The Atmospheric Science Program

Jeff Gaffney and Nancy Marley
Argonne National Laboratory

http://www.asp.bnl.gov

ARGONNE NATIONAL LABORATORY
operated for
the U.S. Department of Energy
by The University of Chicago

ASP

SERVING SCIENCE AND SOCIETY
DOE Biological and Environmental Research Program

Mexico City

AEROSOLS - URBAN

PM-10 - <10 micrometer

PM-2.5 <2.5 micrometer

Primary –

Wind-blown dusts – Pollen, Spores, etc.

Carbonaceous soot – elemental or black C

Secondary -

Sulfate– Sulfuric Acid, Ammonium sulfate

Nitrate – Ammonium Nitrate

Organic Carbon – PAH, Oils, etc.

ATMOSPHERIC CHEMISTRY PROGRAM

ENVIRONMENTAL METEOROLOGY PROGRAM

JUNE 3, 2003

REFOCUS YOUR EFFORTS TOWARDS AEROSOL RADIATIVE EFFECTS

NOVEMBER 2003

BERAC SUBCOMMITTEE MEETING TO DEFINE THE FOCUS OF THE PROGRAM

DOE Program Officers

Mr. Peter Lunn

Mr. Rick Petty

Chief Scientist Named - March 1, 2004 – ASP

Steve Schwartz – Brookhaven National Laboratory

Leadership Team Named – March 4, 2004

Peter Daum – Brookhaven National Laboratory

Jeff Gaffney – Argonne National Laboratory

Steven Ghan – Pacific Northwest National Laboratory

Proposals Reviewed and ASP Science Team Announced – September 04

ASP Team Meeting – January 05

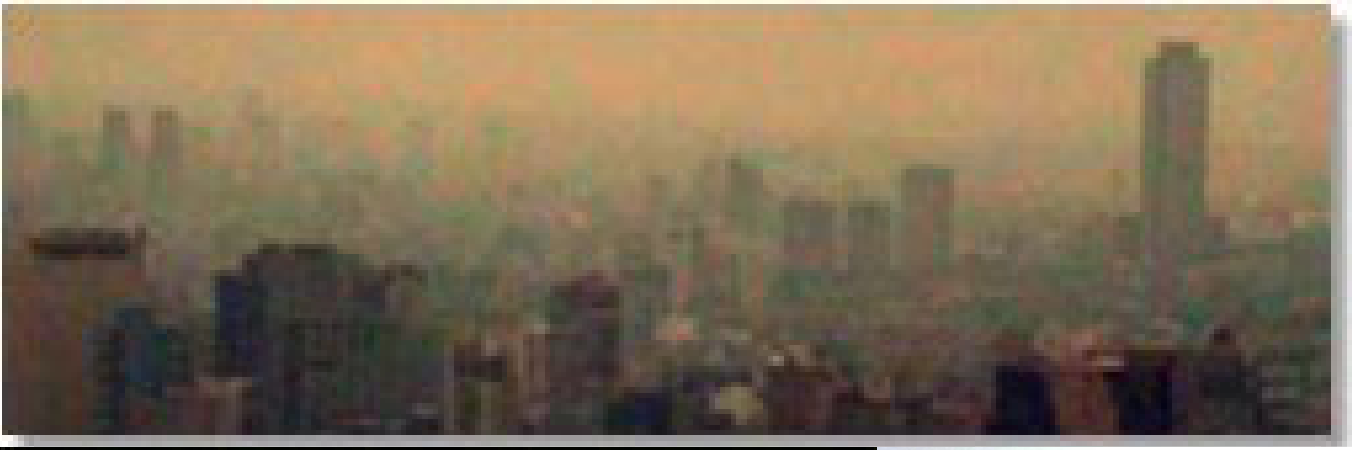
ASP Science Steering Committee. On March 15, 2005 Peter Lunn, DOE Program Director for the Atmospheric Science Program announced the membership of the ASP Science Steering Committee, as follows:

Peter H. Daum	**BNL**
J. Christopher Doran	**PNNL**
Jeffrey S. Gaffney	**ANL**
Steven J. Ghan	**PNNL**
Chris A. Hostetler	**NASA Langley**
Sasha Madronich	**NCAR**
Luisa T. Molina	**MIT**
John H. Seinfeld	**Caltech**

Program Goals

The Atmospheric Science Program (ASP) has both a long-term goal, and a specific science focus that changes from time to time according to national and DOE needs. The long-term goal is to develop a comprehensive understanding of the atmospheric processes that control the transport, transformation, and fate of energy related chemicals and particulate matter, especially in the context of climate change.

Beginning in FY 2005 the specific science focus will be aerosol radiative forcing of climate. Associated with this focus is the objective of enhancing the scientific knowledge needed to simulate and predict radiative forcing and other climatic effects of aerosols.



Photochemical Smog Formation

CLIMATE EFFECTS OF FINE AEROSOLS

Light Scattering – Cooling (short wave)

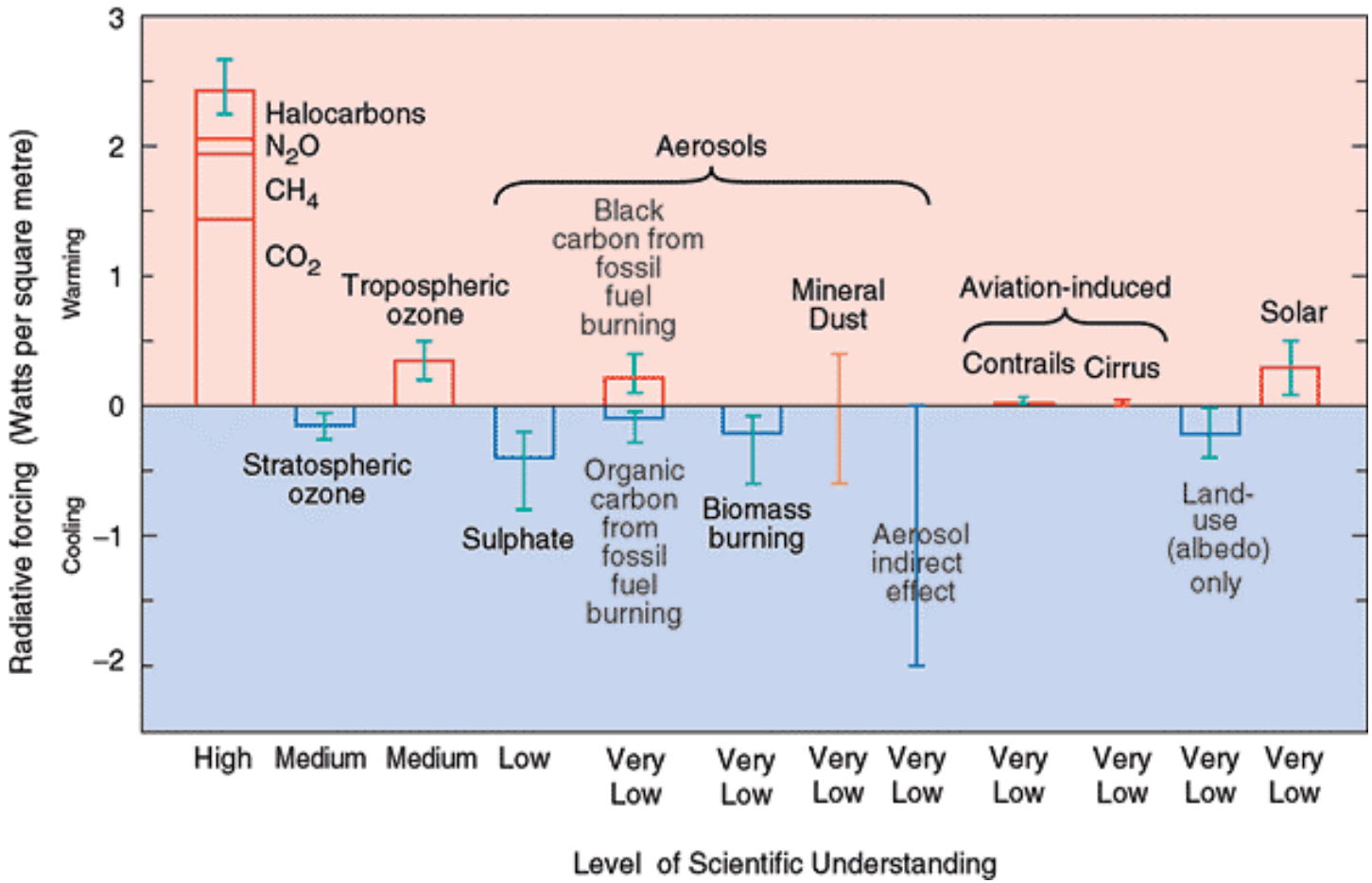
Light Absorption – Heating (long wave- all aerosols!)

Carbonaceous Soot – short and long wave

Indirect – Cloud Condensation Nuclei – Increased Clouds to HAZY SKIES – Depending upon Concentration and Composition.

IMPACT DEPENDS ON POSITION IN THE ATMOSPHERE AND THEIR LIFETIMES

The global mean radiative forcing of the climate system for the year 2000, relative to 1750



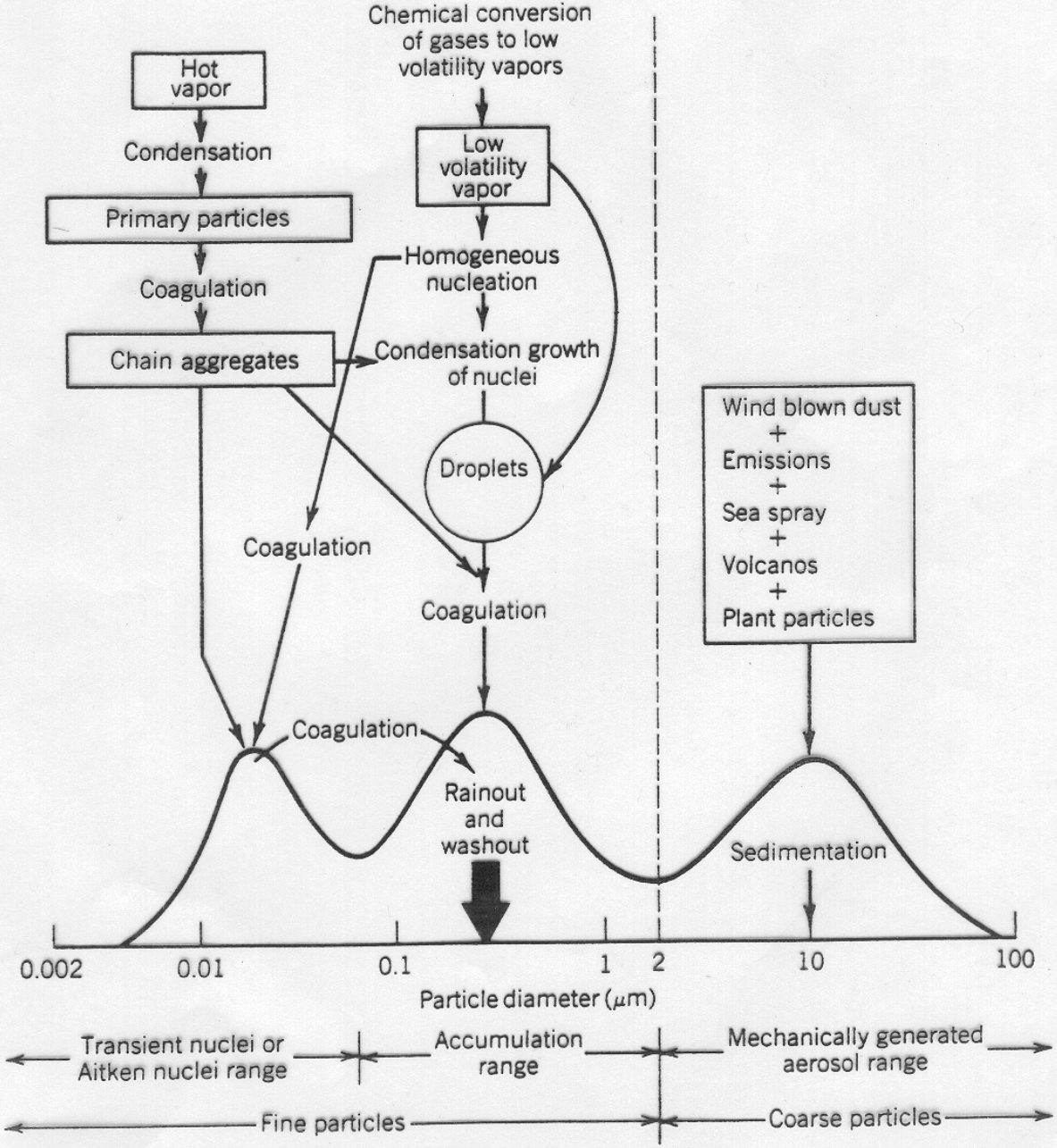
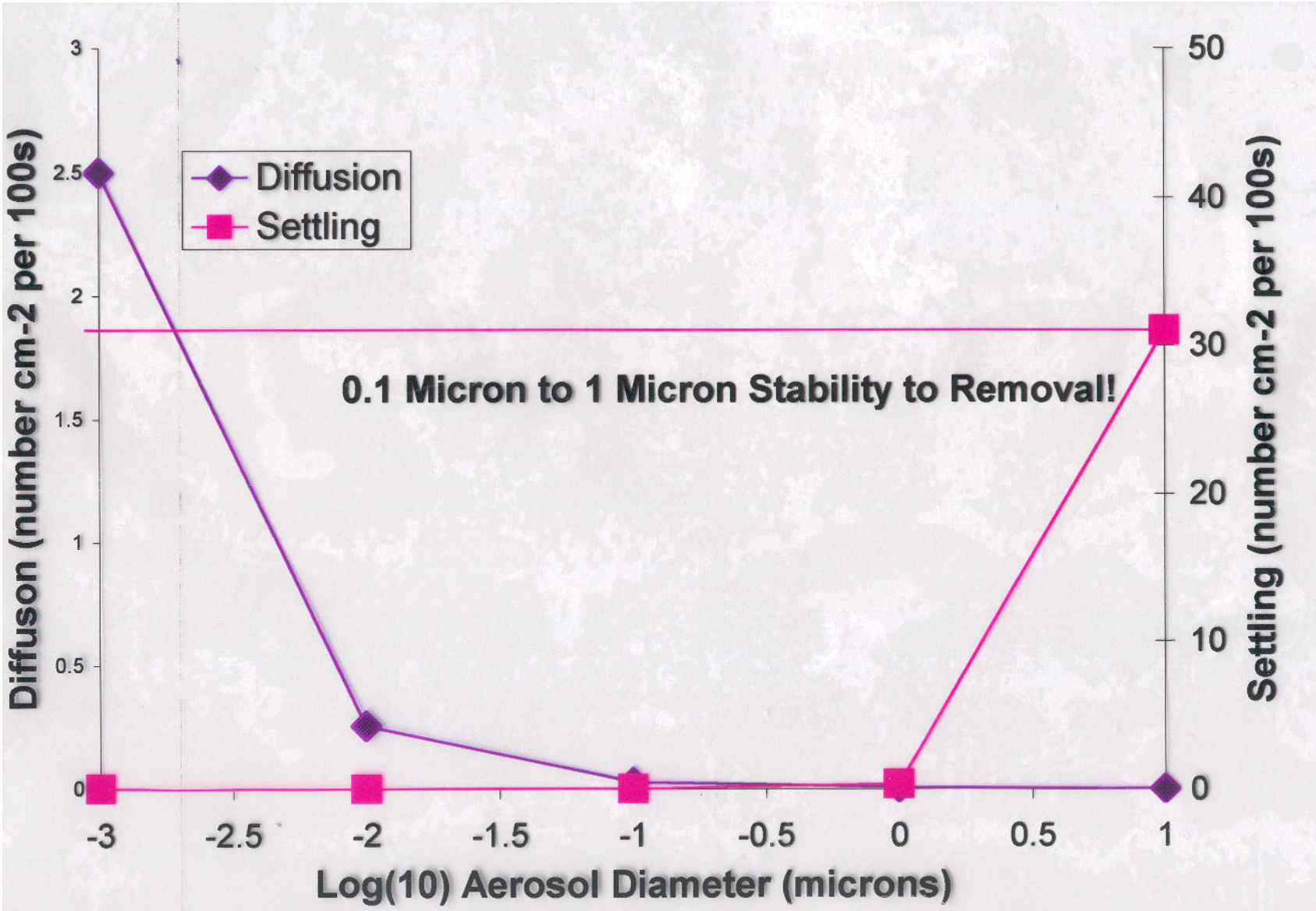


