MODELING SULFATE CHEMISTRY ON HEMISPHERIC AND SUBHEMISPHERIC SCALES

THE KEY, OR THE KEY UNDER THE LAMPPOST?

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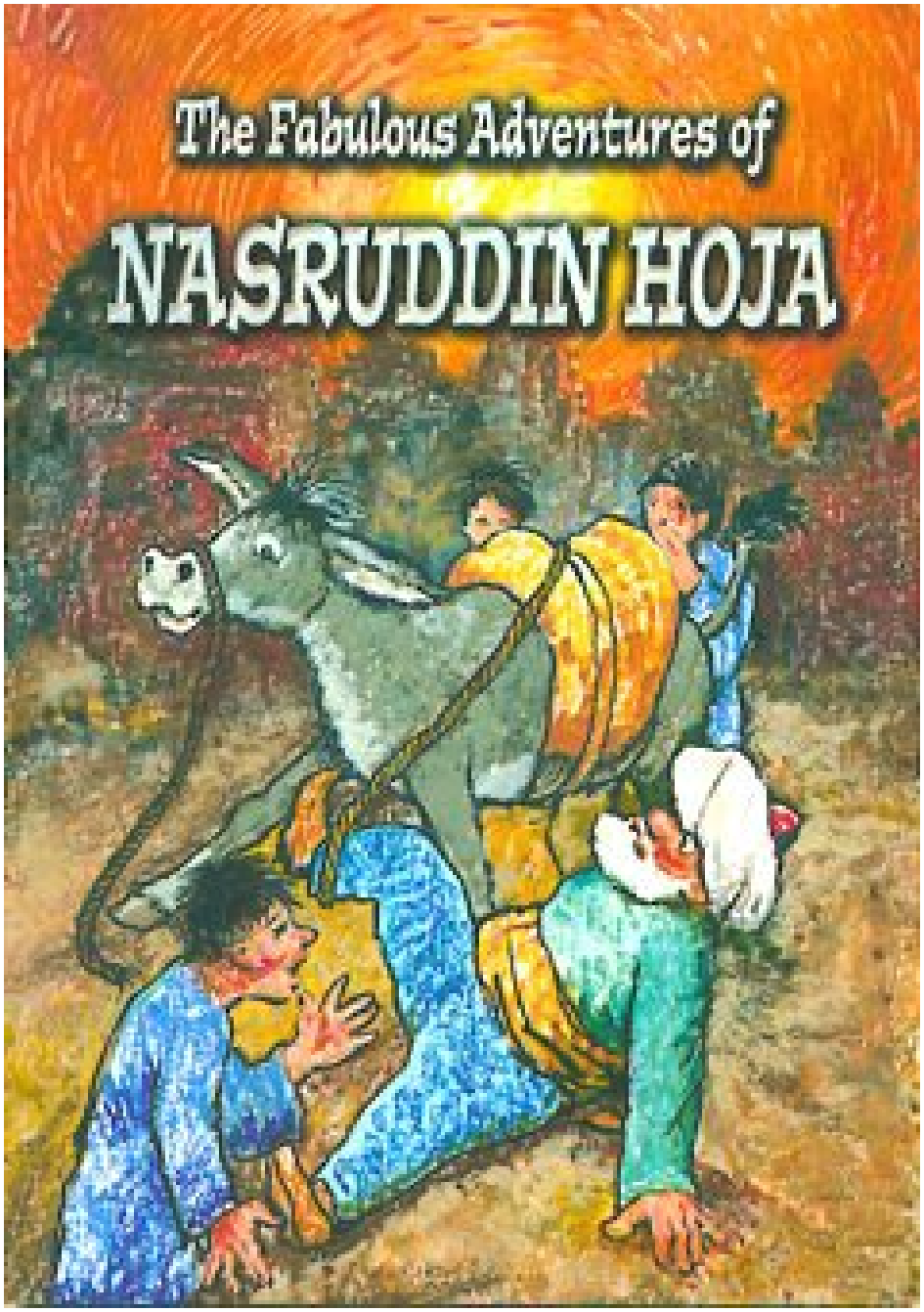
http://www.ecd.bnl.gov/steve/schwartz.html


The Fabulous Adventures of
NASRUDDIN HOJA

The Key under the Lamppost

The Islamic world finds a timeless source of humorous wisdom in the antics of a holy fool, a Mullah called Nasruddin.

One night a neighbor of Mullah Nasruddin was walking home and found Mullah squatting on the ground beside a lamppost evidently looking for something.

"What's the matter Mullah?" asked the concerned neighbor.

"I have lost my key" replied the Mullah.

"Oh! Here let me help you." and the kindly neighbor got down on his knees and started searching for the Mullah's key as well.

After some time spent looking the neighbor straightened up and quite puzzled asked "are you sure you dropped your key here?"

"Oh, I didn't drop it here." replied the Mullah.

"Where did you drop it ?!?" exclaimed the now bewildered neighbor.

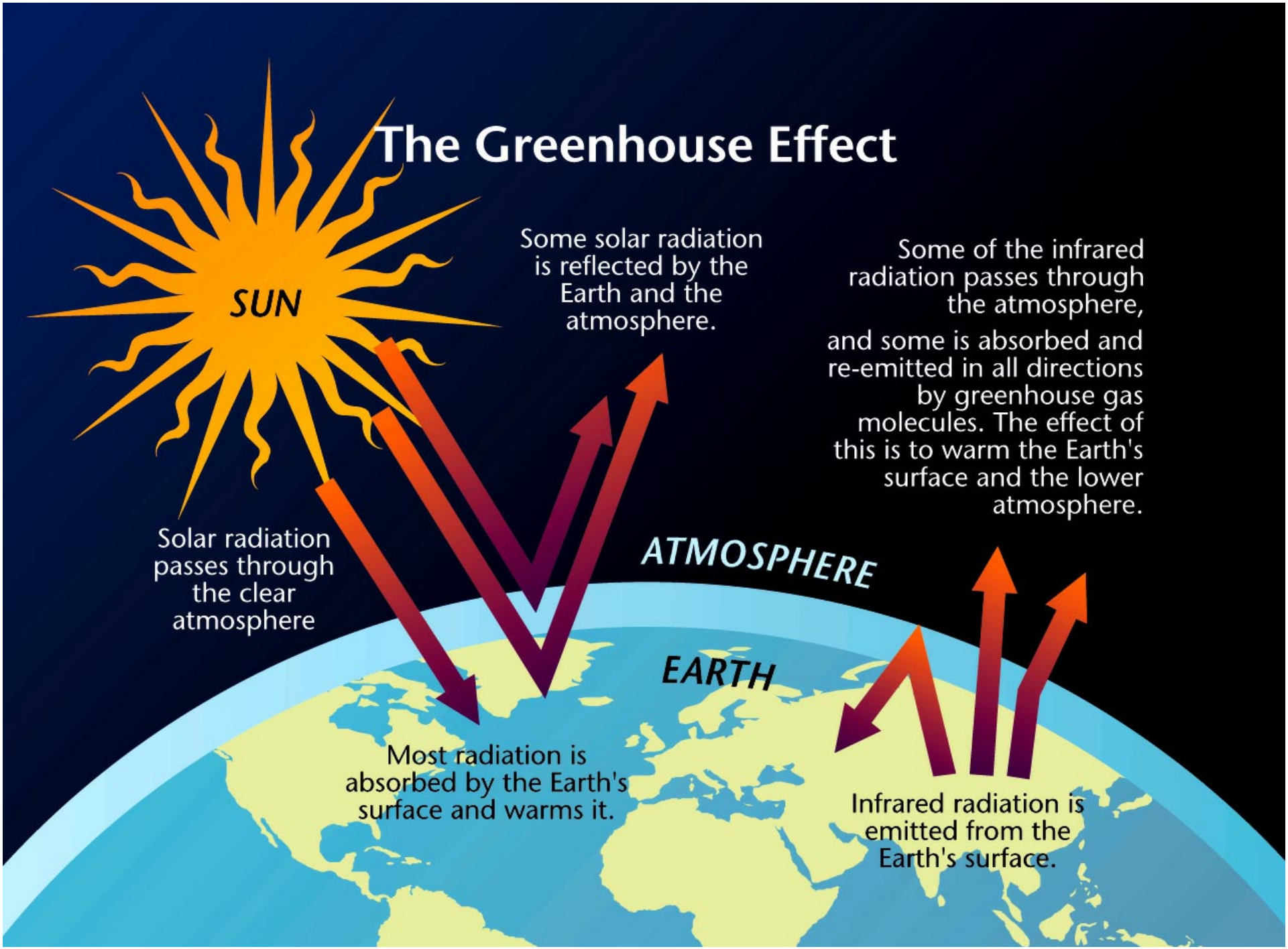
"Over there" and the Mullah pointed to the front of his house that was in darkness.

