	Sampling Rate	Eddy Sampling Technique
IRGA	H_2O/CO_2	50 Hz	EC
O_3	O_3	10 Hz	EC
PTR-MS	C_2-C_{10} VOCs	10 Hz[a]	EC, DEC, DEA
FIS	Isoprene	2 Hz	DEC
Container	C_2-C_{10} VOCs	slow	REA
Solid Sorbent	Monoterpenes (C_{10})	slow	REA
MCCD	C_{10}-C_{20} VOCs	slow	REA

[a] For single analyte monitoring.

preCTEF I

- Location - Boardman Forest
- Observations - Surface Site, Aircraft
- Objectives

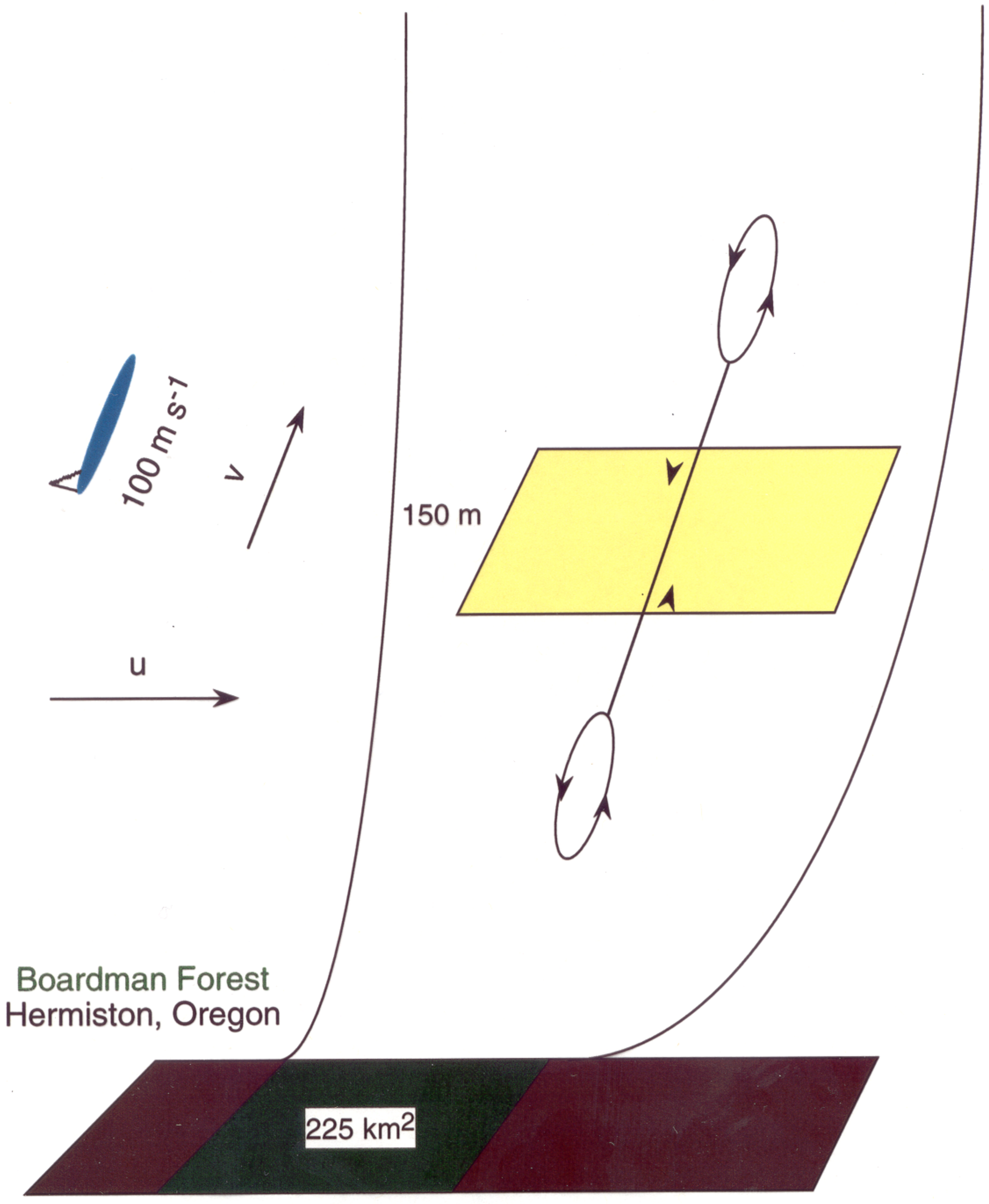
To intercompare instruments and sampling techniques