FIGURE 12.9. Schematic of an atmospheric aerosol size distribution showing the three modes, the main source of mass for each mode, and the principal processes involved in inserting mass into and removing mass from each mode (from Whitby and Sverdrup, 1980).


Diffusion
Settling
0.1 Micron to 1 Micron Stability to Removal!
Diffuson (number cm-2 per 100s)
Settling (number cm-2 per 100s)
Log(10) Aerosol Diameter (microns)
3
2.5
2
1.5
1
0.5
0
50
40
30
20
10
0
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1

Michael Alexander, Pacific Northwest National Laboratory: "Proton Transfer Reaction Ion Trap Mass Spectrometer (PTR-ITMS): Next Generation Aircraft Instrumentation for Gas Phase Organic Analysis"

Patrick Arnott, Desert Research Institute, and **Patrick Sheridan**, NOAA CMDL: "Aerosol Light Absorption and Climate: Quantification by the Photoacoustic Method"

Cynthia Atherton, Lawrence Livermore National Laboratory: "Atmospheric Formation, Transformation, and Radiative Forcing of Acid-Catalyzed Secondary Organic Aerosols"

Carl Berkowitz and **Larry Berg**, Pacific Northwest National Laboratory: "The Effects of Cloud Processes on the Optical Properties of Aerosols"

Peter Daum, Brookhaven National Laboratory: "Aerosol Cloud Interactions: Field Studies and Interpretation"

Paul Davidovits, Boston College: "Effects of Soot Morphology and Chemistry on Particle Hygroscopic and Optical Properties"

Christopher Doran and **Jim Barnard**, Pacific Northwest National Laboratory: "Field Studies of the Evolution of Aerosols Downwind of an Urban Area: The Roles of Black Carbon and Meteorological Processes on Aerosol Radiative Effects"

Jerome Fast, Pacific Northwest National Laboratory: "Synthesis of Field Observations and Multi-Scale Modeling of Aerosol Evolution and Its Impact on Radiative Forcing from Urban to Regional Scales"

Barbara Finlayson-Pitts, UC-Irvine: "Impacts on CCN Properties of Nitrate Aerosols Due to Exposure to Irradiated VOC-NOx Mixtures"

Jeffrey Gaffney, Argonne National Laboratory: "Determining Aerosol Mean Residence Times and Black Carbon Washout Rates with Natural Radionuclides and Isotopic Signatures"

Steven Ghan, Pacific Northwest National Laboratory: "Superparameterization of Aerosol Transport, Transformation, and Removal by Clouds"

Mary Gilles, Lawrence Berkeley National Laboratory: "Soft X-ray Spectromicroscopy of Black Carbon Aerosols"

Chris Hostetler, NASA Langley: "Characterizing Aerosol Distributions and Optical Properties using Airborne Active and Passive Remote Sensing"

James Hudson, Desert Research Institute, "CCN Spectral Measurements"

Lawrence Kleinman, Brookhaven National Laboratory: "Field Studies on the Life Cycle of Aerosols and Their Direct Radiative Impacts"

Rao Kotamarthi, Argonne National Laboratory: "Process-Scale Modeling of ASP Field Measurements"

Alexander Laskin, Pacific Northwest National Laboratory: "Laboratory Studies of Optical and Hygroscopic Properties of Field Collected Atmospheric Aerosols"

Yin-Nan Lee, Brookhaven National Laboratory: "Characterization of Aerosol Organic Matter: Detection, Formation and Optical and Radiative Effects"

Sasha Madronich, NCAR: "Impacts of Secondary Organics on the Evolution of Climate-Relevant Aerosol Properties During Lagrangian Aerosol Plume Experiments"

Nancy Marley, Argonne National Laboratory: "Aerosol Precursors and Aerosol Instrumentation: Field Measurements and Method Development"

Robert McGraw, Brookhaven National Laboratory: "New Particle Formation: Mechanisms and Influence on Atmospheric Aerosol Properties"

Peter McMurry, University of Minnesota: "Nucleation and Growth of Atmospheric Aerosols"

Mario Molina, MIT, **Charles Kolb**, Aerodyne, and **Jose Jimenez**, University of Colorado: "Characterization of Fine Particulate Matter (PM) and Secondary PM Precursor Gases in the Mexico City Metropolitan Area"

John Ogren, NOAA CMDL: "Cloud-Driven Changes in Aerosol Optical Properties"

Mikhail Ovtchinnikov and **Dick Easter**, Pacific Northwest National Laboratory: "Aerosol Processing by Clouds: Model Evaluation and Parameterization Development"

Suzanne Paulson, UCLA: "Black Carbon and Organic Carbon Aerosol Mass and Optical Properties: Comparability and Causes of Uncertainties"

Stephen Schwartz and **Douglas Wright**, Brookhaven National Laboratory: "Modeling Aerosol Processes in the DOE Atmospheric Science Program"

Arthur Sedlacek, Brookhaven National Laboratory: "Measurement of Aerosol Absorption Using Photothermal Interferometry"

John Seinfeld, California Institute of Technology: "Mechanisms of Formation of Secondary Organic Aerosols and Implications for Global Radiative Forcing"

Jian Wang, Brookhaven National Laboratory: "Fast Measurements of Aerosol Size Distribution, Hygroscopicity, and Volatility for Aircraft Deployment"

Judith Weinstein-Lloyd, SUNY-Old Westbury: "Secondary Aerosol: Precursors and Formation Mechanisms"

Paul Ziemann, **Roger Atkinson**, and **Janet Arey**, UC-Riverside: "Laboratory Studies of Processing of Carbonaceous Aerosols by Atmospheric Oxidants"

Infrastructure Projects (5):

Richard Coulter, Argonne National Laboratory: "Instrumentation and Deployment in Support of ASP Field Studies"

John Hubbe, Pacific Northwest National Laboratory: "Research Aircraft Operations"

Stephen Schwartz, Brookhaven National Laboratory: "Chief Scientist for the Atmospheric Science Program"

William Shaw, Pacific Northwest National Laboratory: "Meteorology and Aerosol Measurements for DOE's Atmospheric Science Program"

Stephen Springston, Brookhaven National Laboratory: "Chemistry and Microphysics of the Troposphere: Core Measurements for Field Programs"

Atmospheric Science Program:

DOE Research Aircraft Facility

Gulfstream 159 Aircraft for Airborne Atmospheric Research

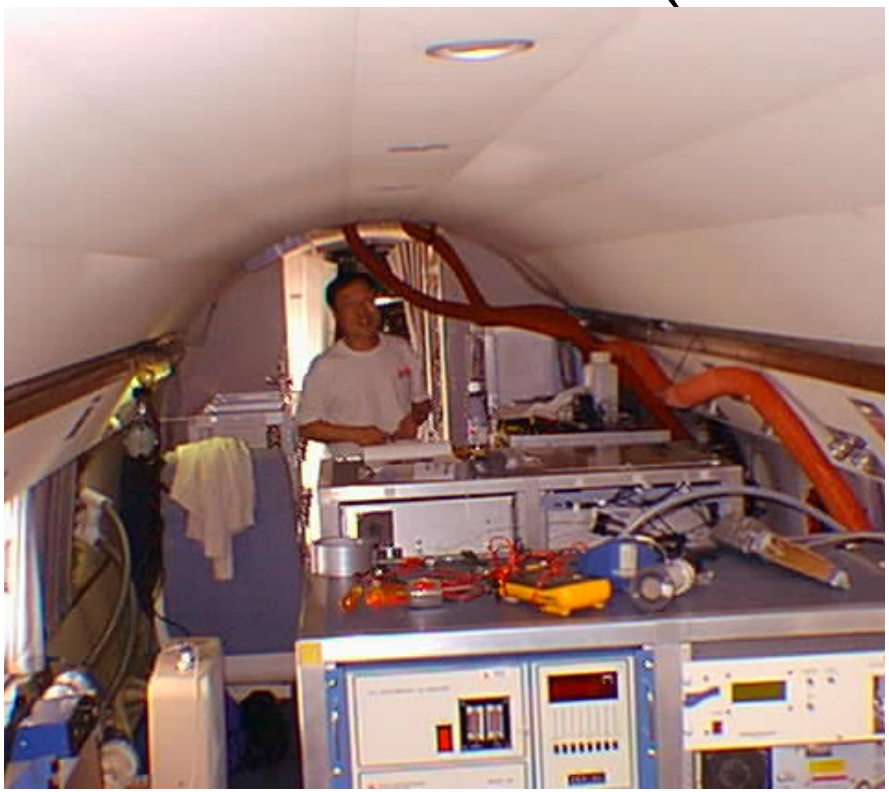
John Hubbe/Bob Hannigan

Pacific Northwest National Lab

DOE Research Aircraft Facility

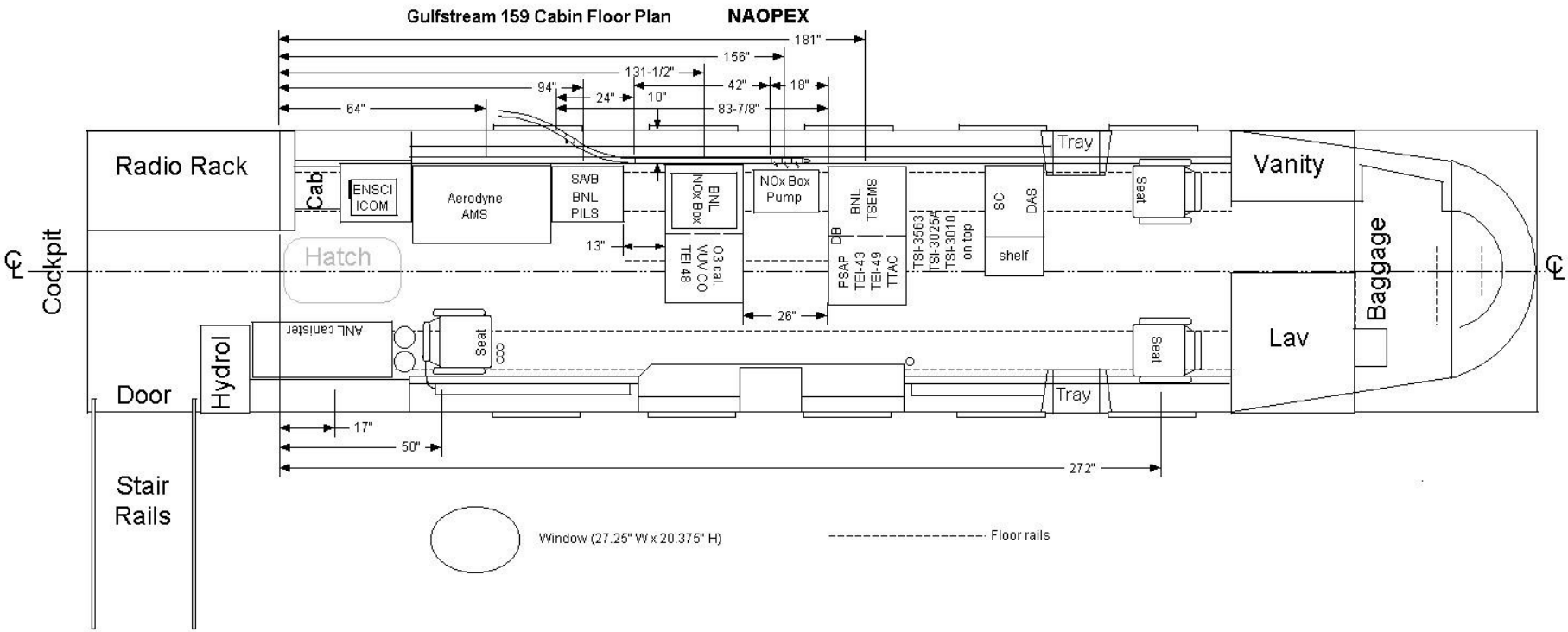
Grumman Gulfstream 159 (G-1) twin turboprop aircraft

Instrumentation on G-1
(continued)



Instrumentation Racks

Cabin Configuration for FY02 Field Studies



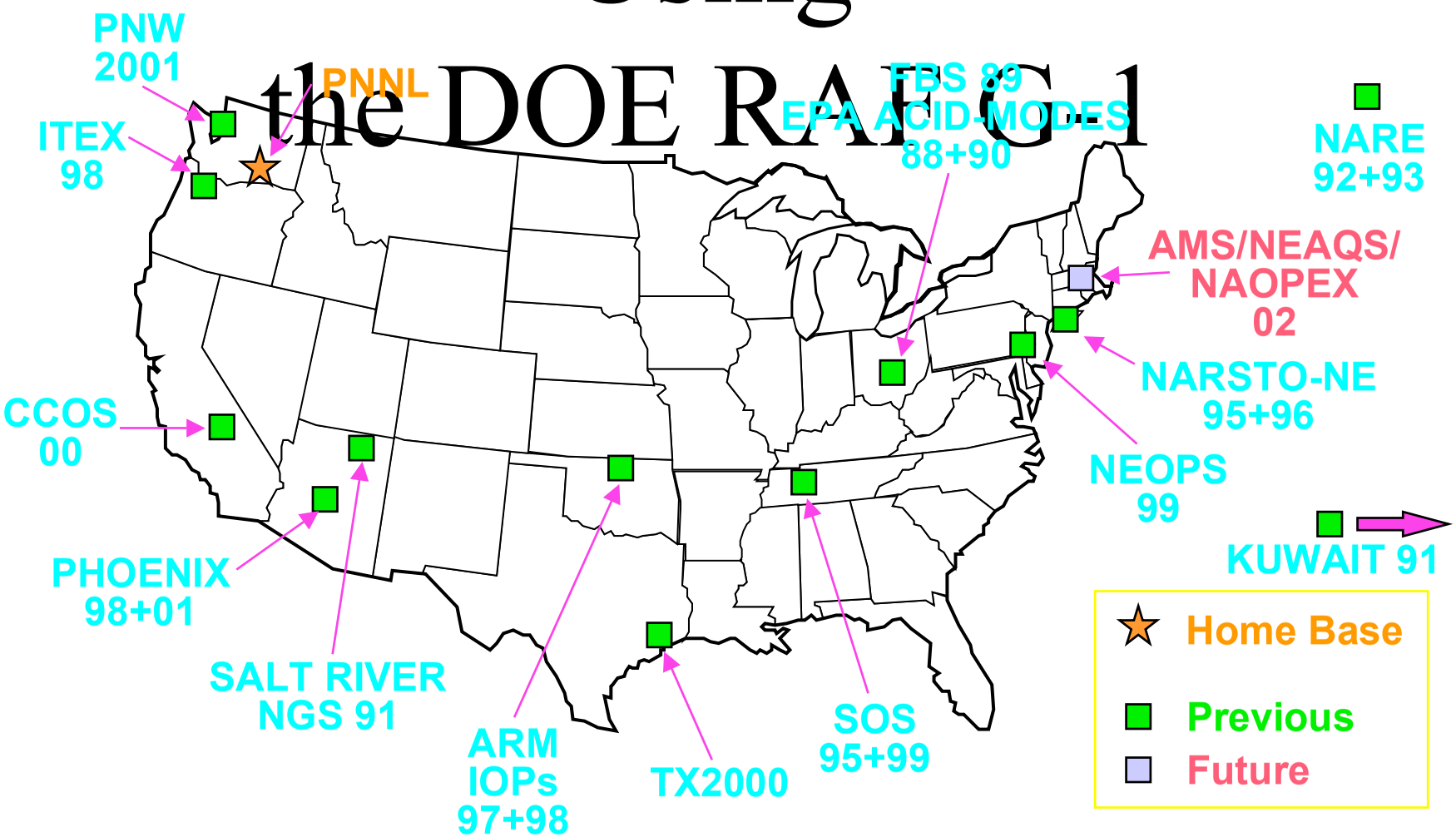
2700 lb equipment

4 scientific crew

5000 VA @ 110 VAC

2900 VA @ 220 VAC

Locations of ACP Projects Using the DOE RAEG-1



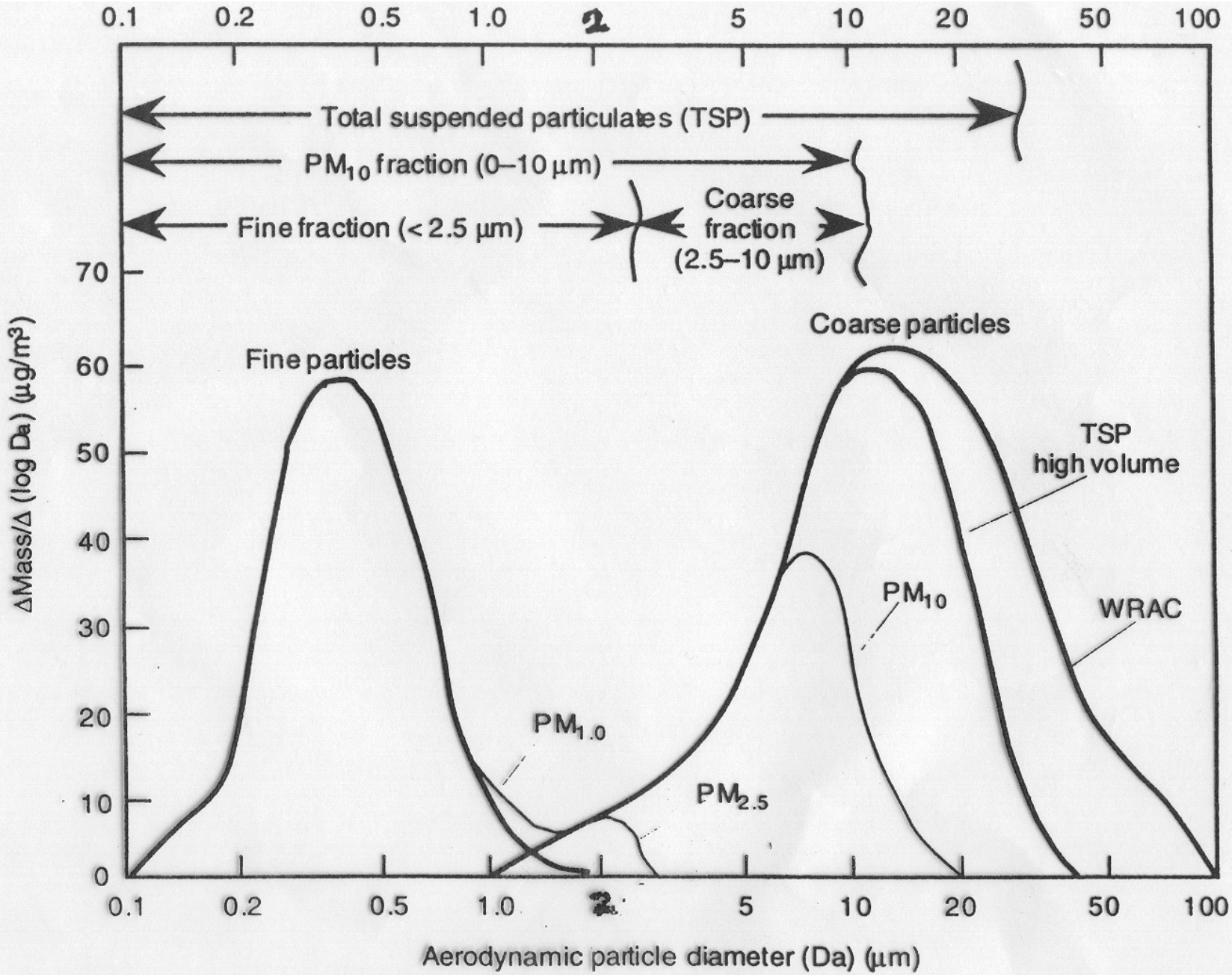
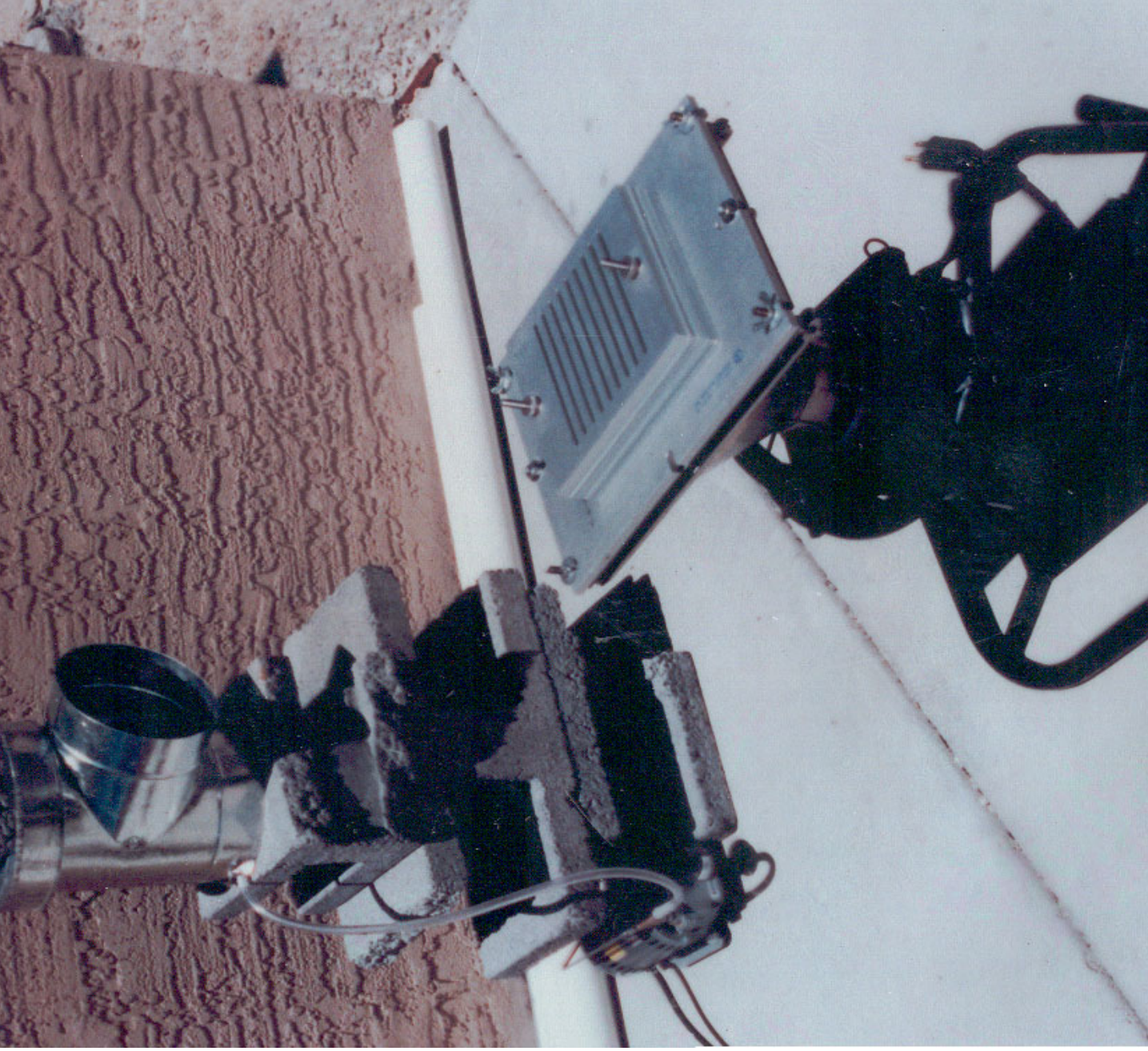
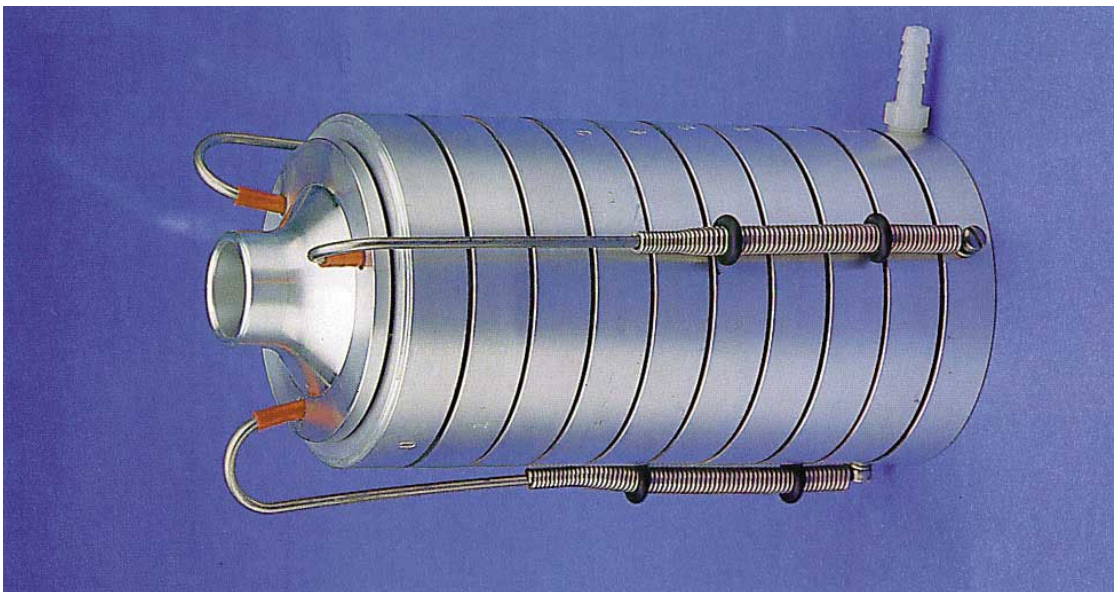