"So why are you looking for it here ??!!??" exclaimed the now exasperated neighbor.

"Because the light is better over here." replied the Mullah.

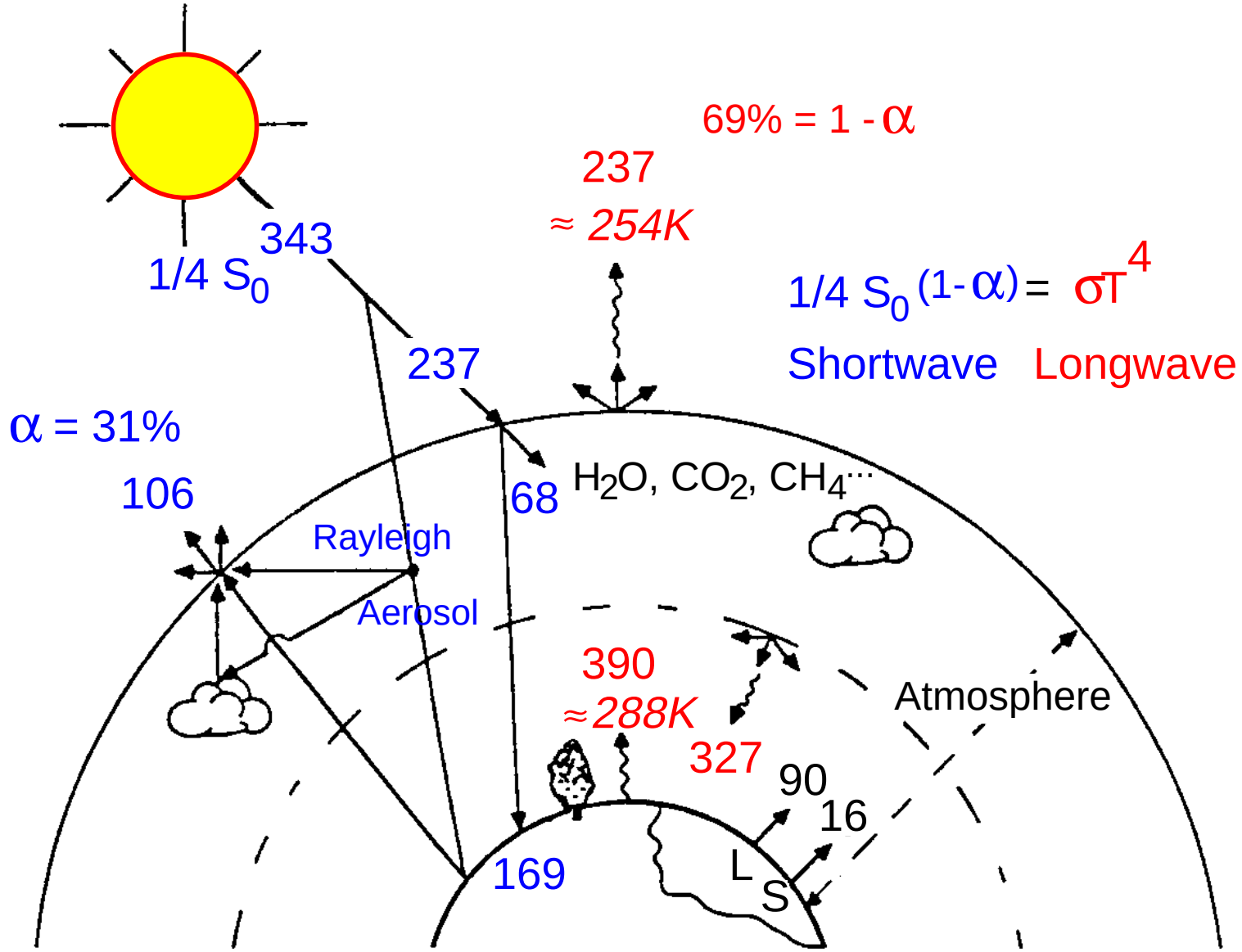
OUTLINE

- Earth's radiation budget
- Radiative forcing of climate change by greenhouse gases
- Radiative forcing of climate change by aerosols
- Why focus on sulfate?
- BNL chemical transport model for sulfate - description and results
- Representing aerosol size
- Summary


The Greenhouse Effect
SUN
Some solar radiation is reflected by the Earth and the atmosphere.
Some of the infrared radiation passes through the atmosphere,
and some is absorbed and re-emitted in all directions by greenhouse gas molecules. The effect of this is to warm the Earth's surface and the lower atmosphere.
Solar radiation passes through the clear atmosphere
ATMOSPHERE
EARTH
Most radiation is absorbed by the Earth's surface and warms it.
Infrared radiation is emitted from the Earth's surface.