To measure vertical profiles of the isoprene flux and concentration

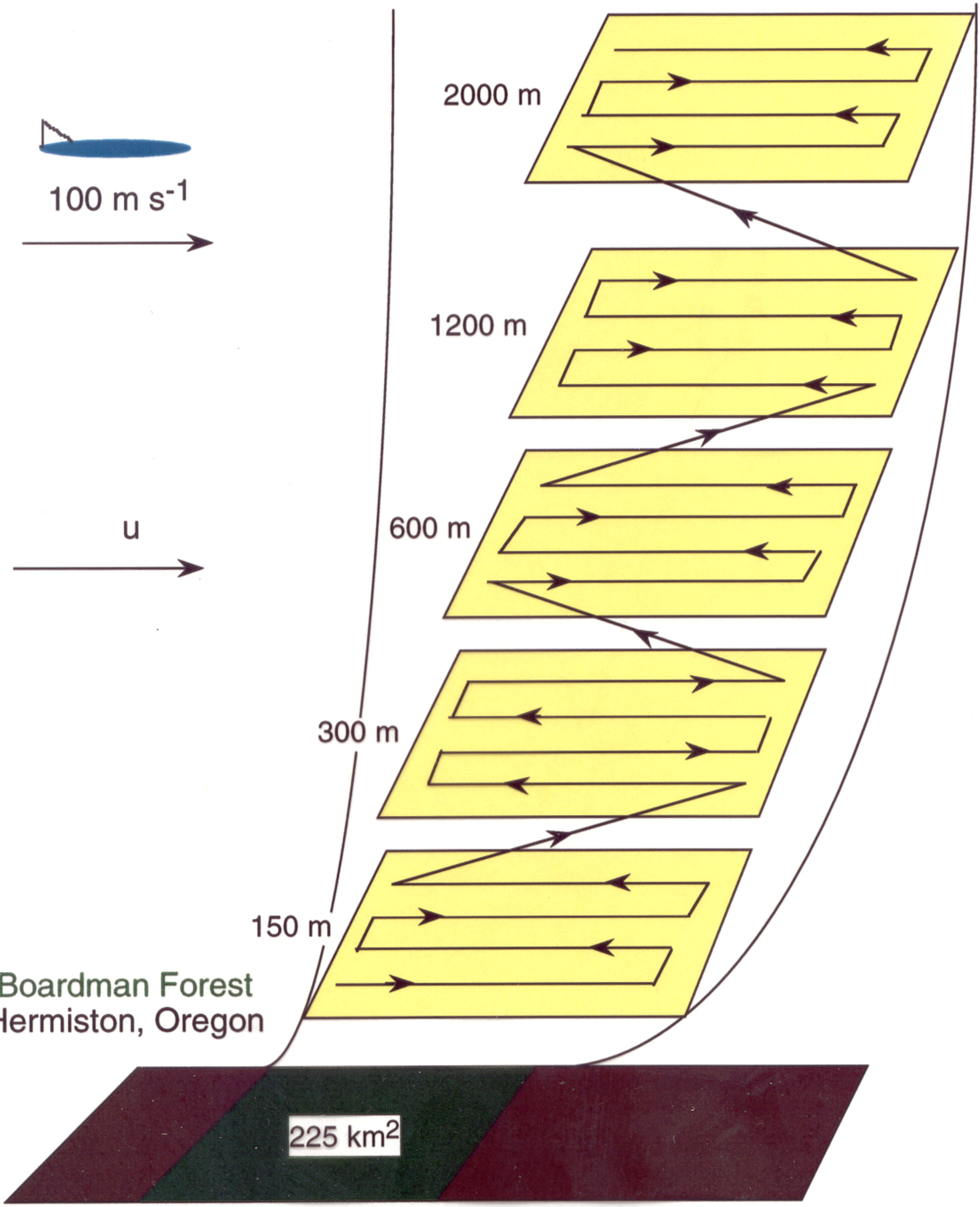
To evaluate meteorological chemical transport models