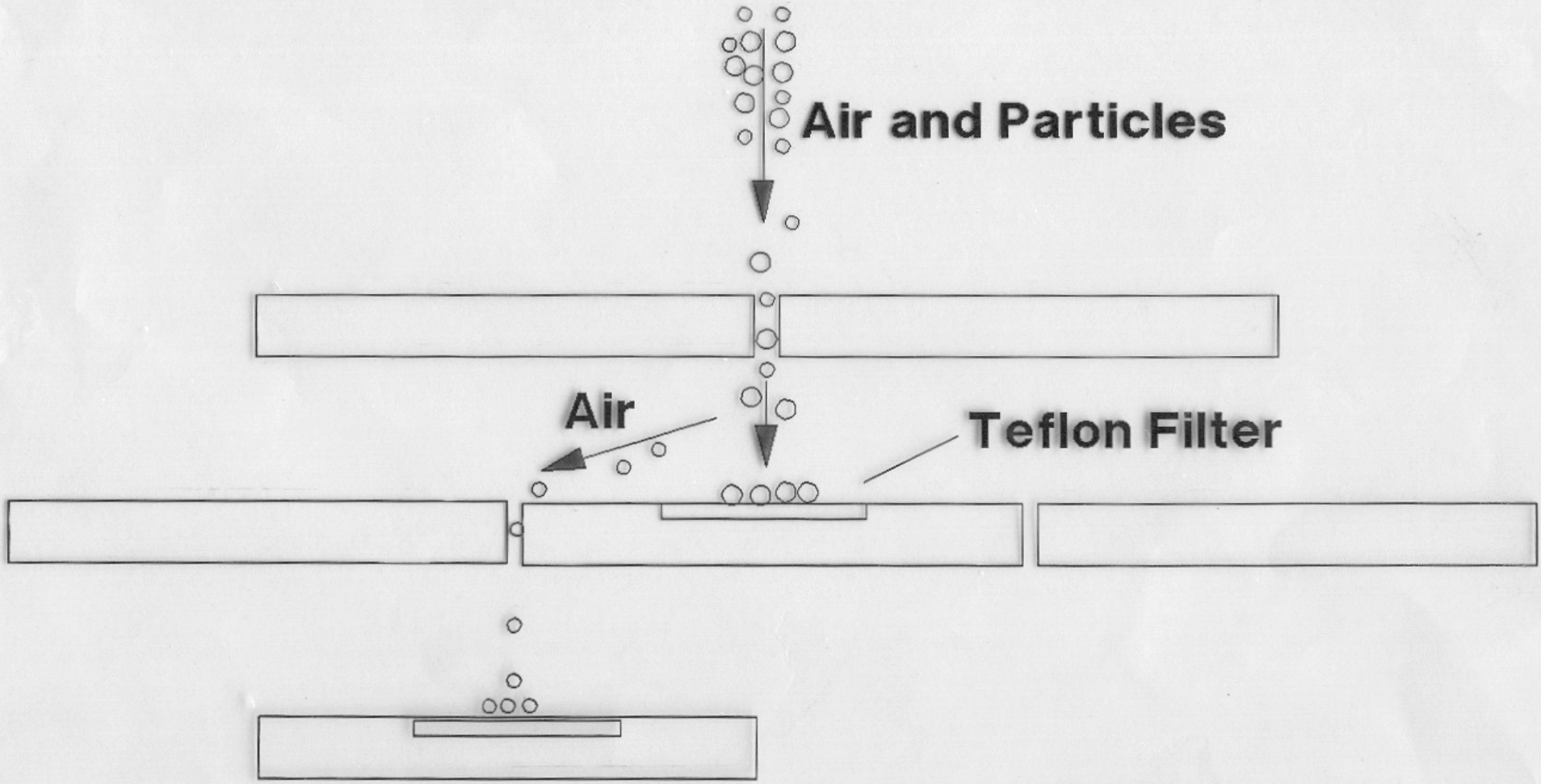
Figure 5
The interrelationship between different parameters used to describe the size distribution of airborne particulate matter. (Adapted from Wilson and Suh, 1997.)