GLOBAL ENERGY BALANCE

Global and annual average energy fluxes in watts per square meter



Schwartz, 1996, modified from Ramanathan, 1987

ATMOSPHERIC RADIATION

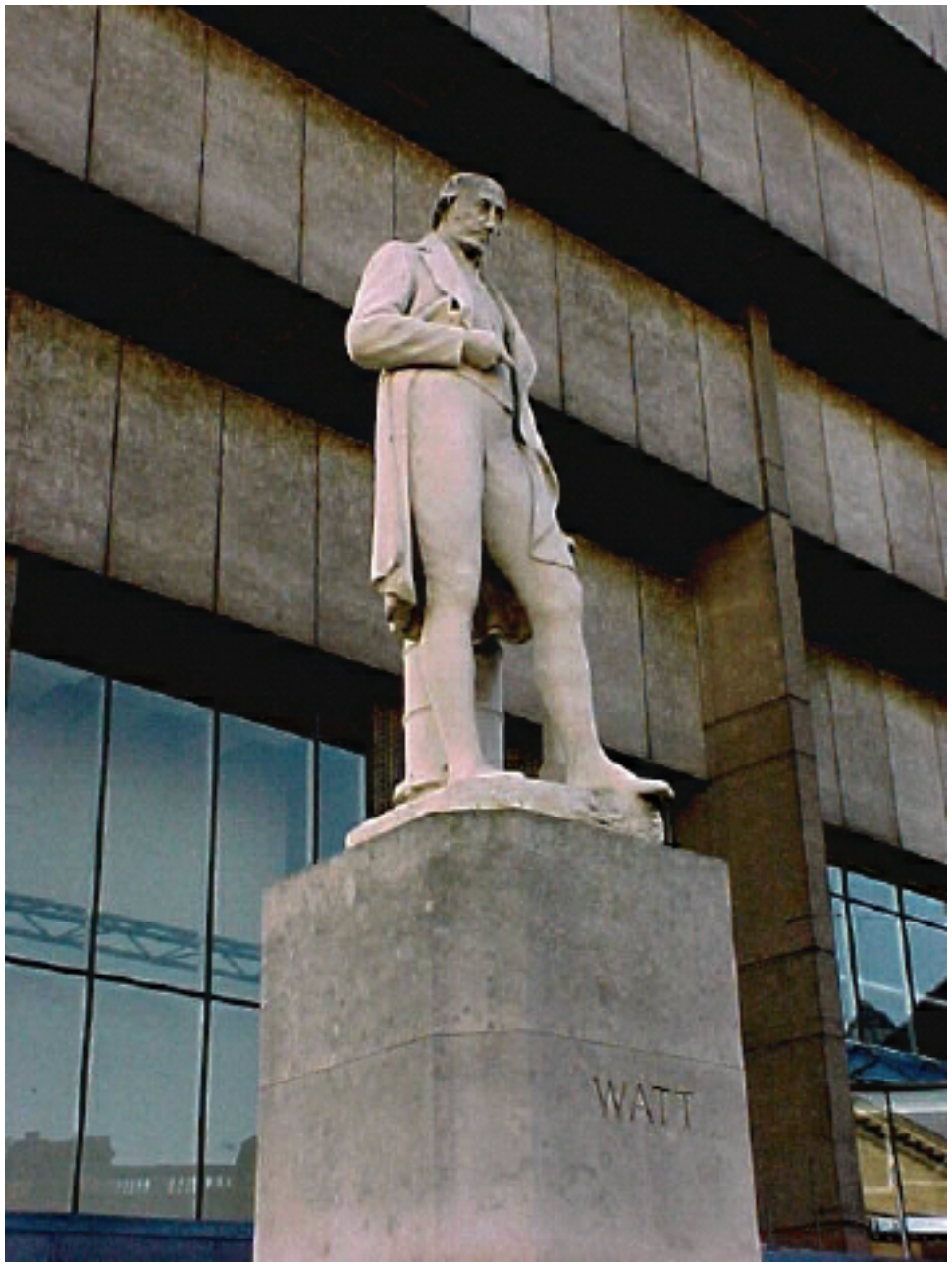
Energy per area per time

Power per time

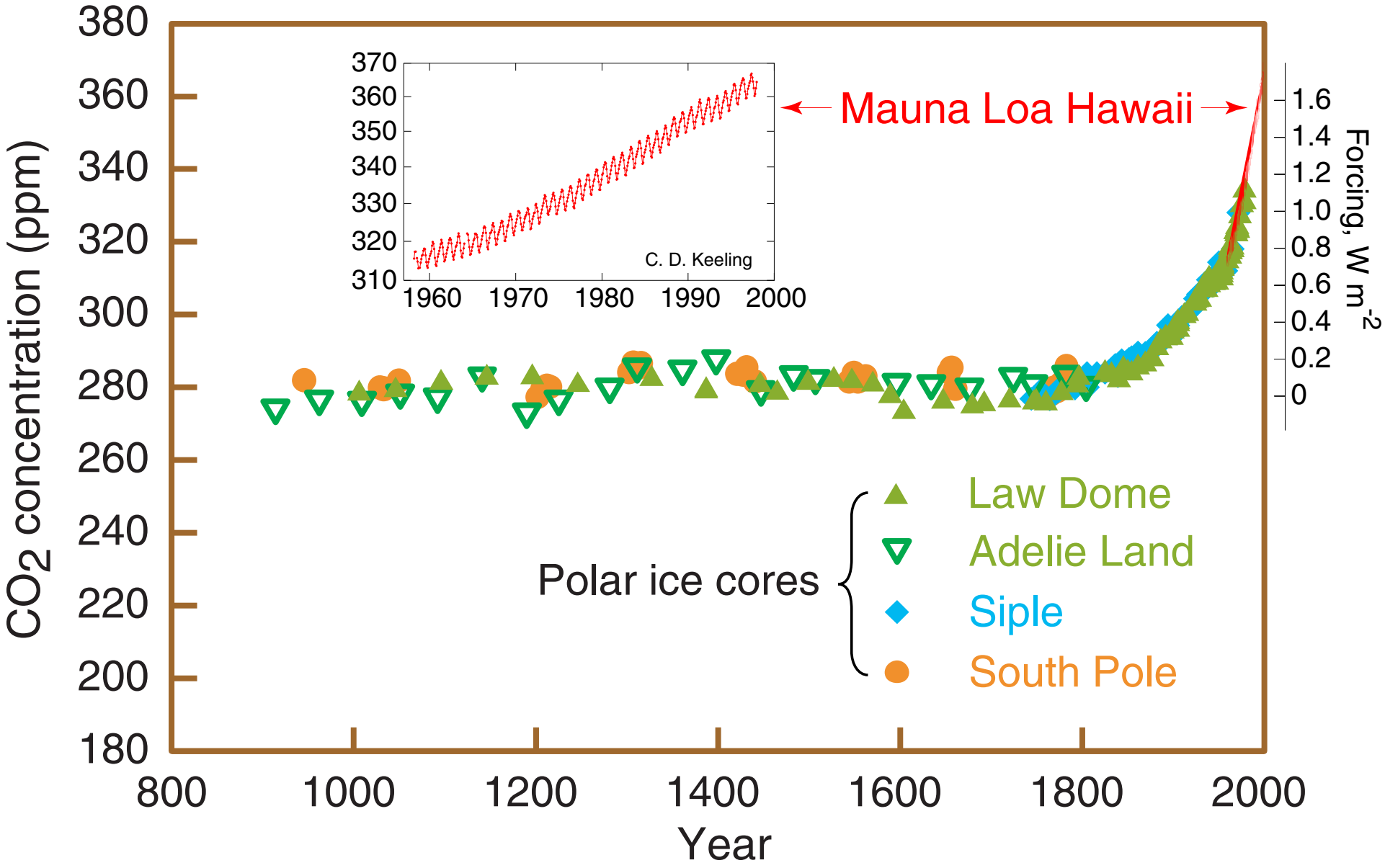
Unit:

Watt per square meter

$W\ m^{-2}$

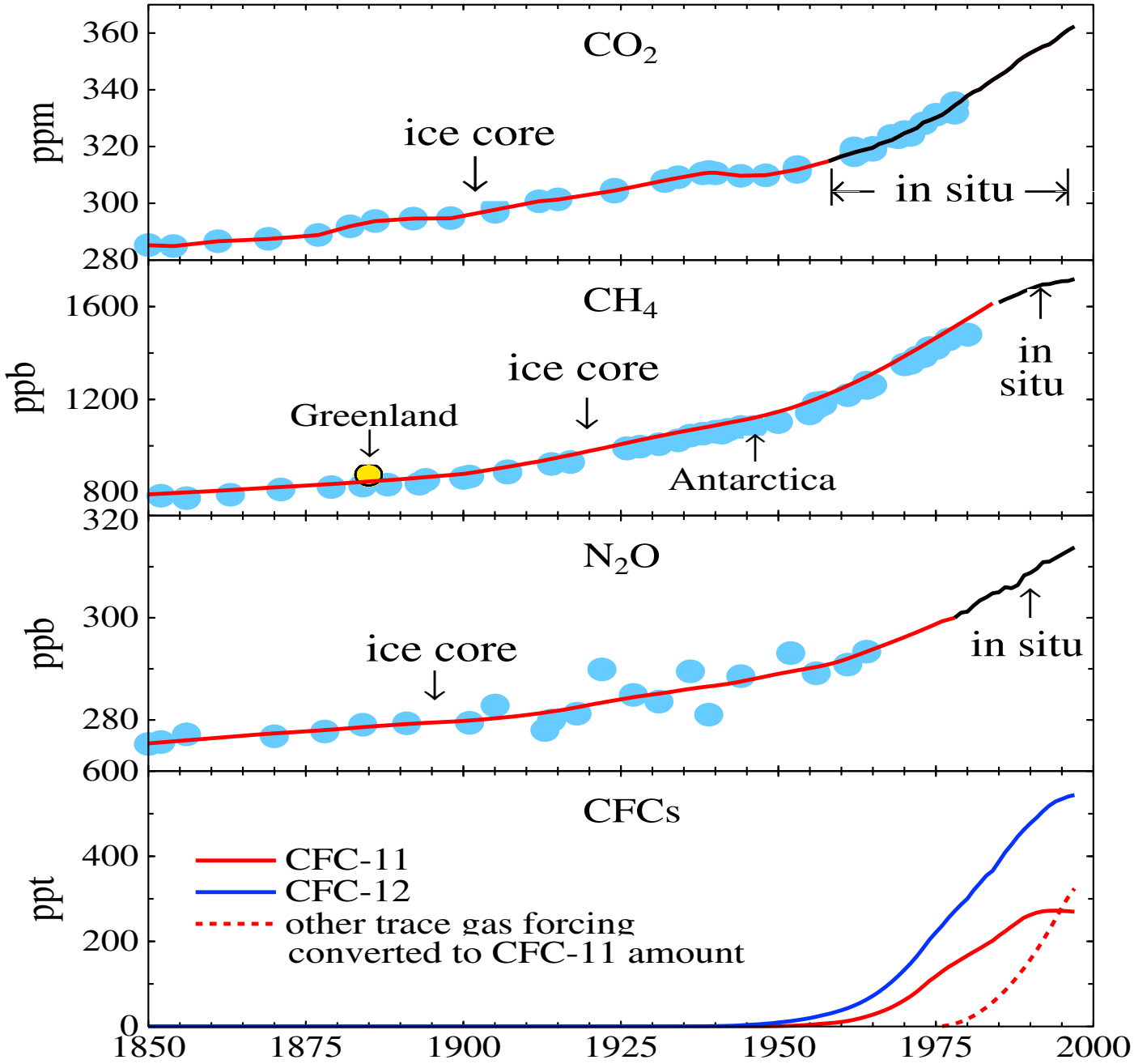


ATMOSPHERIC CARBON DIOXIDE IS INCREASING



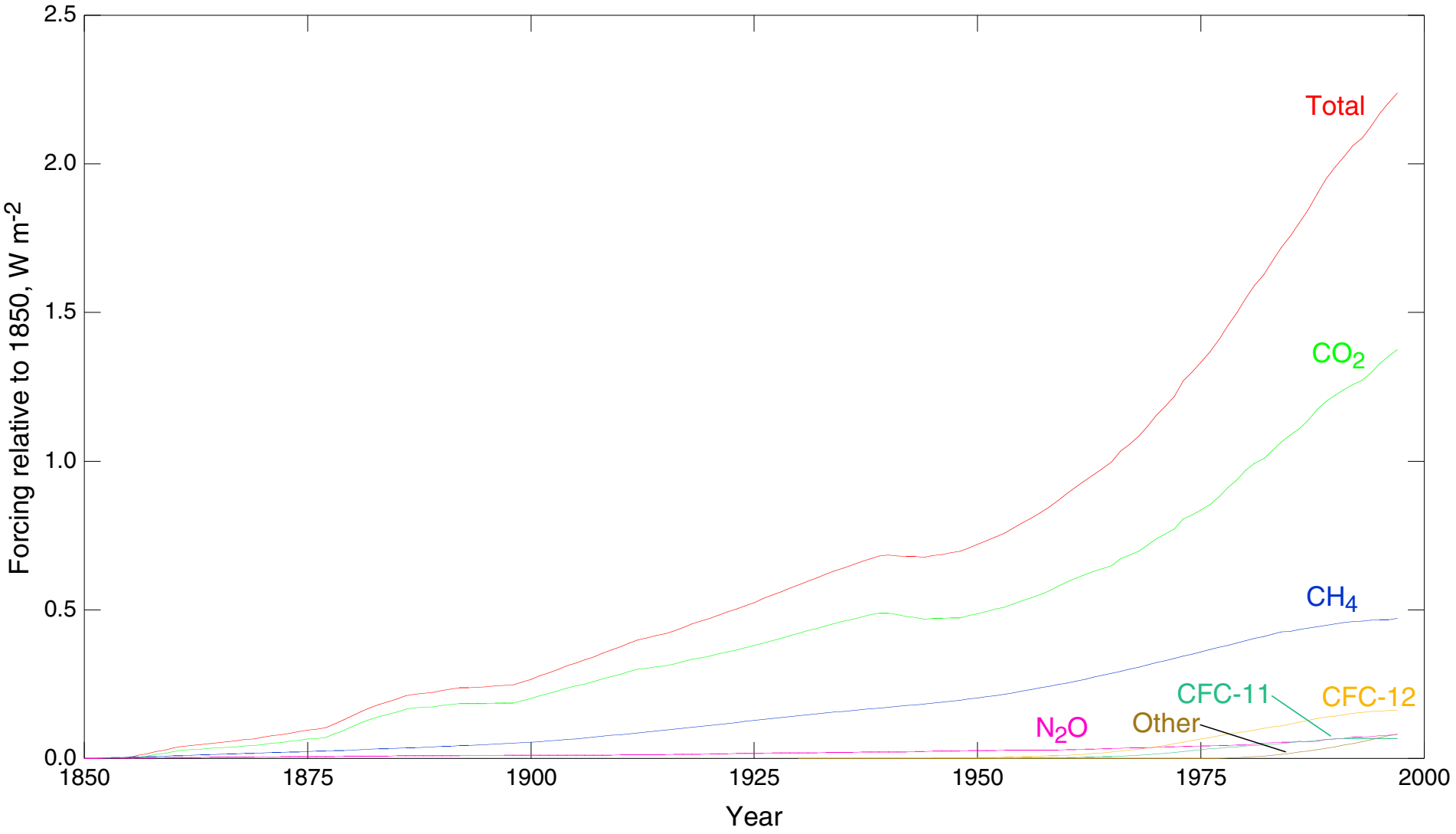
Global carbon dioxide concentration and infrared radiative forcing over the last thousand years