Air-Surface Exchange
↑↓
Atmospheric Chemistry
↑↓
Transport

Flight Plan for Instrument Intercomparison

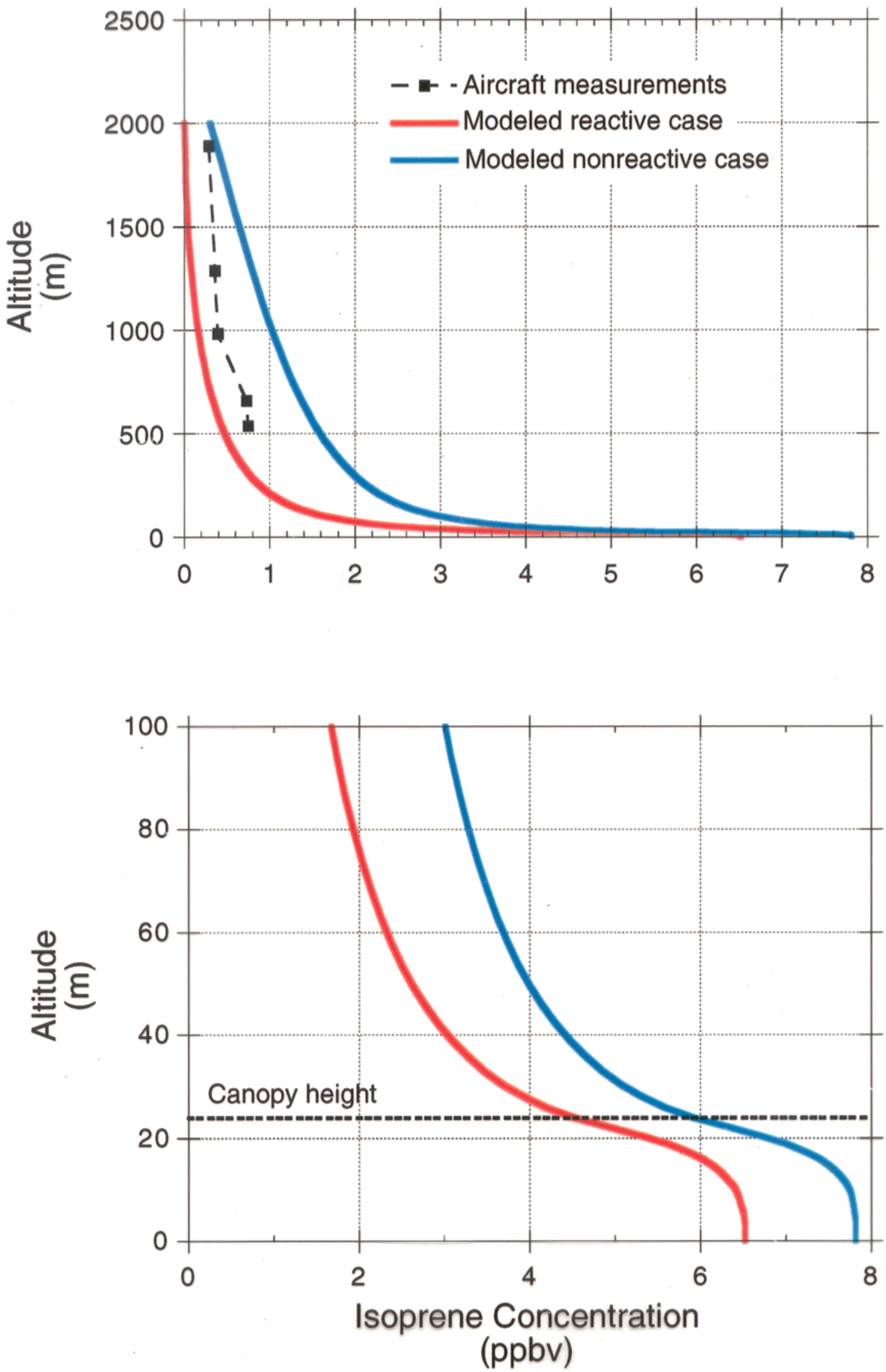


Flight Plan for Isoprene Flux Measurements

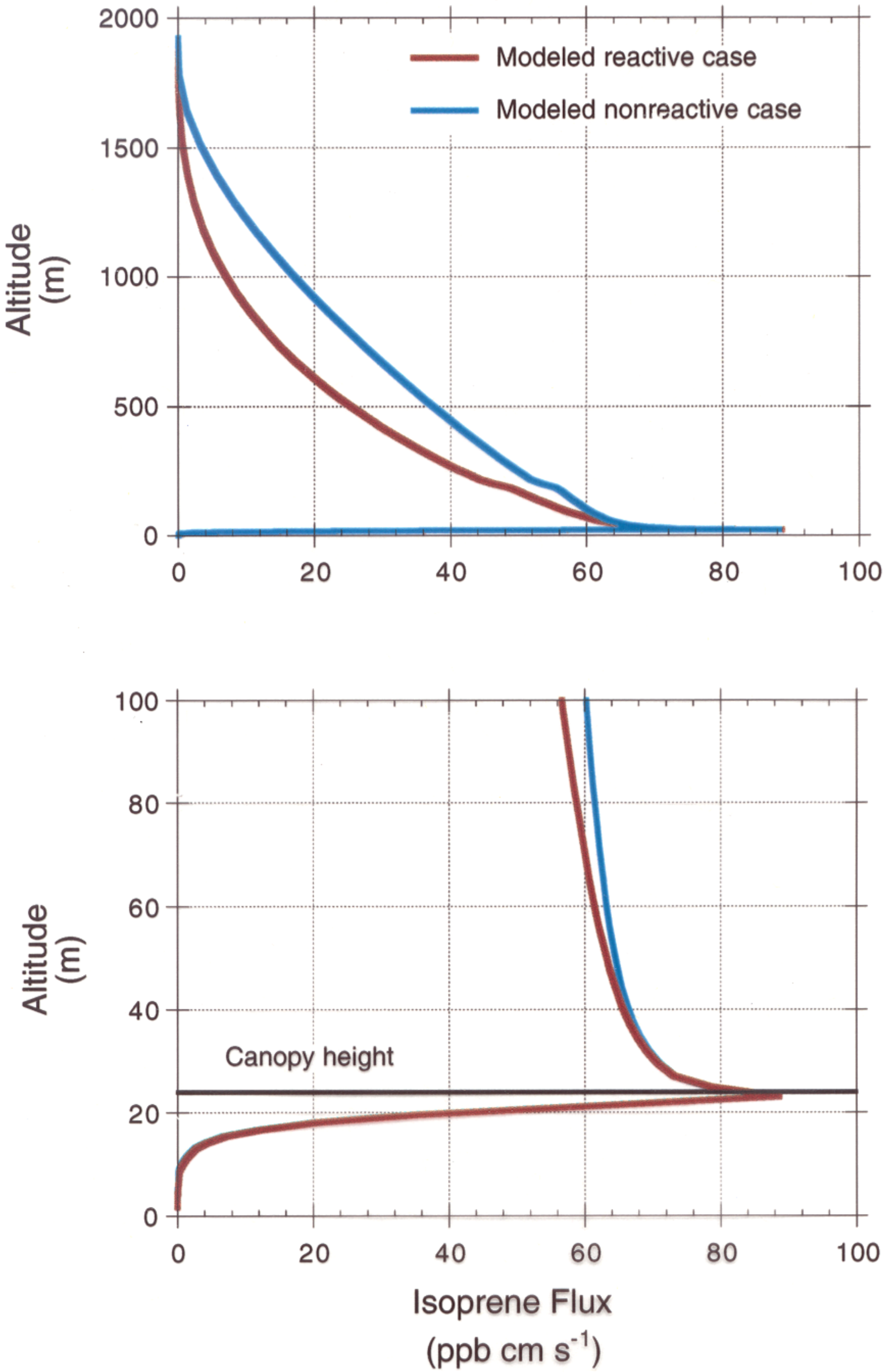


	Task 1 Instrument and Sampling Technique Intercomparison	Task 2 Vertical Profiling of Isoprene Flux and Concentration
Elevation (m)	150	150, 300, 600, 1200, 2000
Transects (#)	Crosswind (4)	Upwind/Downwind (4)[a]
Duration (s)	600	600[a]
Sample Collections		
EC	6000	6000[a]
DEC	1200	1200[a]
REA	4	1[a]
Whole-air	4	1[a]