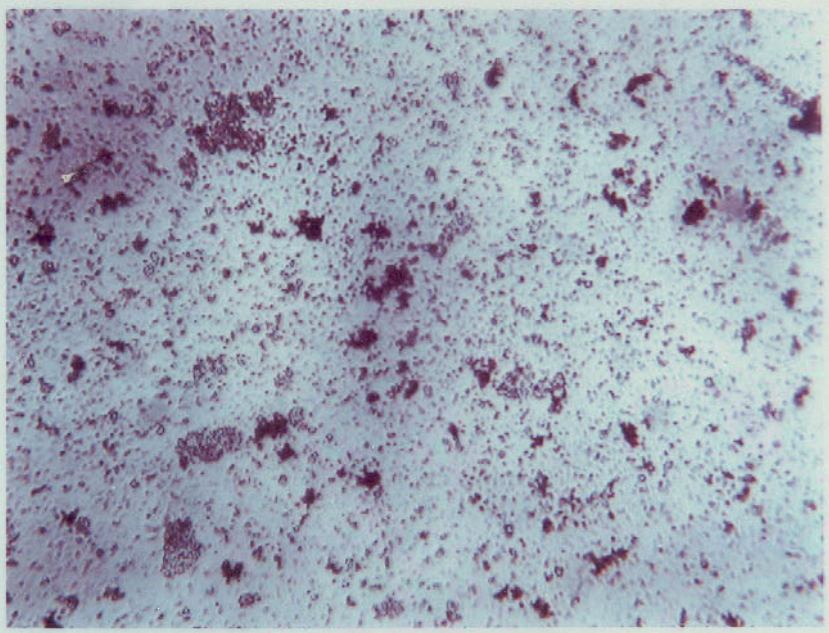


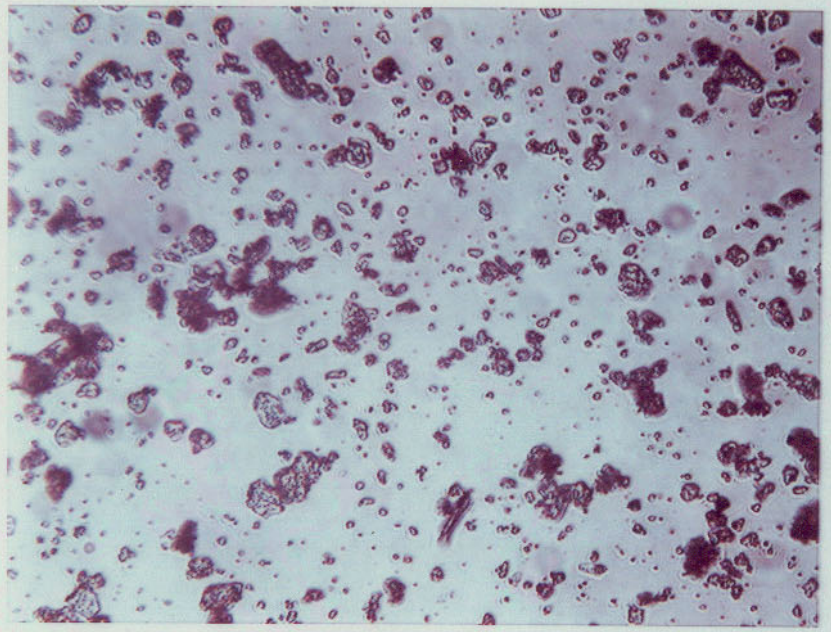


BASIC PHYSICS OF AN IMPACTOR

Sizing Dependent on Flow Velocity and Geometry



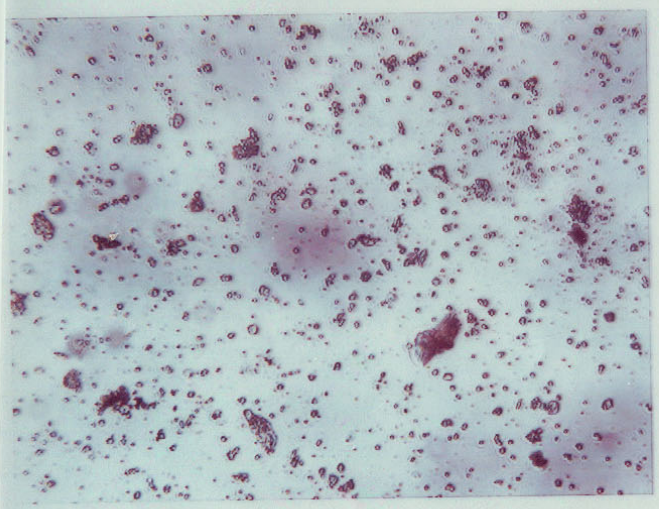


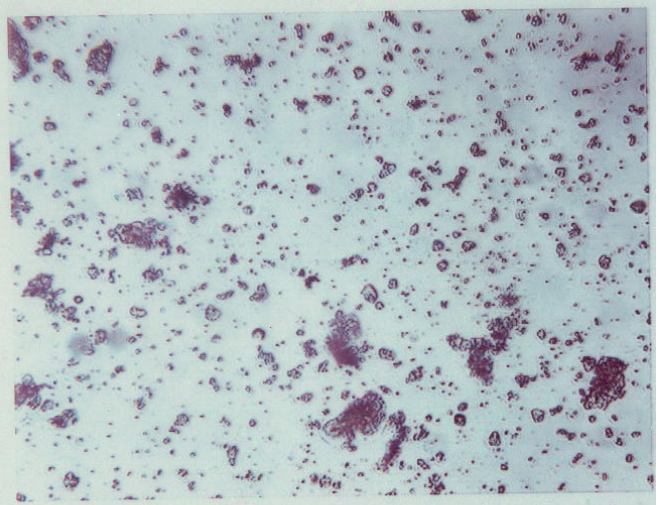


STAGE 5
50% CUTOFF 0.5 µm

STAGE 4
50% CUTOFF 1.0 µm

1 cm = 25µm





STAGE 3
50% CUTOFF 2.0 µm

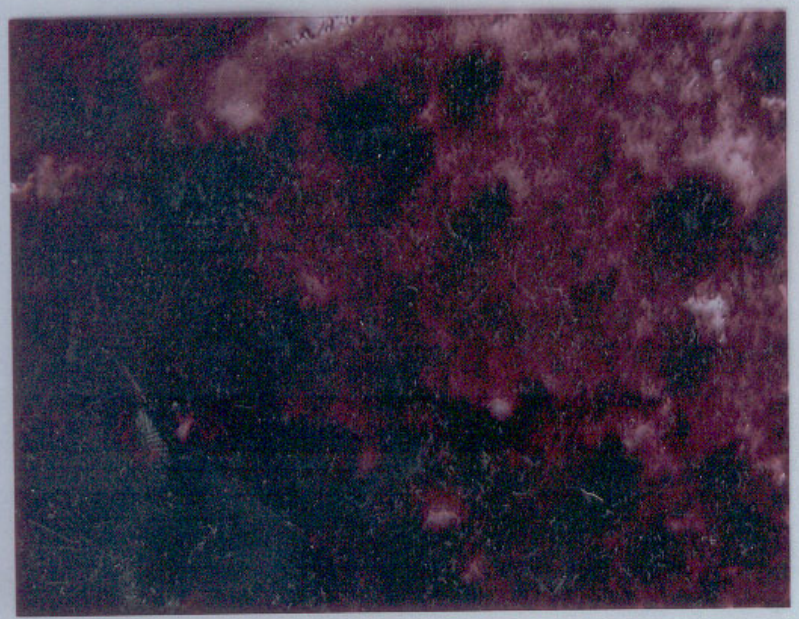
STAGE 2
50% CUTOFF 4.0 µm

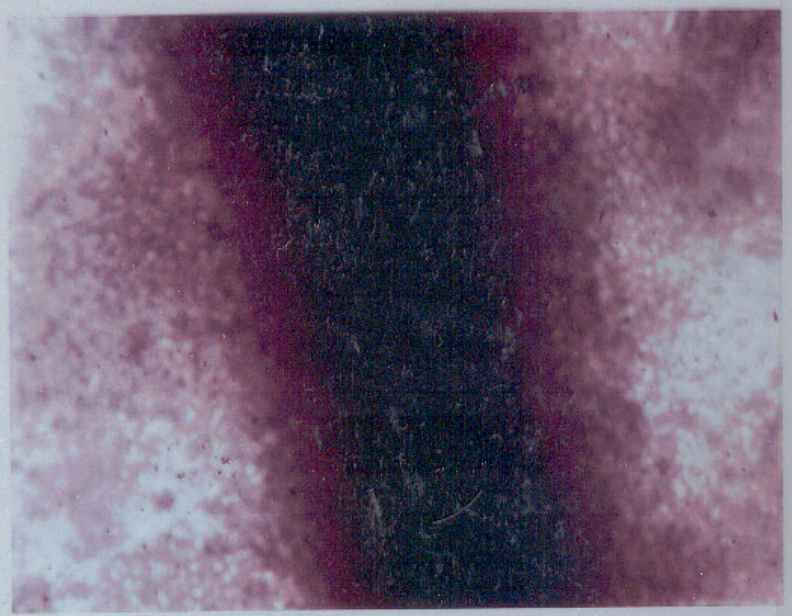
1 cm = 25µm

Aerosol Samples - Argonne, IL

1 cm = 25 um

1 cm = 158 um





Size Fraction 5; 0.5 um.

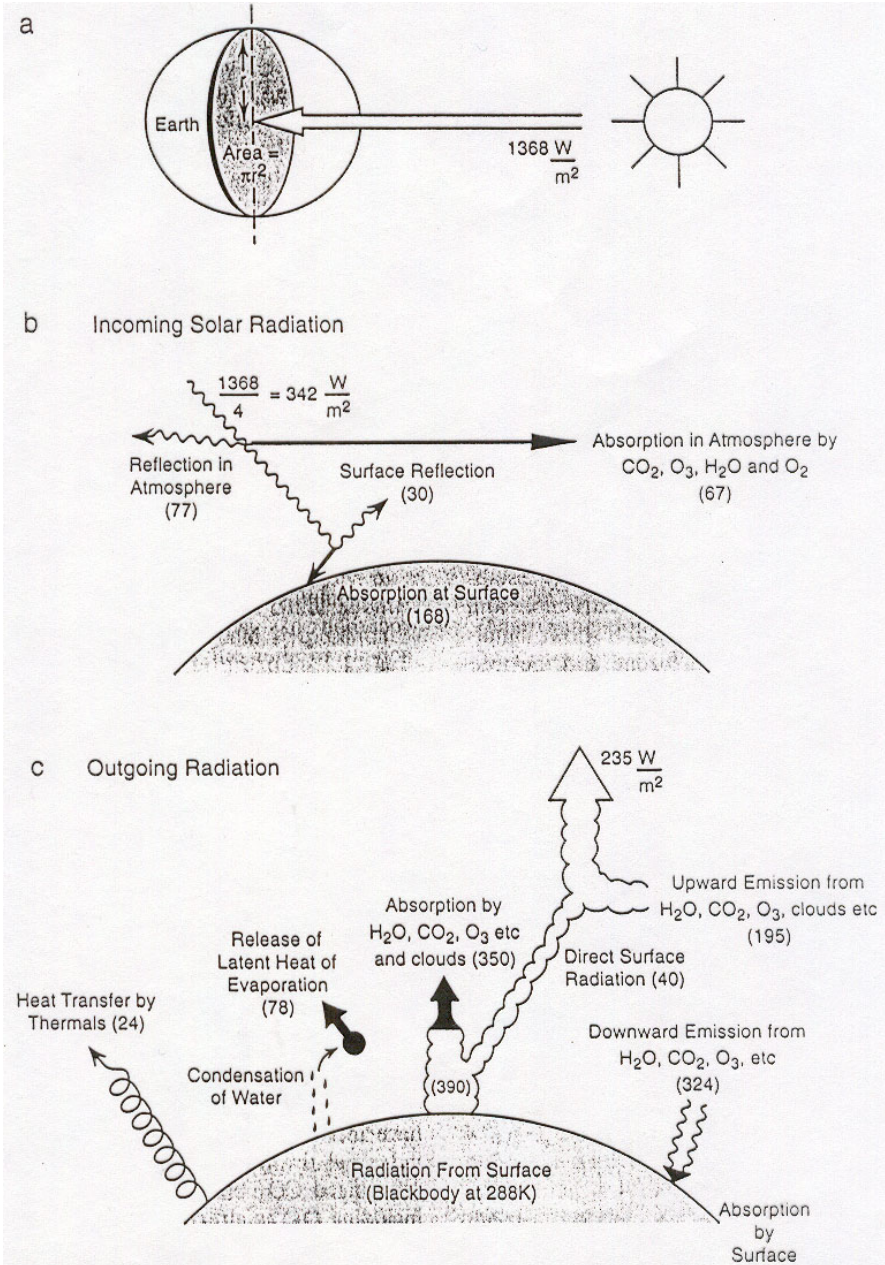
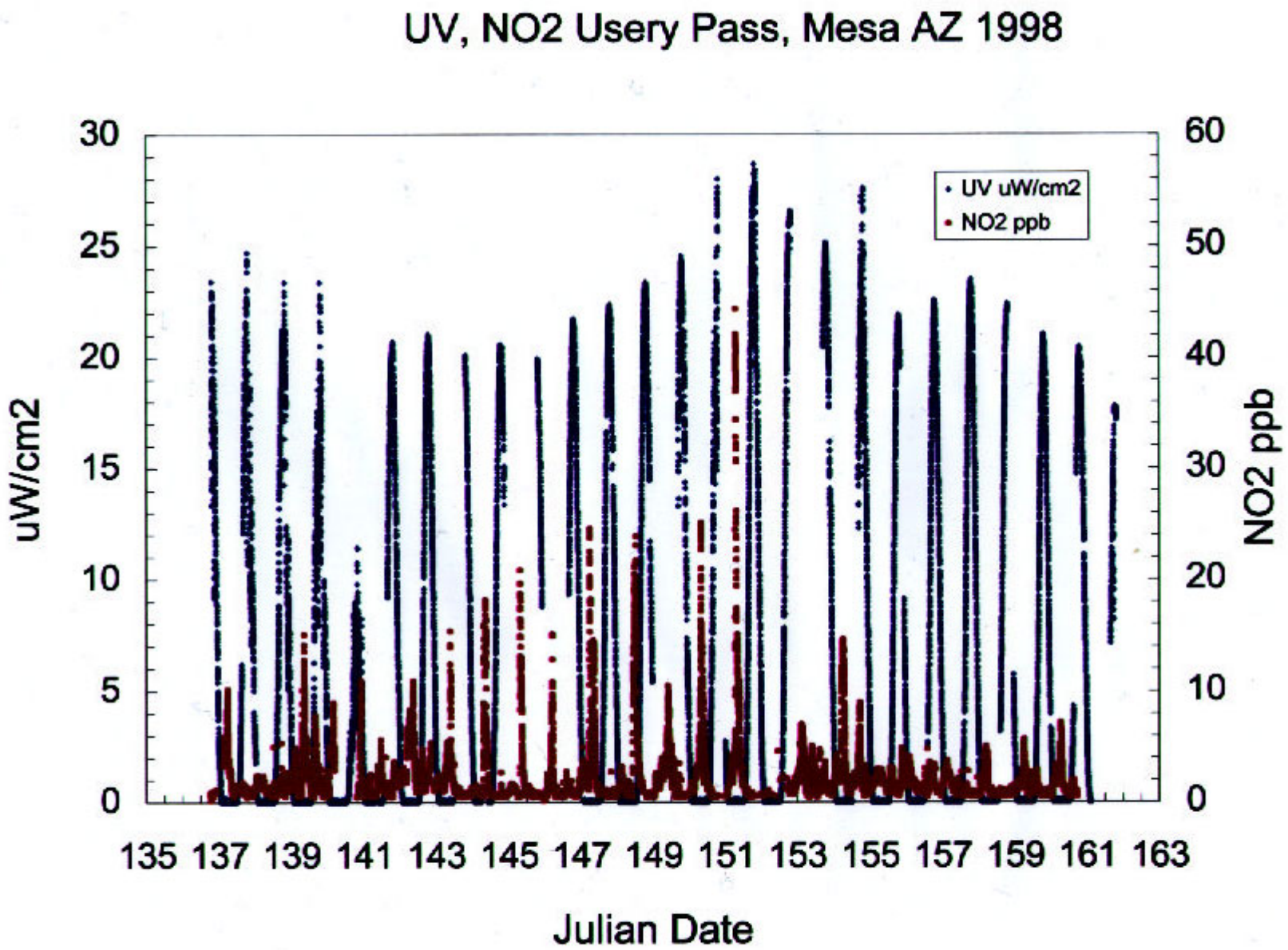
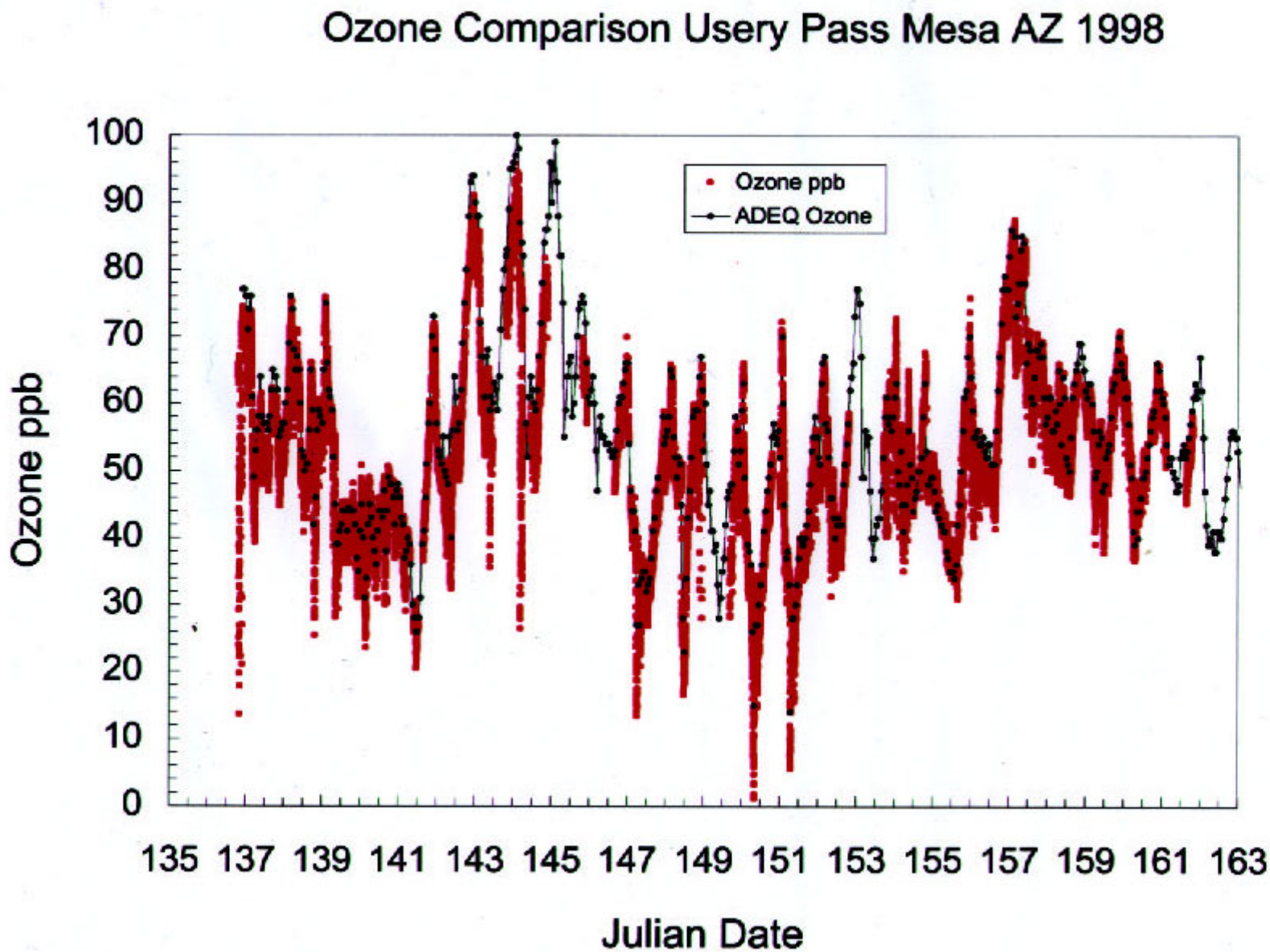
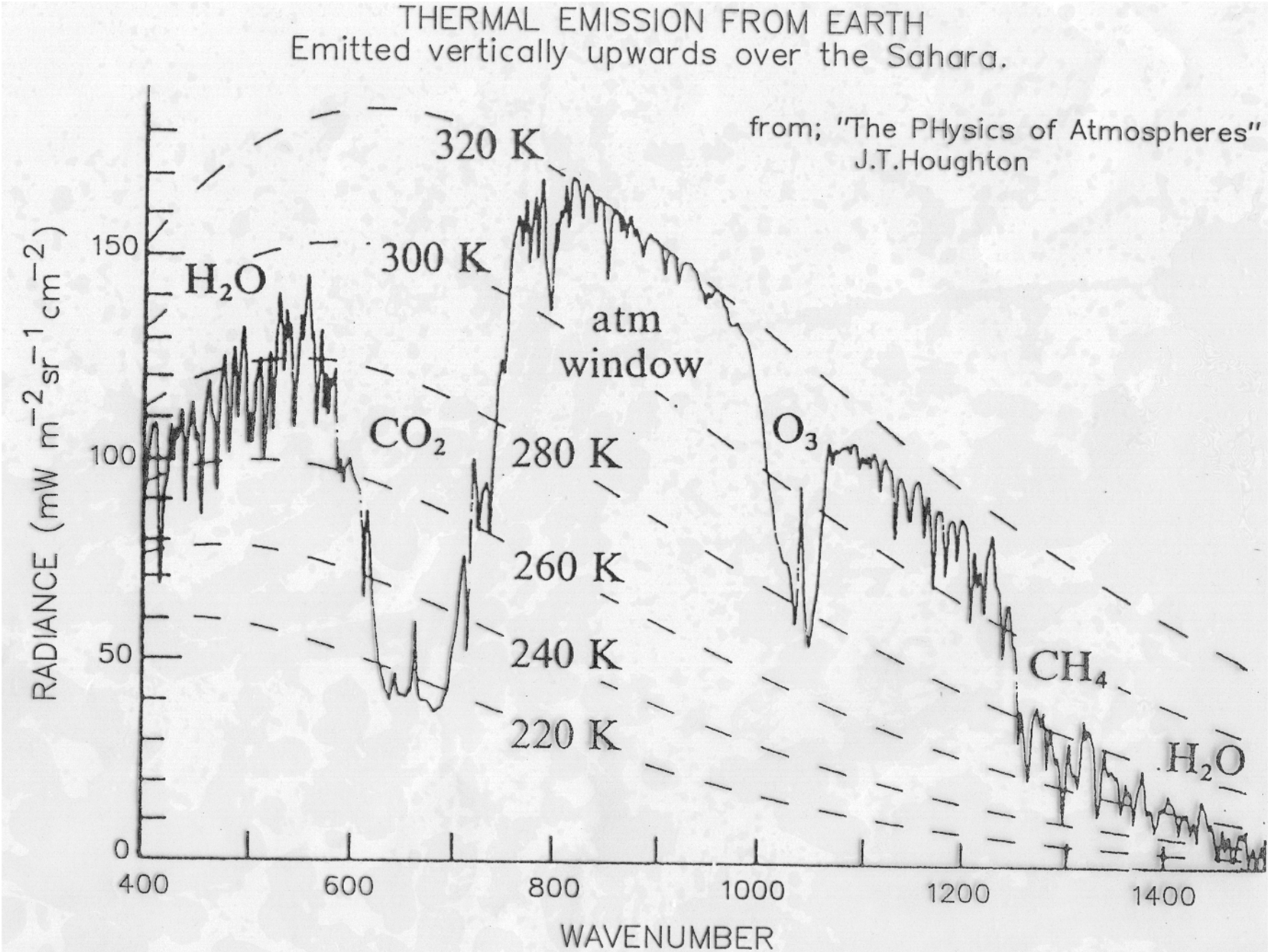