GREENHOUSE GAS MIXING RATIOS OVER THE INDUSTRIAL PERIOD



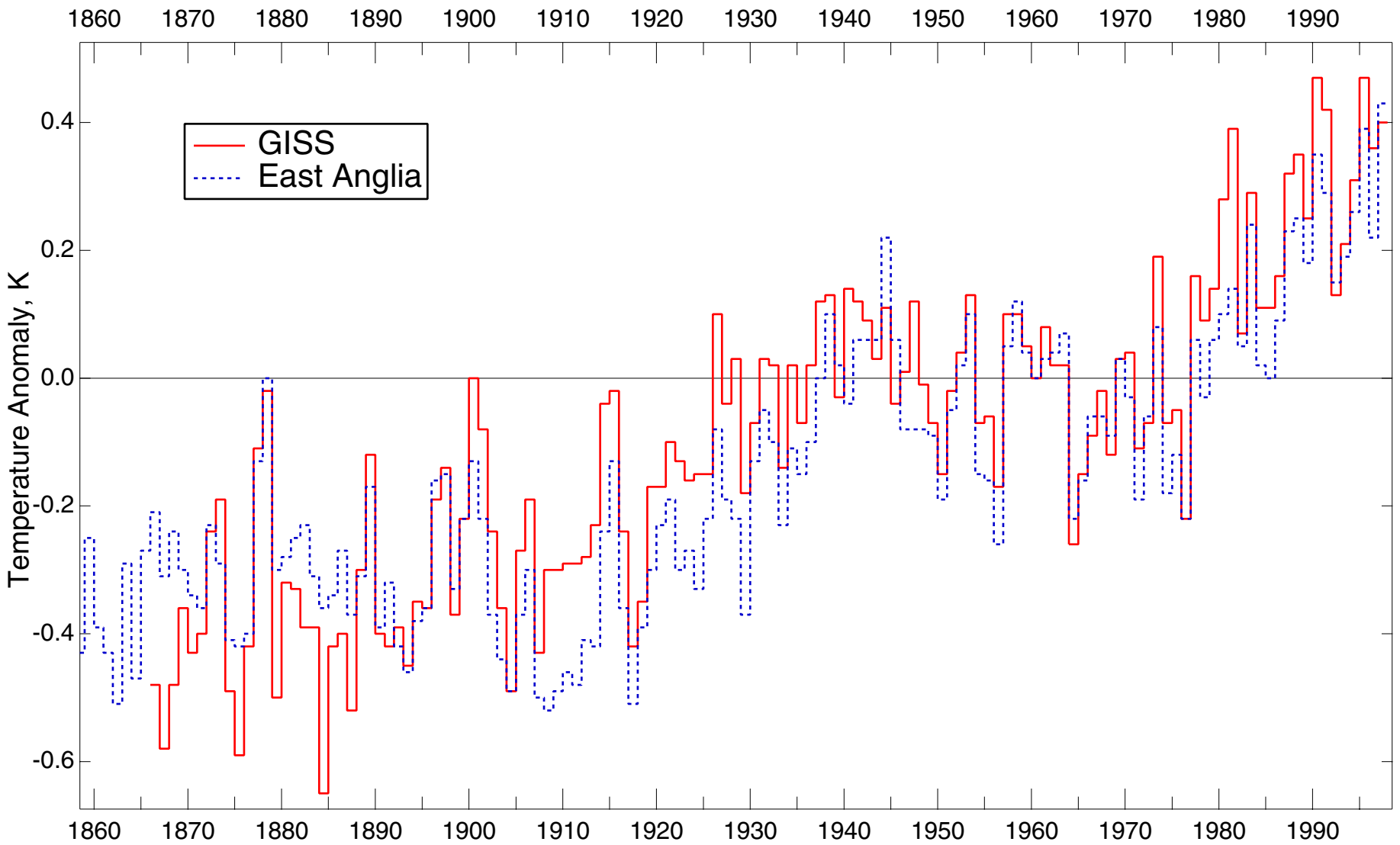
Hansen *et al.*, PNAS. 1998

GREENHOUSE GAS FORCINGS OVER THE INDUSTRIAL PERIOD

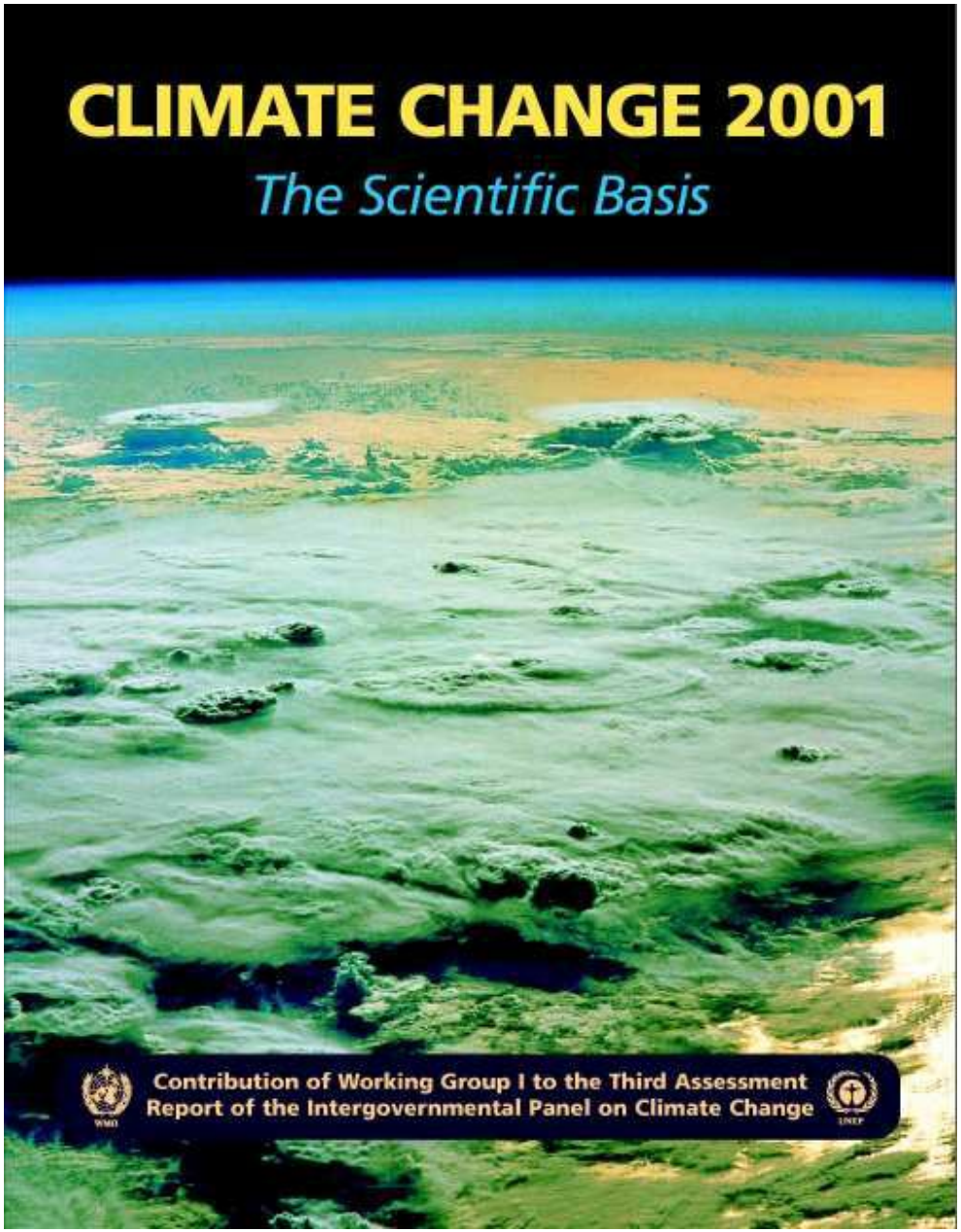


Data: GISS

GLOBAL TEMPERATURE TREND OVER THE INDUSTRIAL PERIOD



THE "BIBLE" OF CLIMATE CHANGE RESEARCH



Cambridge University Press, 2001

CLIMATE CHANGE SENSITIVITY

Summary of Current Models

Units: K / (W m^{-2})

Number of Models	Mean	Standard Deviation	Range
15	0.87	0.23	0.5 - 1.25

Climate Change 2001, Cambridge University Press, 2001

EMPIRICAL TEMPERATURE SENSITIVITY

Greenhouse forcing over the industrial period is 2.5 W m^{-2}

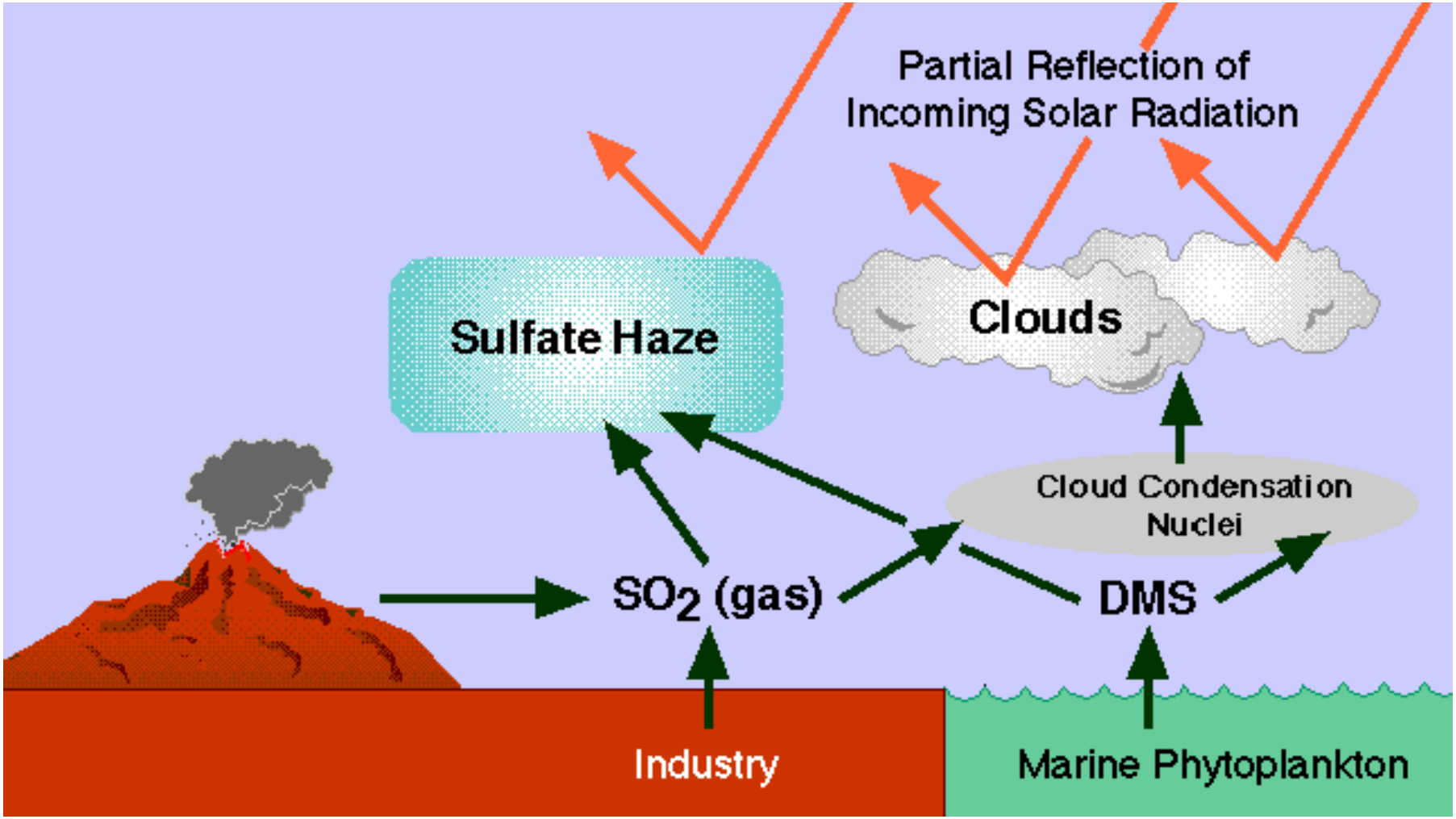
Temperature increase over the industrial period is 0.6 K.

Empirical Sensitivity: $\lambda = \frac{dT}{dF} = \frac{0.6 \text{ K}}{2.5 \text{ W m}^{-2}} = 0.24 \text{ K / (W m}^{-2})$

This value is much lower than model predictions.

WHY?