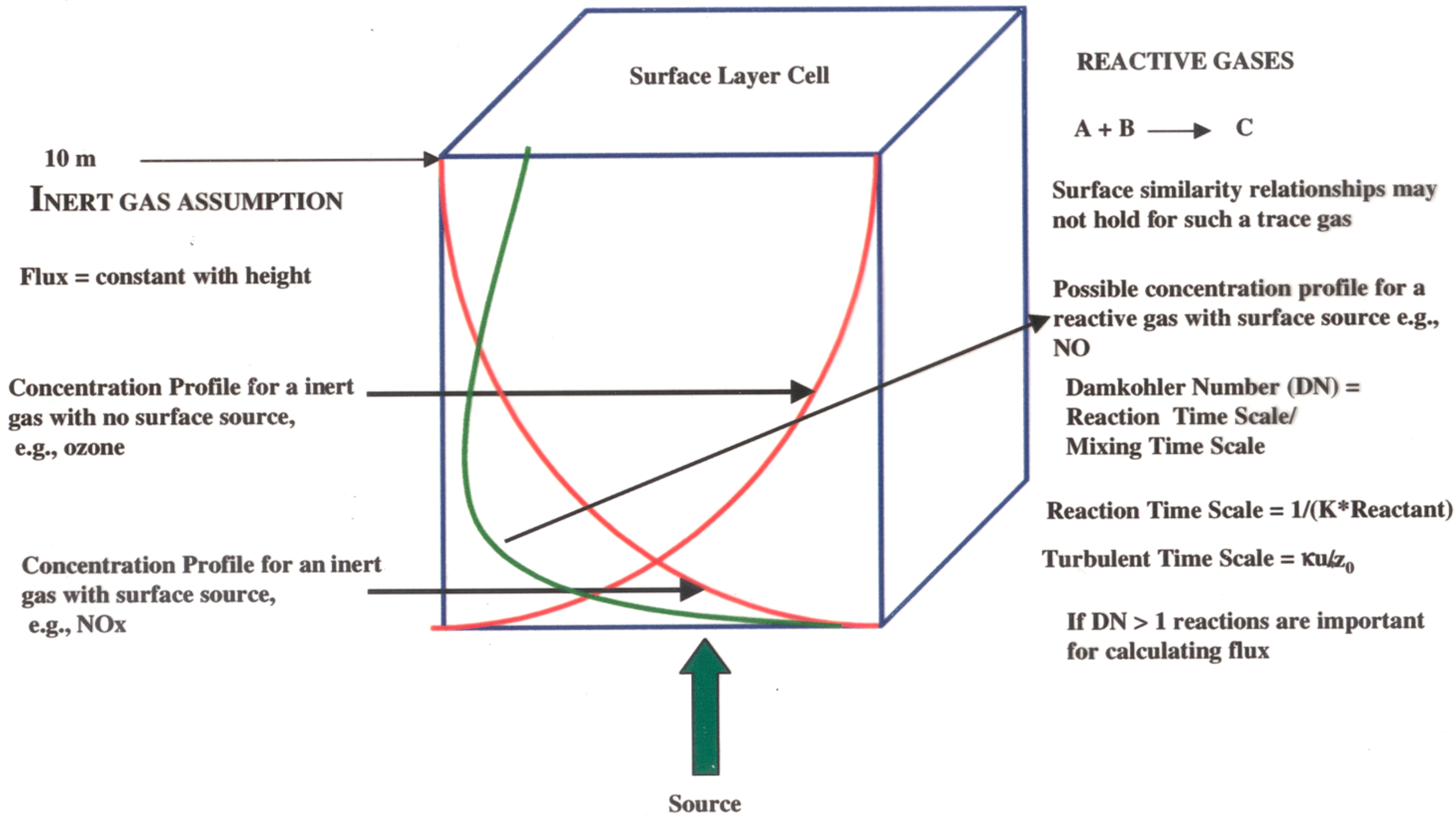
[a] At each elevation.



(Doskey, P. V. and W. Gao, J. Geophys. Res, 104, 21,263-21,274, 1999.)