FIGURE 1.9 Global average mean radiation and energy balance per unit of earth's surface [adapted with permission from IPCC (1996) with numbers from Kiehl and Trenberth (1997)].


UV, NO2 Usery Pass, Mesa AZ 1998
UV uW/cm2
NO2 ppb
uW/cm2
NO2 ppb
Julian Date
0
5
10
15
20
25
30
0
10
20
30
40
50
60
135 137 139 141 143 145 147 149 151 153 155 157 159 161 163


Ozone Comparison Usery Pass Mesa AZ 1998
Ozone ppb
ADEQ Ozone
Ozone ppb
100
90
80
70
60
50
40
30
20
10
0
135 137 139 141 143 145 147 149 151 153 155 157 159 161 163
Julian Date


THERMAL EMISSION FROM EARTH
Emitted vertically upwards over the Sahara.
from; "The PHysics of Atmospheres"
J.T.Houghton
320 K
300 K
280 K
260 K
240 K
220 K
H_2O
CO_2
atm
window
O_3
CH_4
H_2O
RADIANCE (mW $m^{-2}sr^{-1}cm^{-2}$)
150
100
50
0
400
600
800
1000
1200
1400
WAVENUMBER

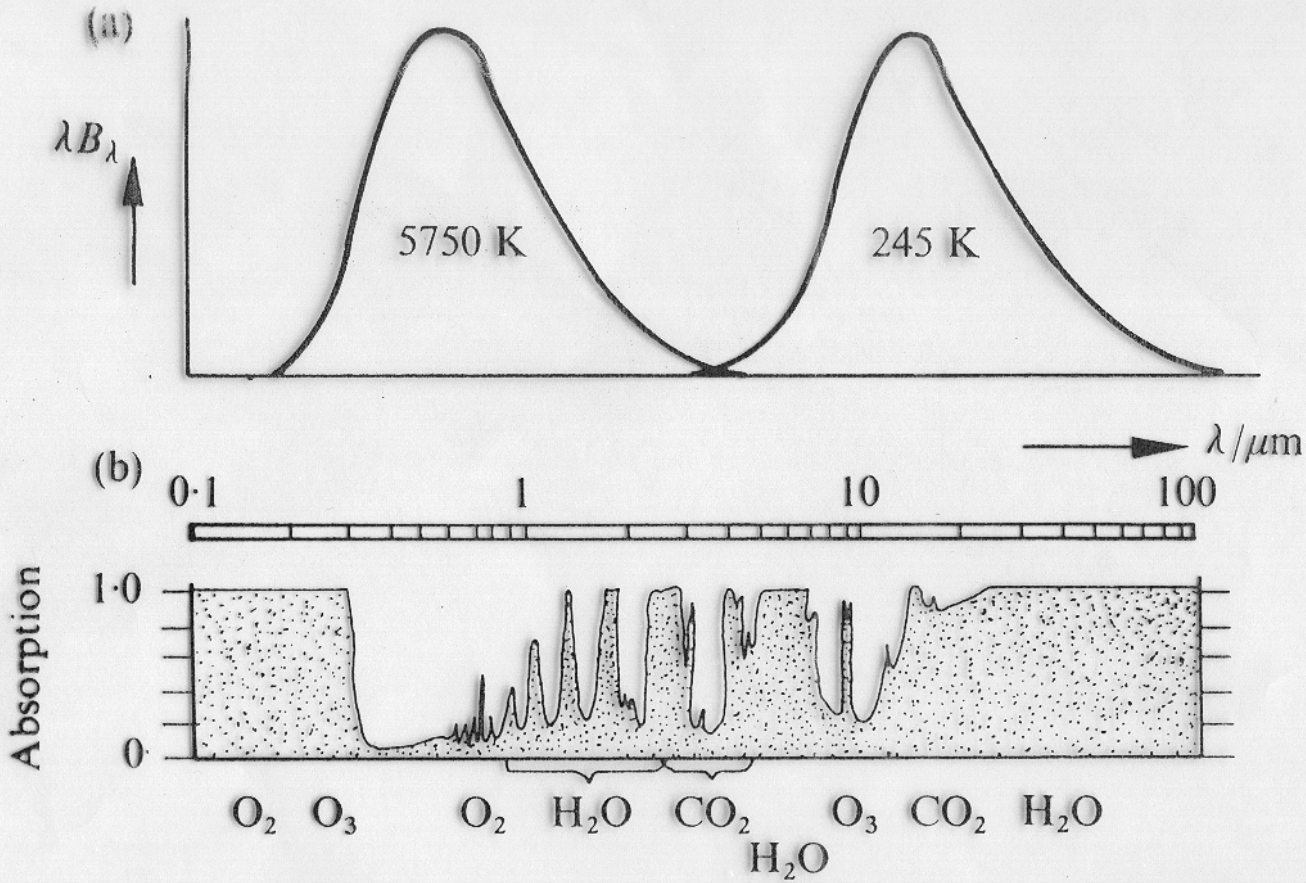
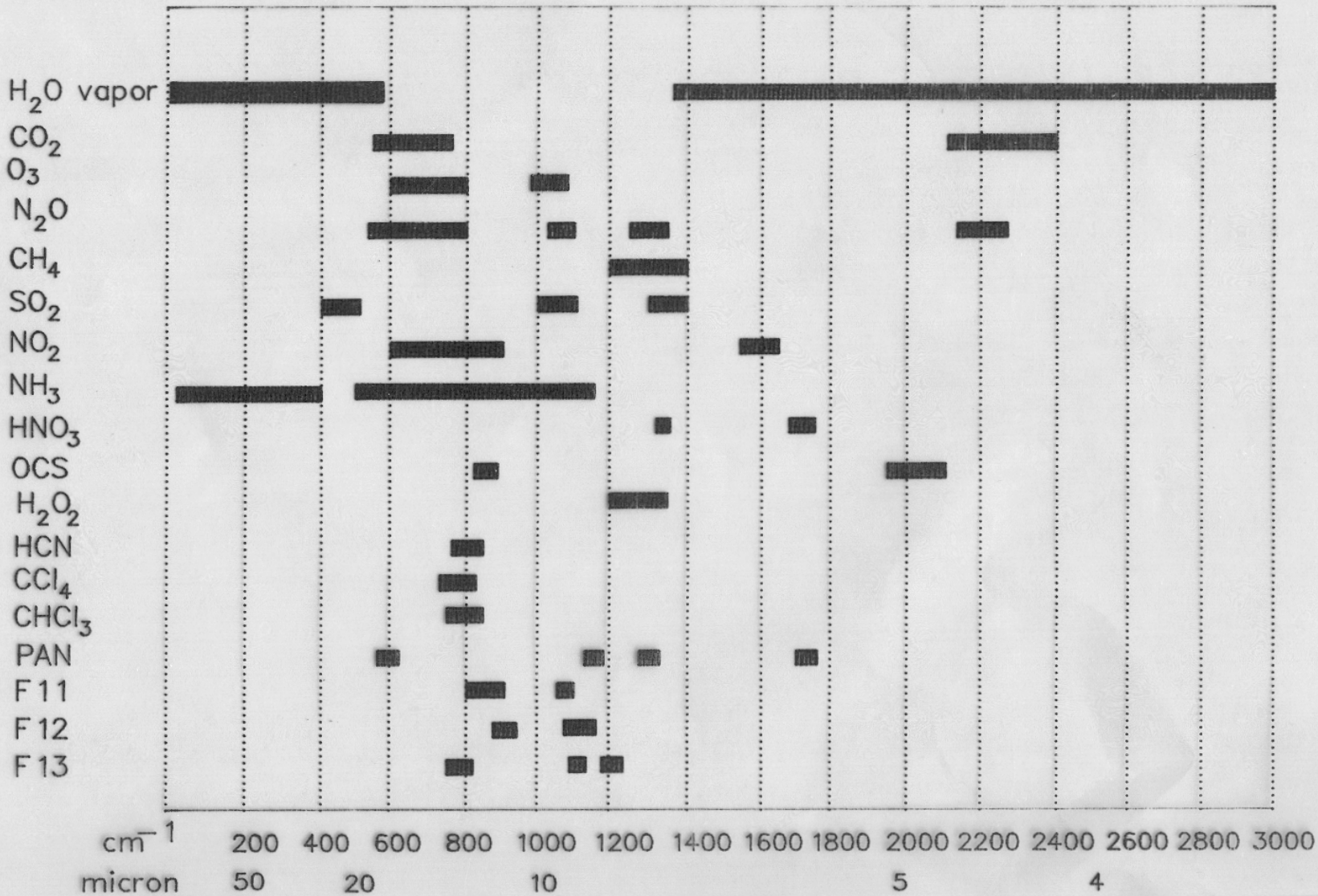
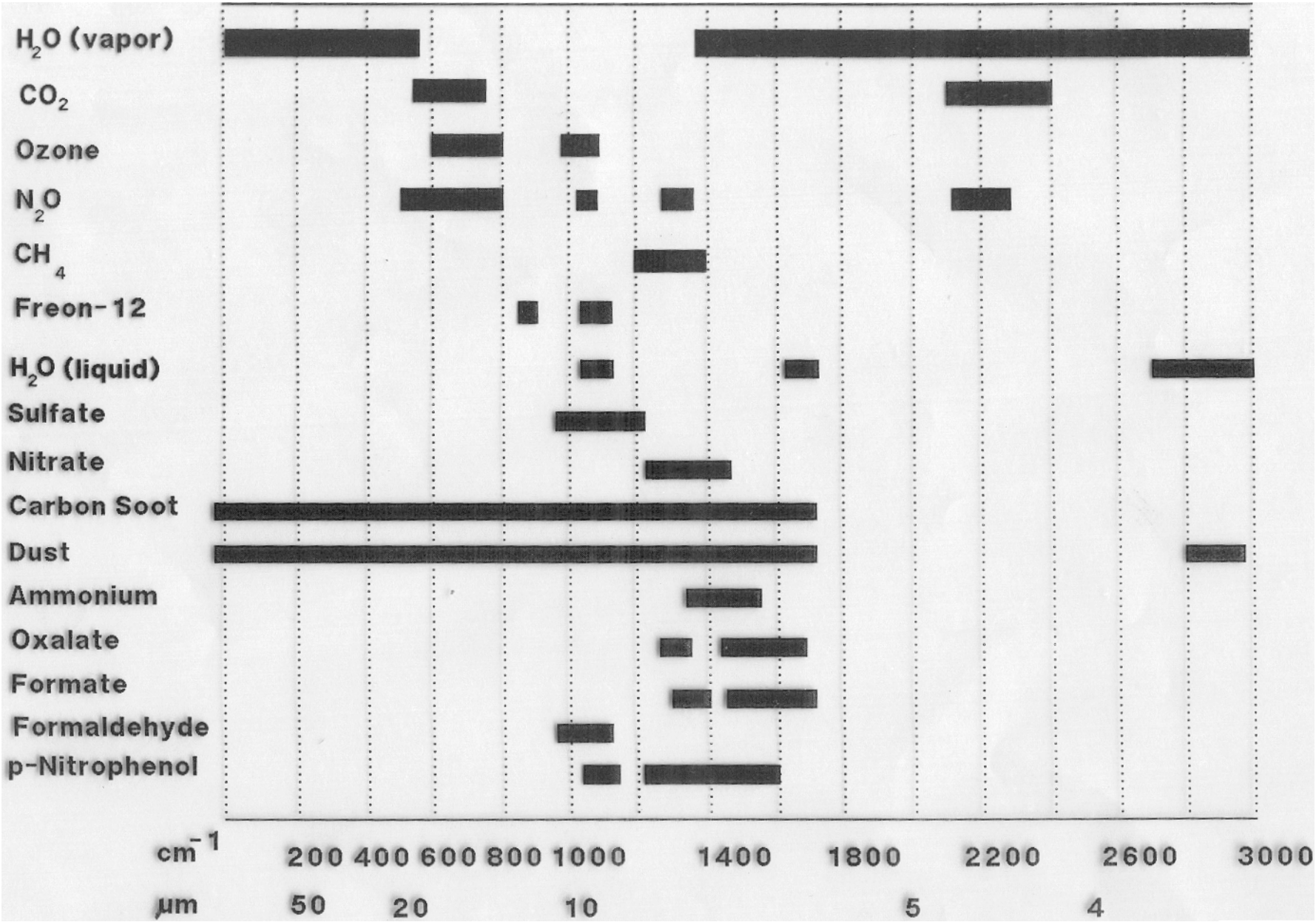