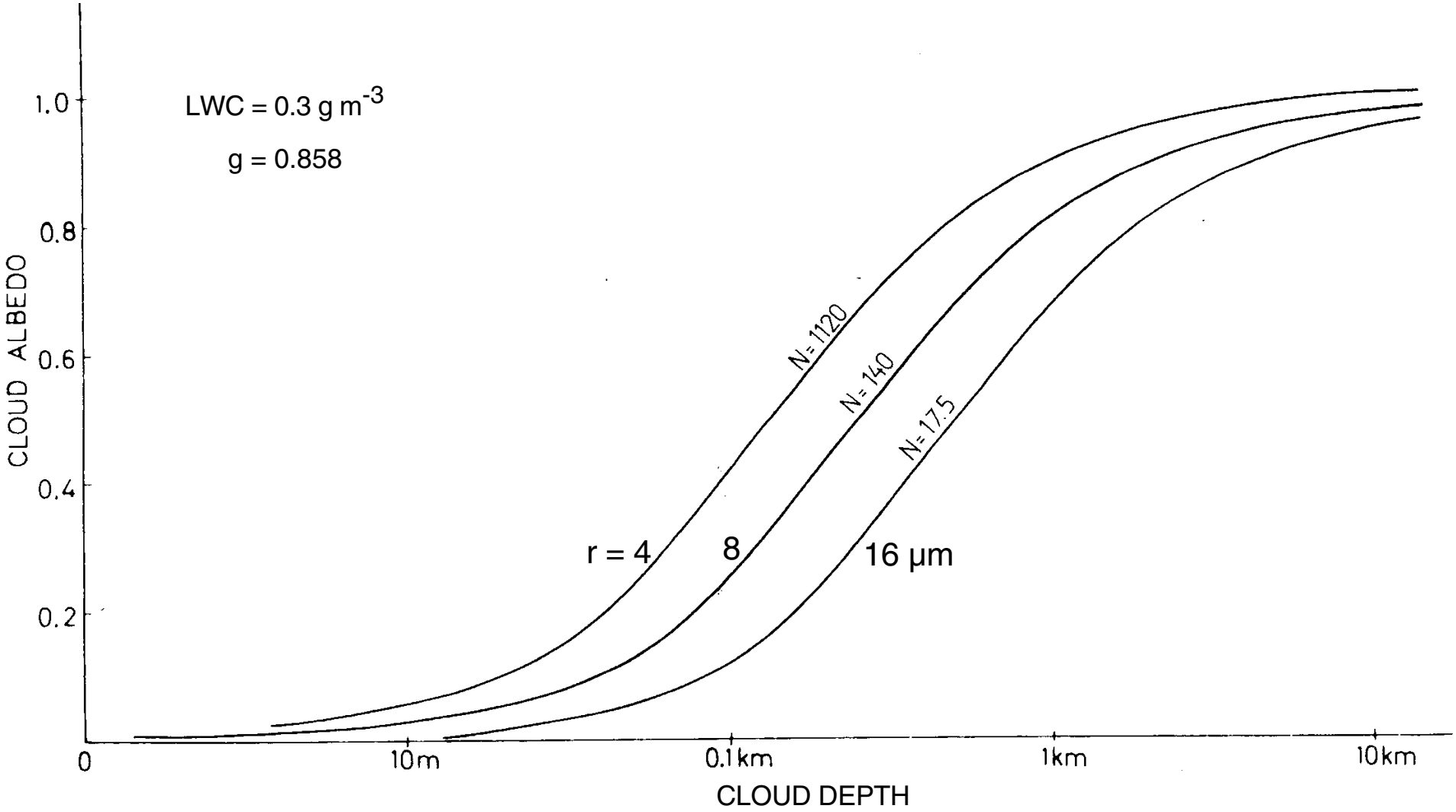
CLIMATE FORCING BY SULFATE AEROSOL



BIOMASS BURNING AND WIDESPREAD AEROSOL
Northeastern Oklahoma, 2000-12-01

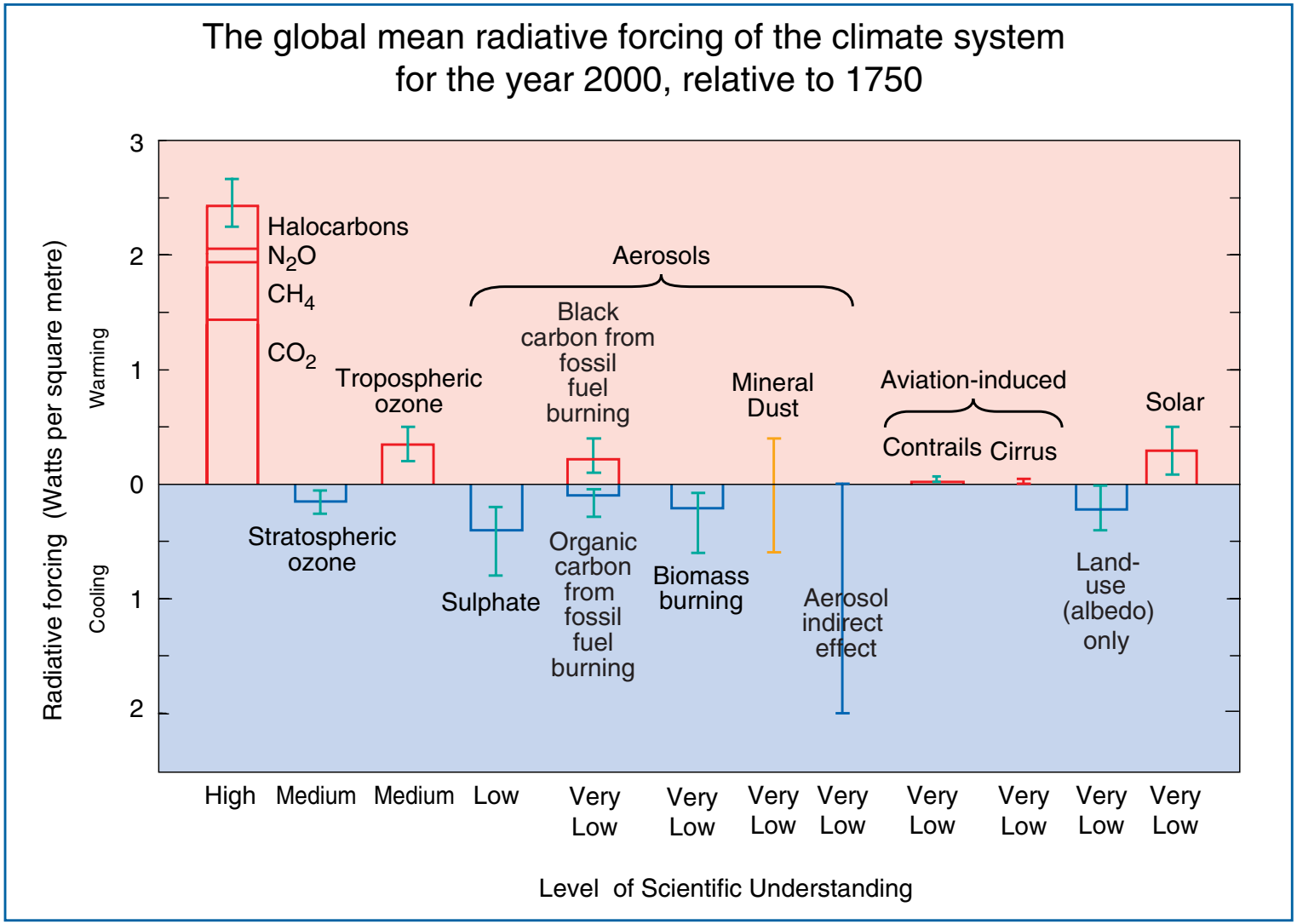
DEPENDENCE OF CLOUD ALBEDO ON CLOUD DEPTH

Influence of Cloud Drop Radius and Concentration



Twomey, *Atmospheric Aerosols*, 1977

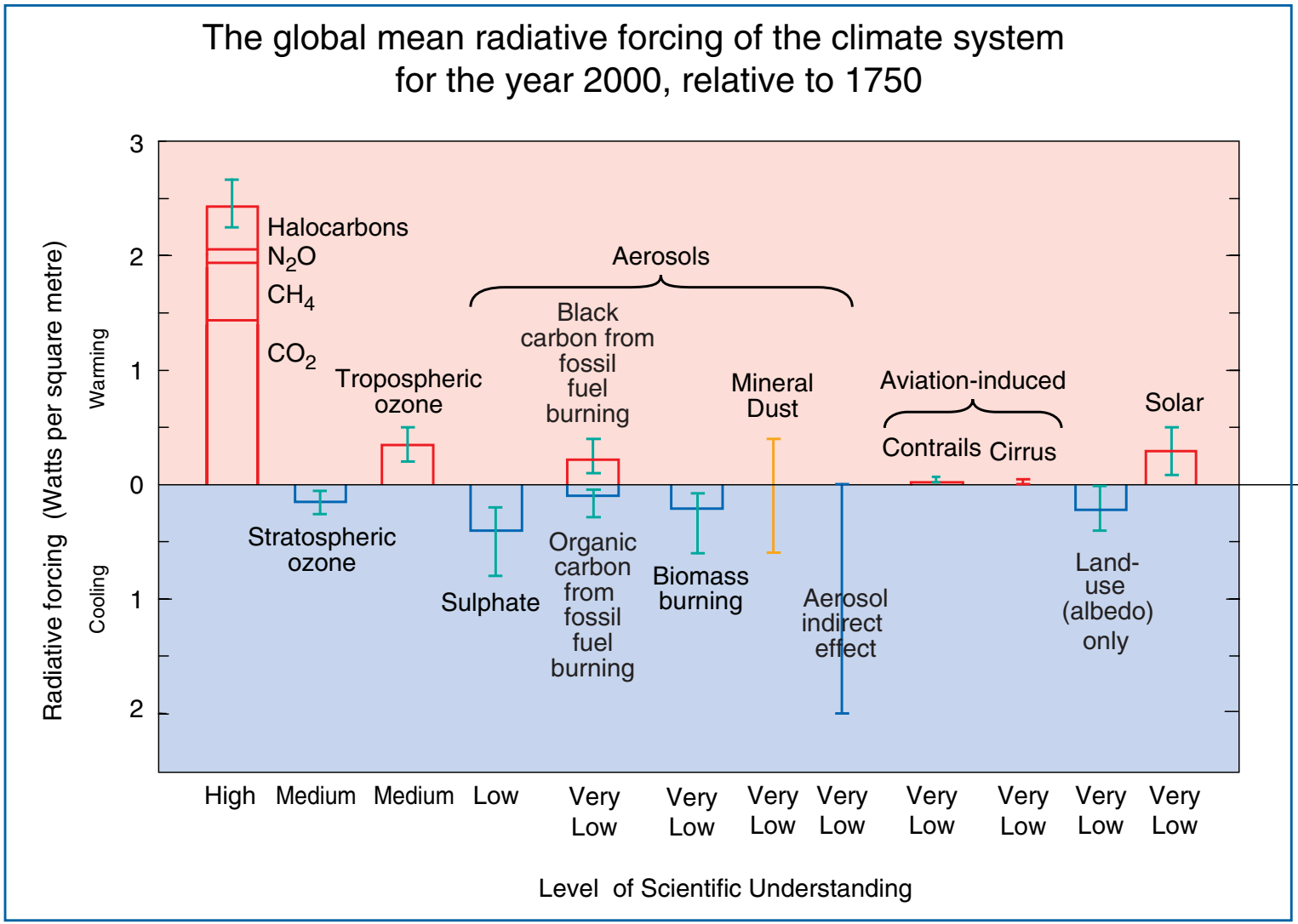
RADIATIVE FORCING OVER THE INDUSTRIAL PERIOD
IPCC (2001)