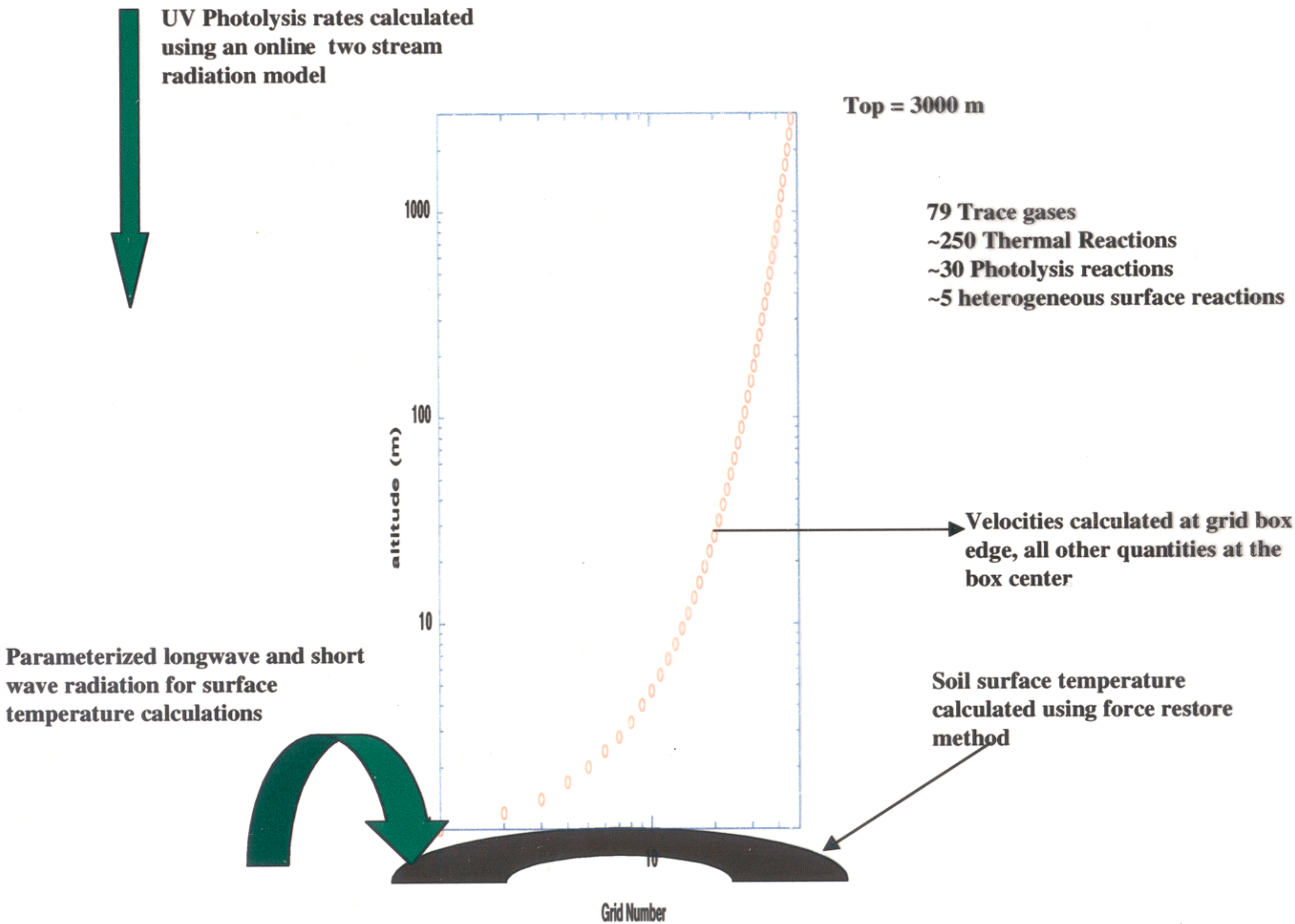


Modeled reactive case
Modeled nonreactive case
Altitude (m)
2000
1500
1000
500
0
0
20
40
60
80
100
Altitude (m)
100
80
60
40
20
0
Canopy height
0
20
40
60
80
100
Isoprene Flux
(ppb cm s-1)