Fig. 2.1. (a) Curves of black-body energy B_λ at wavelength λ for 5750 K (approximating to the sun's temperature) and 245 K (approximating to the atmosphere's mean temperature). The curves have been drawn of equal areas since integrated over the earth's surface and all angles the solar and terrestrial fluxes are equal.
(b) Absorption by atmospheric gases for a clear vertical column of atmosphere. The positions of the absorption bands of the main constituents are marked.

SPECTRAL LOCATIONS OF THE MAJOR INFRARED ABSORPTION BANDSFOR THE GREENHOUSE GASSES




H_2O (vapor)
CO_2
Ozone
N_2O
CH_4
Freon-12
H_2O (liquid)
Sulfate
Nitrate
Carbon Soot
Dust
Ammonium
Oxalate
Formate
Formaldehyde
p-Nitrophenol
cm^{-1}
200 400 600 800 1000 1400 1800 2200 2600 3000
µm
50 20 10 5 4

SOME ISSUES

ATMOSPHERIC LIFETIMES

- Course Aerosol - Hours
- Fine Aerosols - Days, Months?

LOCAL SOURCE EMISSION CONTROLS?

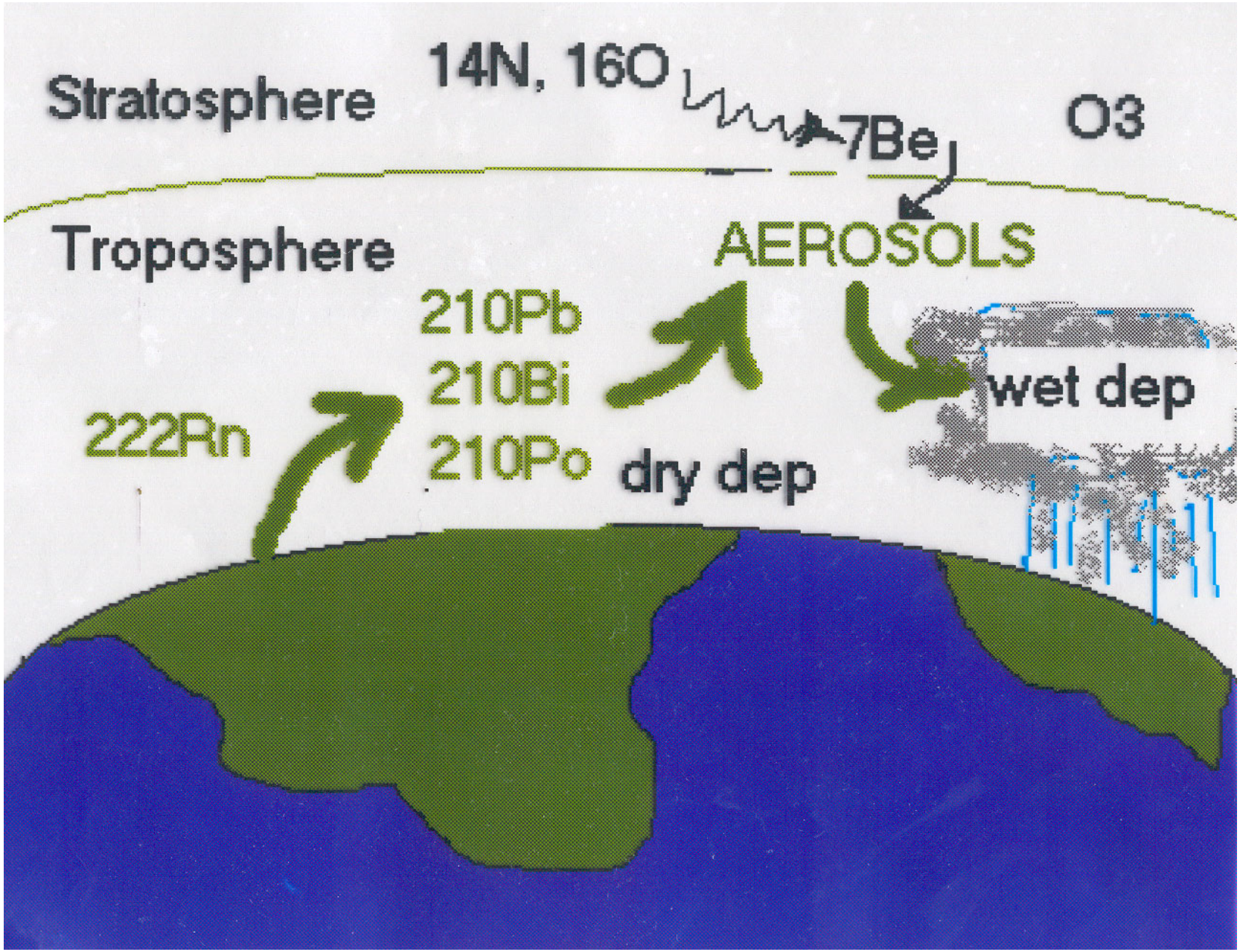
REGIONAL EMISSION CONTROLS?

COMBUSTION SOURCES - CARBONACEOUS AEROSOL

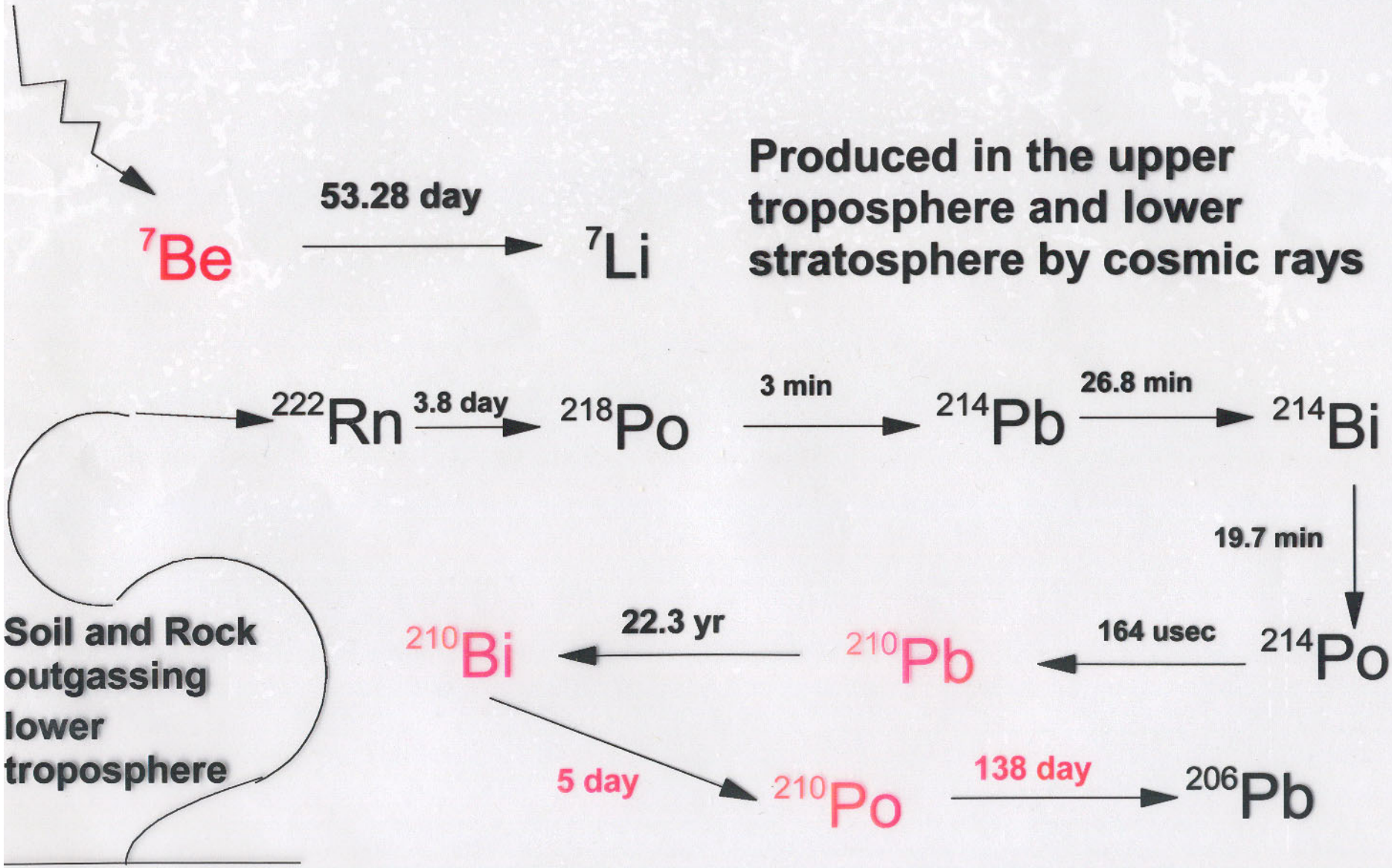
- Diesel Engines
- Jet Engines
- Incineration of Wastes