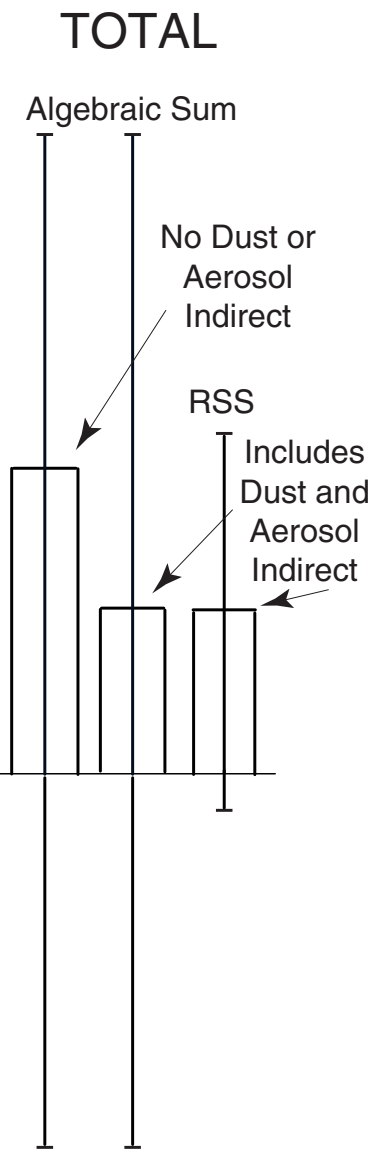


Summary for Policymakers

A Report of Working Group I of the Intergovernmental Panel on Climate Change

RADIATIVE FORCING OVER THE INDUSTRIAL PERIOD
IPCC (2001)
With totals and overall uncertainties by 3 approaches





WHY MODELING SULFATE IS "EASY"

The key under the lamppost

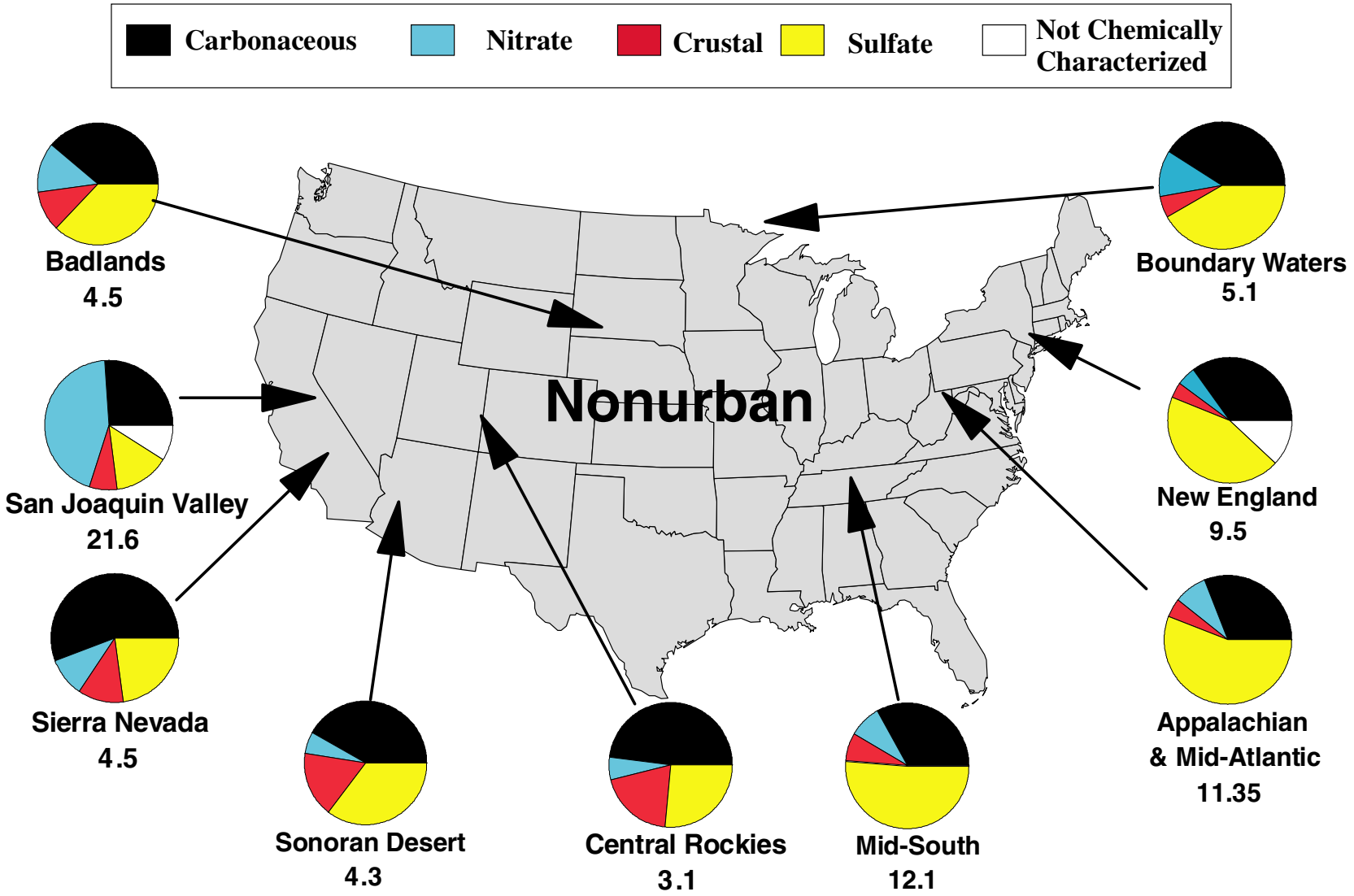
- Conservation of matter
- Emissions
- Chemistry
- Measurements

WHY MODELING SULFATE IS IMPORTANT

The key

- Major anthropogenic aerosol constituent
- Test ability to model
- Examine for aerosol influences
- Examine climate sensitivity

AEROSOL COMPOSITION AND MASS-LOADING
PM2.5 ($\mu g\ m^{-3}$) at nonurban U. S. locations
Several-year average