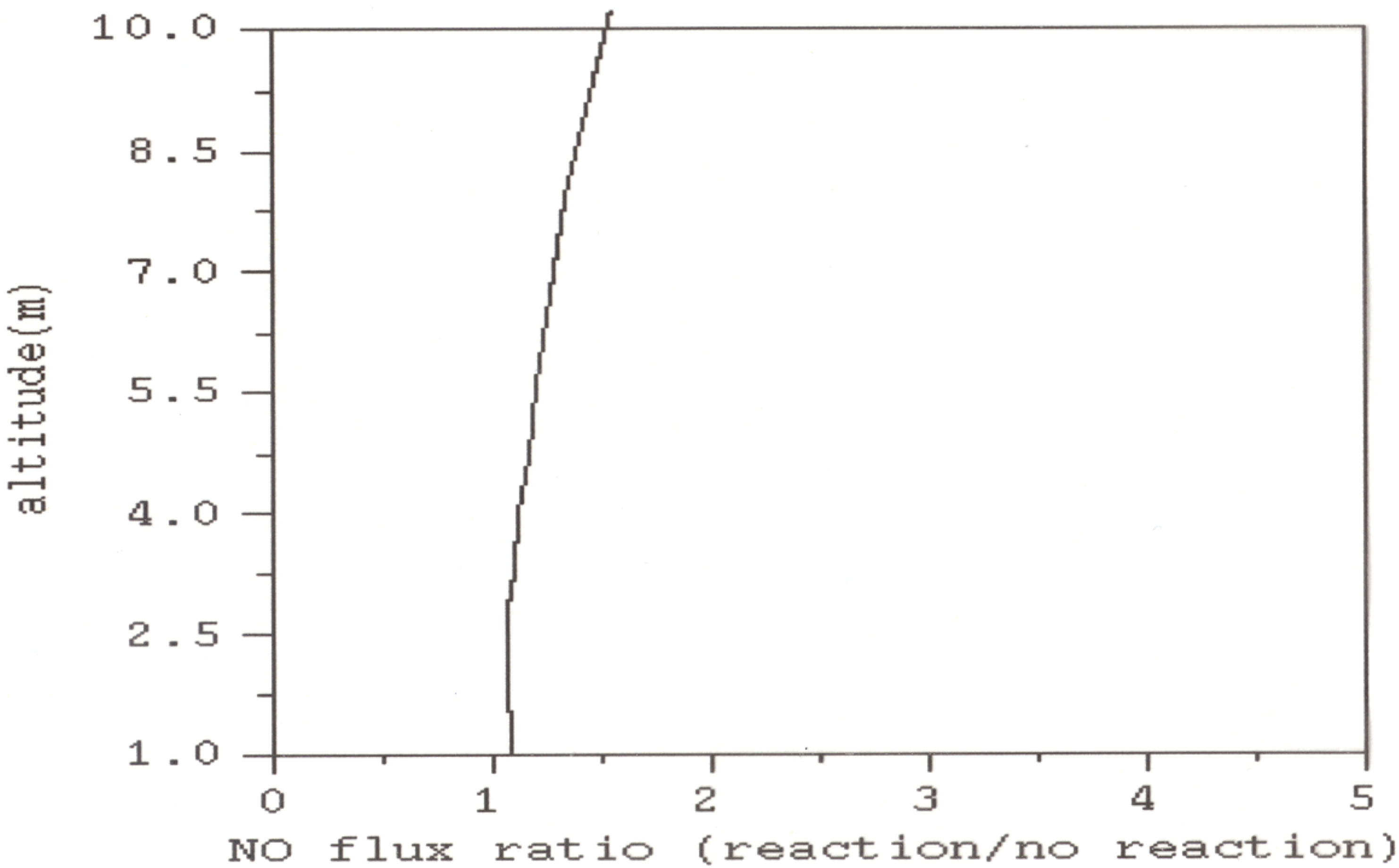


Surface Layer Cell
10 m
INERT GAS ASSUMPTION
Flux = constant with height
Concentration Profile for a inert gas with no surface source, e.g., ozone
Concentration Profile for an inert gas with surface source, e.g., NOx
Source
REACTIVE GASES
A + B → C
Surface similarity relationships may not hold for such a trace gas
Possible concentration profile for a reactive gas with surface source e.g., NO
Damkohler Number (DN) = Reaction Time Scale/ Mixing Time Scale
Reaction Time Scale = 1/(K*Reactant)
Turbulent Time Scale = $\kappa u/z_0$
If DN > 1 reactions are important for calculating flux