PM-2.5 & AIR TOXICS

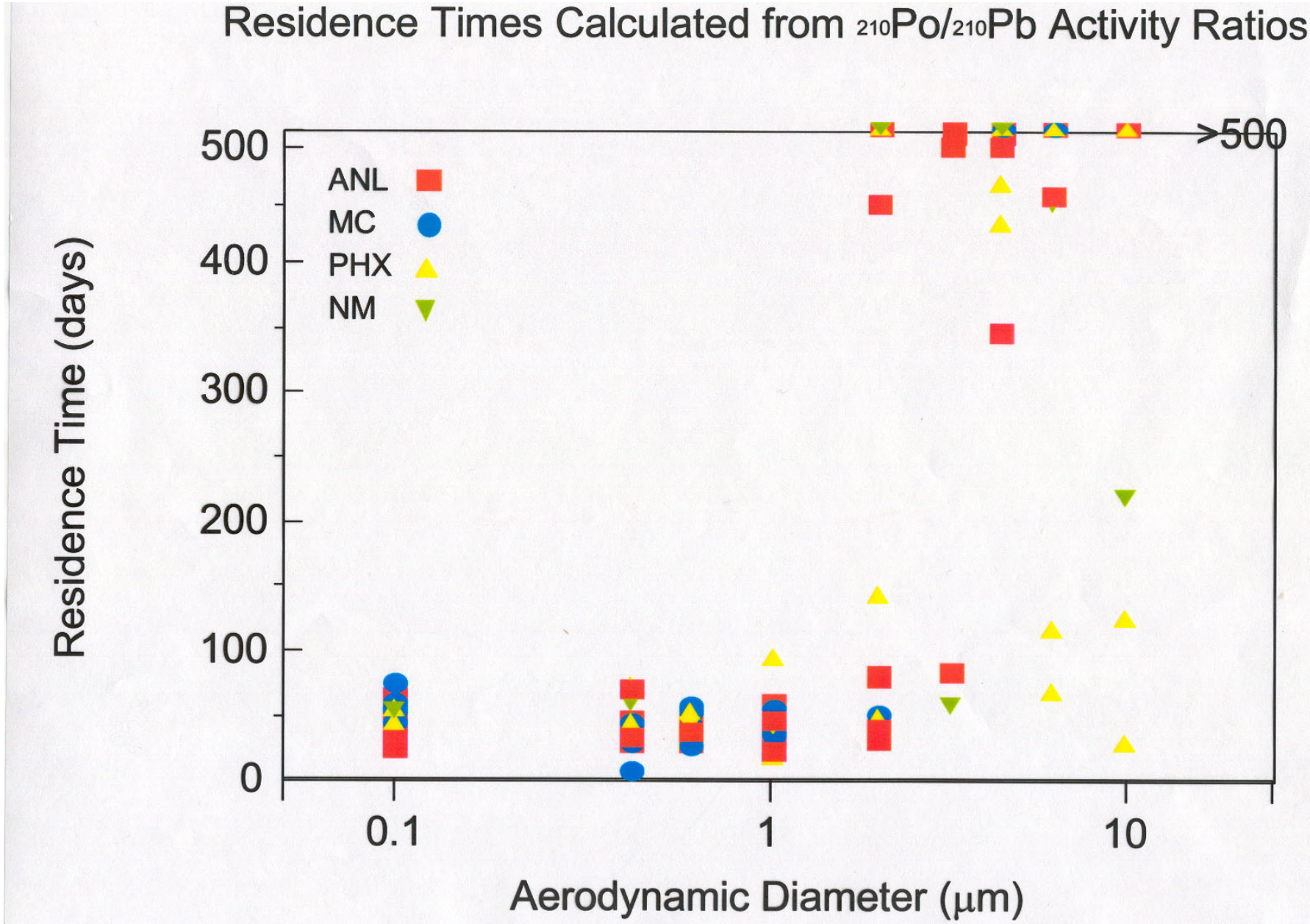
- Toxic Metals
- PAH, PCBs, etc.


Stratosphere
14N, 16O
7Be
O3
Troposphere
AEROSOLS
210Pb
210Bi
210Po
222Rn
dry dep
wet dep

Radioactive Decay of Natural Atmospheric Tracers



4/4/2002 20:03

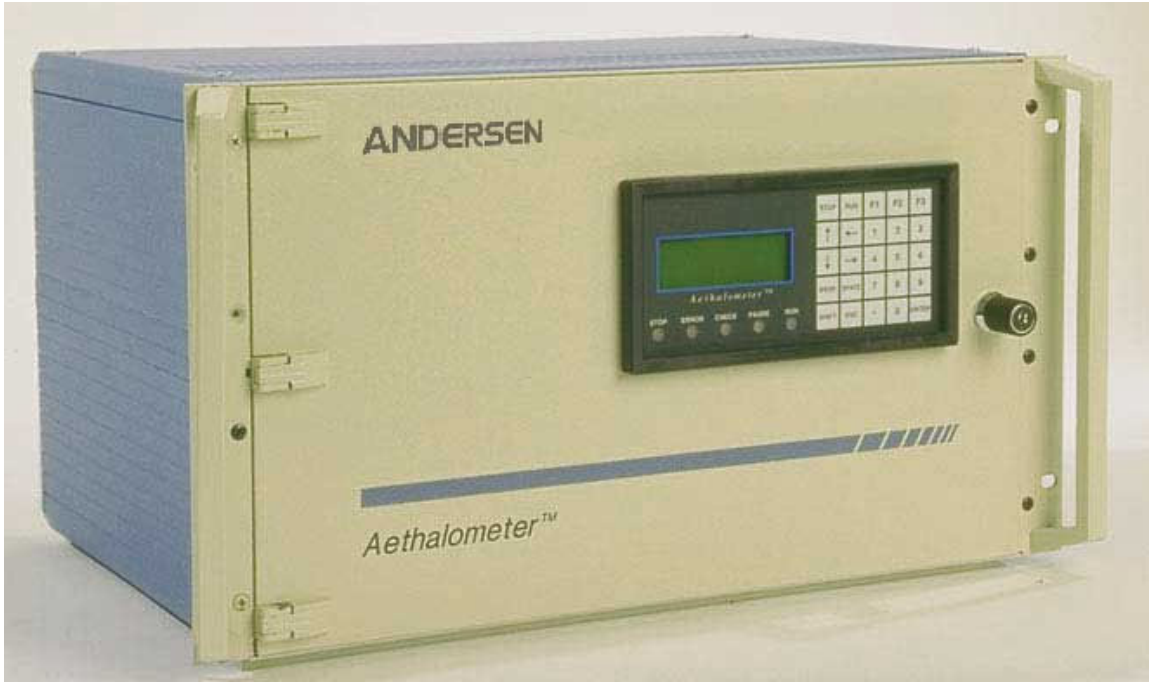

Residence Times Calculated from 210Po/210Pb Activity Ratios
Residence Time (days)
500
400
300
200
100
0
>500
ANL
MC
PHX
NM
0.1
1
10
Aerodynamic Diameter (μm)

Apparent Ages for Aerosols – NETL

Sample	SIZE(μm)	CORR. AGE (days)
PA1	<1	17
PA2	>1	11
PA5	<1	19
PA6	>1	20
PA9	<1	21
PA10	>1	12
PA11	<1	18
PA12	>1	15
PA13	<1	30
PA14	>1	27
PA17	<1	10
PA18	>1	30
PA21	<1	12
PA22	>1	25
PA25	<1	24
PA26	>1	32
PA29	<1	31
PA30	>1	46

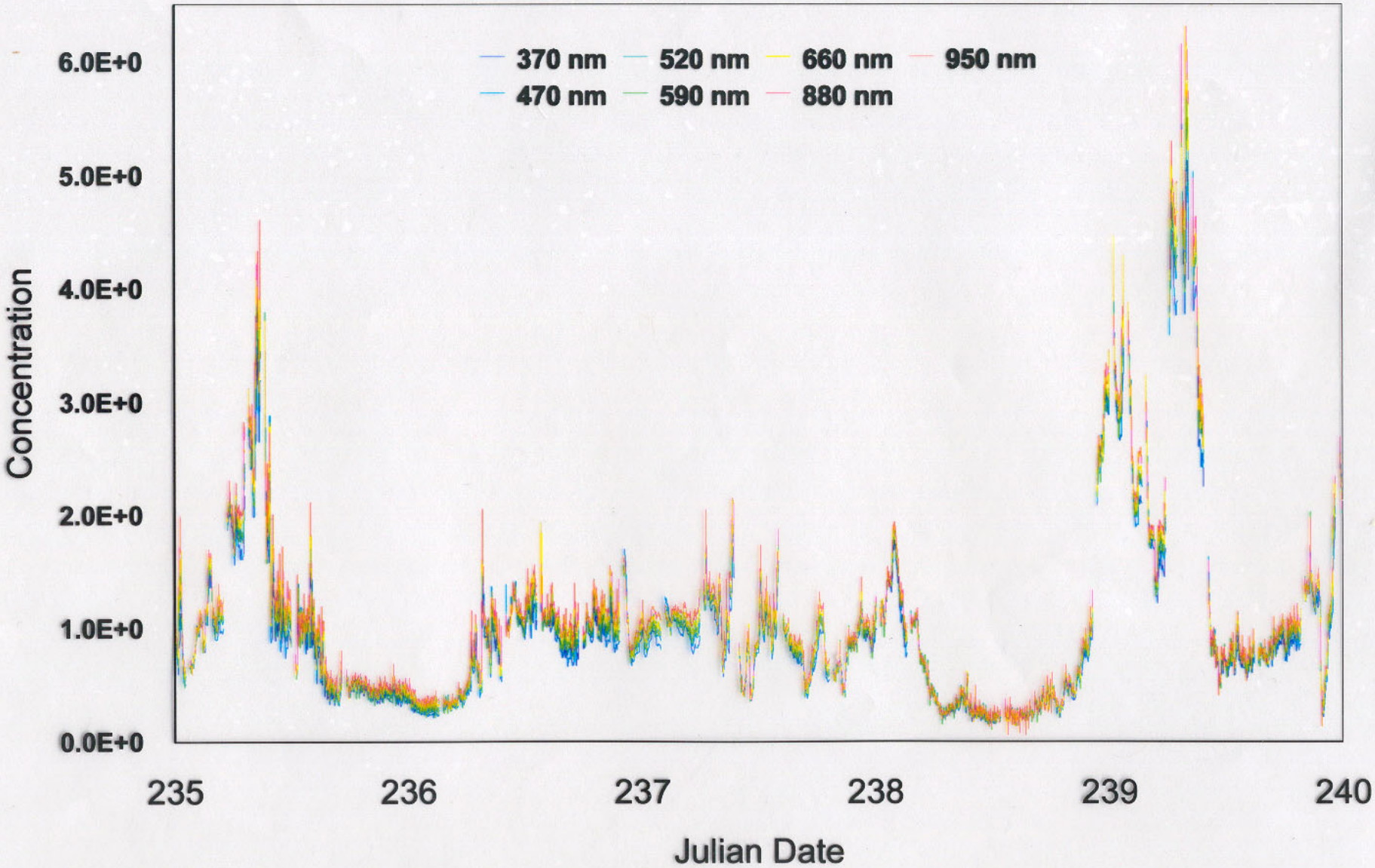
OK SO WHAT IS CAUSING THIS?

BLACK CARBON?


ANDERSEN
Aethalometer™

Aethalometry

Chicago, IL (2001)



Daytime Attack!

O_3 OH NO NO_2 hν

Nighttime Attack! - NO_3

```
H H H   H H H H H H H H H H   H H H H H H H H   H
\ \ \   \ \ \ \ \ \ \ \ \ \   \ \ \ \ \ \ \ \ \   \
~C-C-C=C-C-C-C-C-C-C-C-C=C-C-C=C-C-C-C-C=C~
 / /     / / / / / / /       /     / / /
 H H     H H H H H H H       H     H H H
```

OILY CARBONACEOUS SOOT SURFACE

After Reaction – STILL PRETTY HYDROPHOBIC!

```
H H H  H  HO H H H H H  H H H H H HO H  H   H
\  \ \  \    \ \ \ \ \ \  \ \ \  \ \   \ \ \   \
~C-C-C =O  O=C-C-C-C-C-C-C-C-C=O  O=C-C-C=C-
 /  /            / / / /  / / /          /
 H  H           H H H H H H  H          H
```

OILY CARBONACEOUS SOOT SURFACE

AEROSOL INDIRECT

EFFECTS

CLOUD FORMATION

PARTICLES IN CLOUDS?