1-D PBL Dynamics Chemistry Model



The ratio of NO fluxes calculated for the lowest 10 m of the model



CTEF I

Chemical Processing of Terpene Emissions from Forests - Isoprene

- Intensive Field Campaign

- Observations - Surface Sites, Aircraft, Tethersondes

  Chemistry

  Tracer Studies

  Meteorology

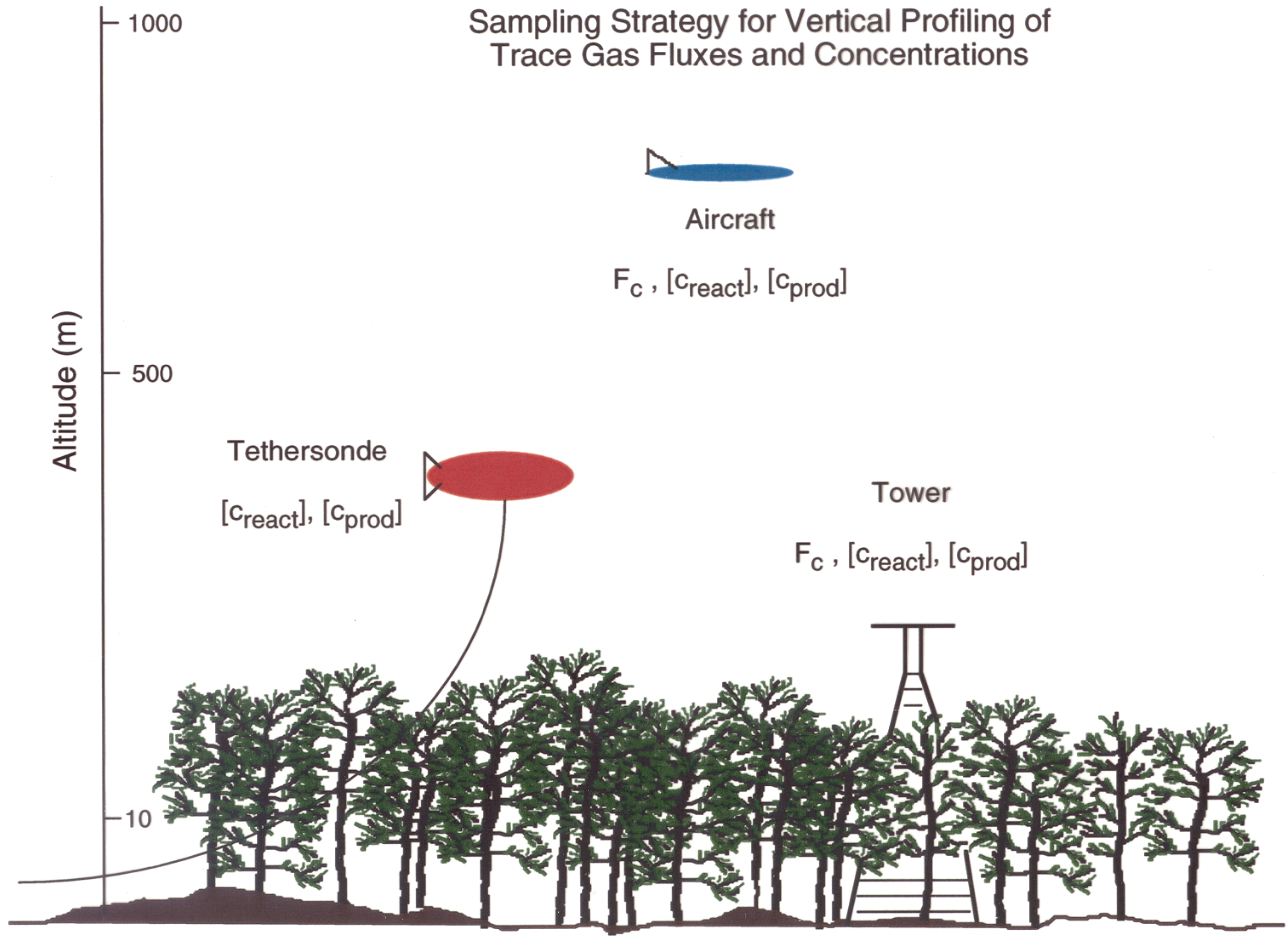
Air-Surface Exchange

↑↓

- Modeling Studies → Atmospheric Chemistry

↑↓

Transport


Sampling Strategy for Vertical Profiling of
Trace Gas Fluxes and Concentrations
1000
500
10
Altitude (m)
Aircraft
F_c , $[c_{react}]$, $[c_{prod}]$
Tethersonde
$[c_{react}]$, $[c_{prod}]$
Tower
F_c , $[c_{react}]$, $[c_{prod}]$

CTEF - I
Potential Collaborators and Field Sites

- Collaborators
    - Alex Guenther - NCAR
    - Paul Shepson - Purdue University
    - Hal Westberg - Washington State University
    - ASP Investigators
        - Tom Jobson
        - John Hubbe
        - Russell Dietz
        - Yin-Nan Lee
- Field Sites
    - NE Texas
    - Ozarks
    - Oak Ridge

Aerosol Field Studies

- Locations

  Coniferous Forest

  Urban Area - Mexico City, Houston

- Intensive Field Campaign

  Observations - Surface Sites, Aircraft, Tethersondes

  Chemistry

  Optical Depth

  Meteorology

Air-Surface Exchange

↑↓

- Modeling Studies → Atmospheric Chemistry and Radiative Forcing

↑↓

Transport

Acknowledgments

- Funding

  Peter Lunn, Program Manager
  Atmospheric Sciences Program
  Department of Energy