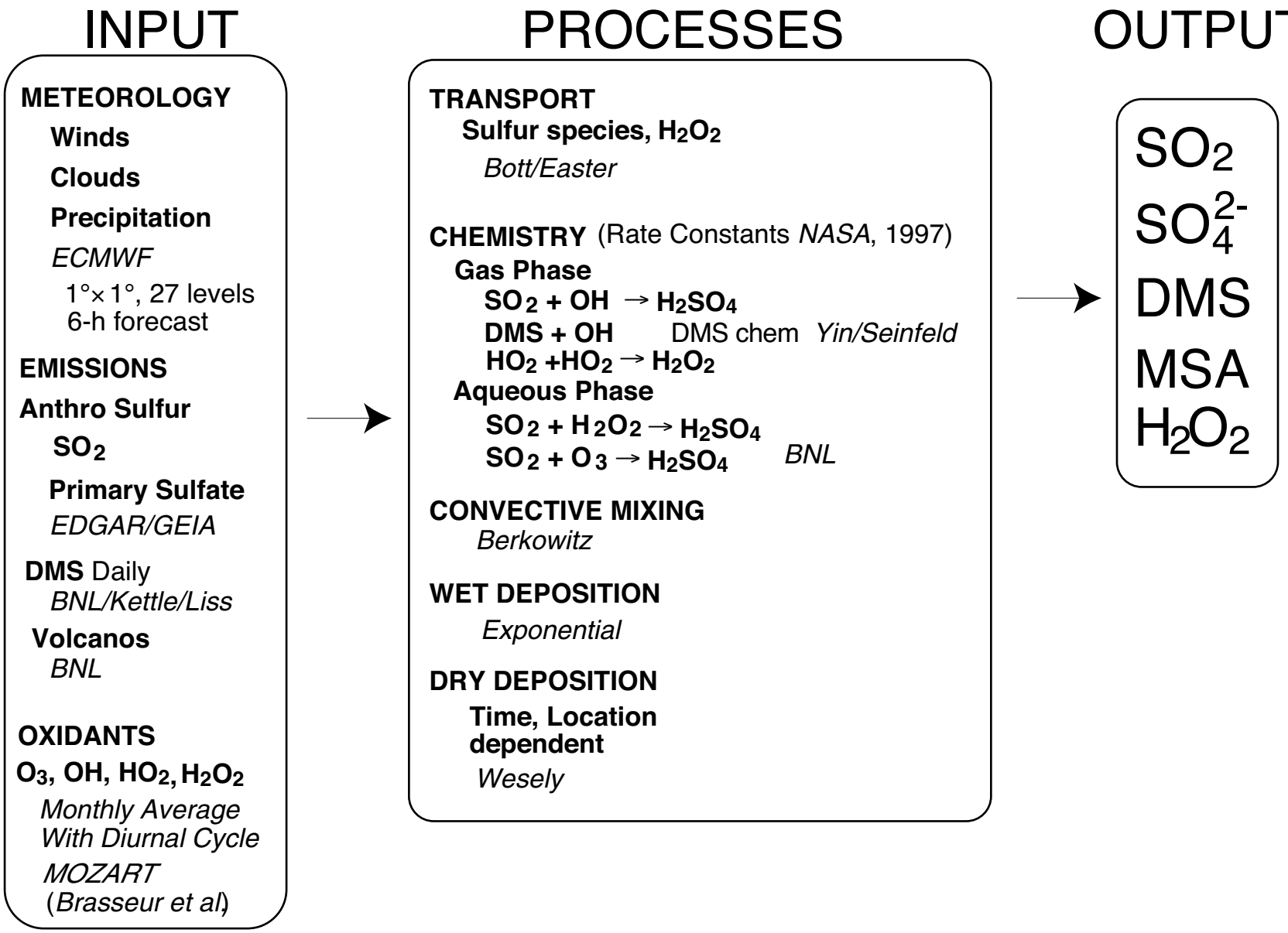


Source - EPA

Aerosol Chemical Transport Model GChM-O

Global **Ch**emistry **M**odel Driven by **O**bservation-Derived Meteorological Data

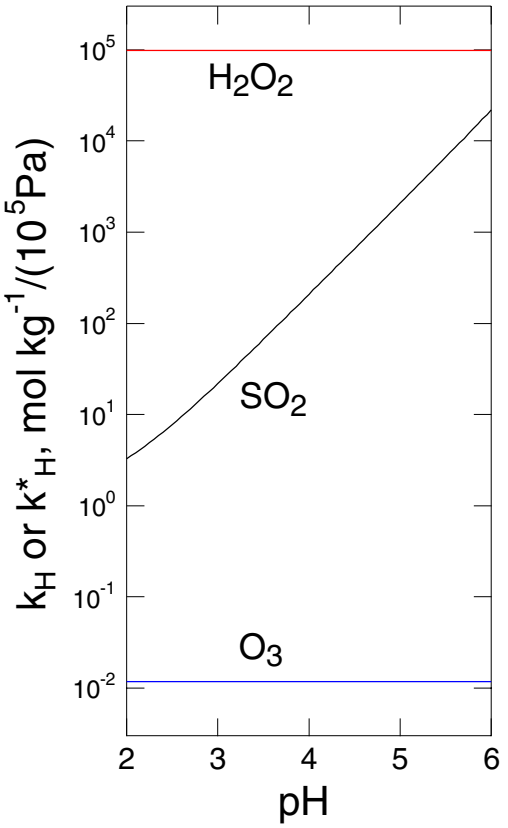
Benkovitz, Schwartz, et al., 1994 - 2003



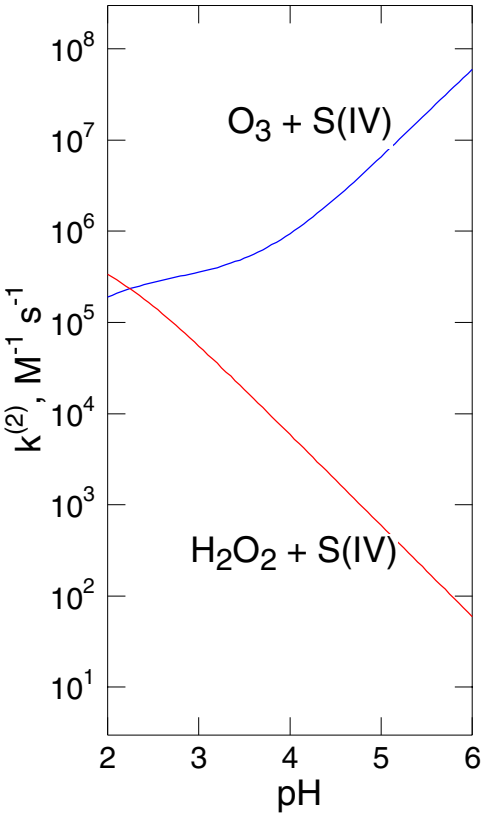
AQUEOUS OXIDATION OF S(IV) BY H_2O_2 AND O_3

pH Dependence of solubility and kinetics

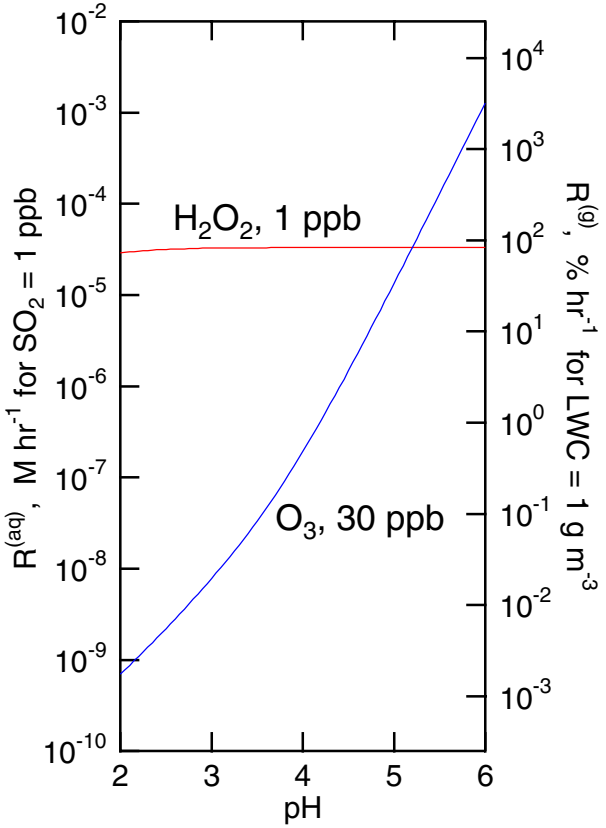
Solubility



Rate Constant



Rate



$$R_{\mathrm{aq}} = -\frac{d[\mathrm{S(IV)}]}{dt} = \frac{d[\mathrm{S(VI)}]}{dt} = H^*_{\mathrm{SO}_2} H_{\mathrm{O}_3} k^{(2)}_{\mathrm{aq}} p_{\mathrm{SO}_2} p_{\mathrm{O}_3}$$

$$R_{\mathrm{g}} = -\frac{dp_{\mathrm{SO}_2}}{dt} = LRTR_{\mathrm{aq}}$$

L = Liquid water content
R = Universal gas constant
T = Temperature

DAYS OF RECKONING

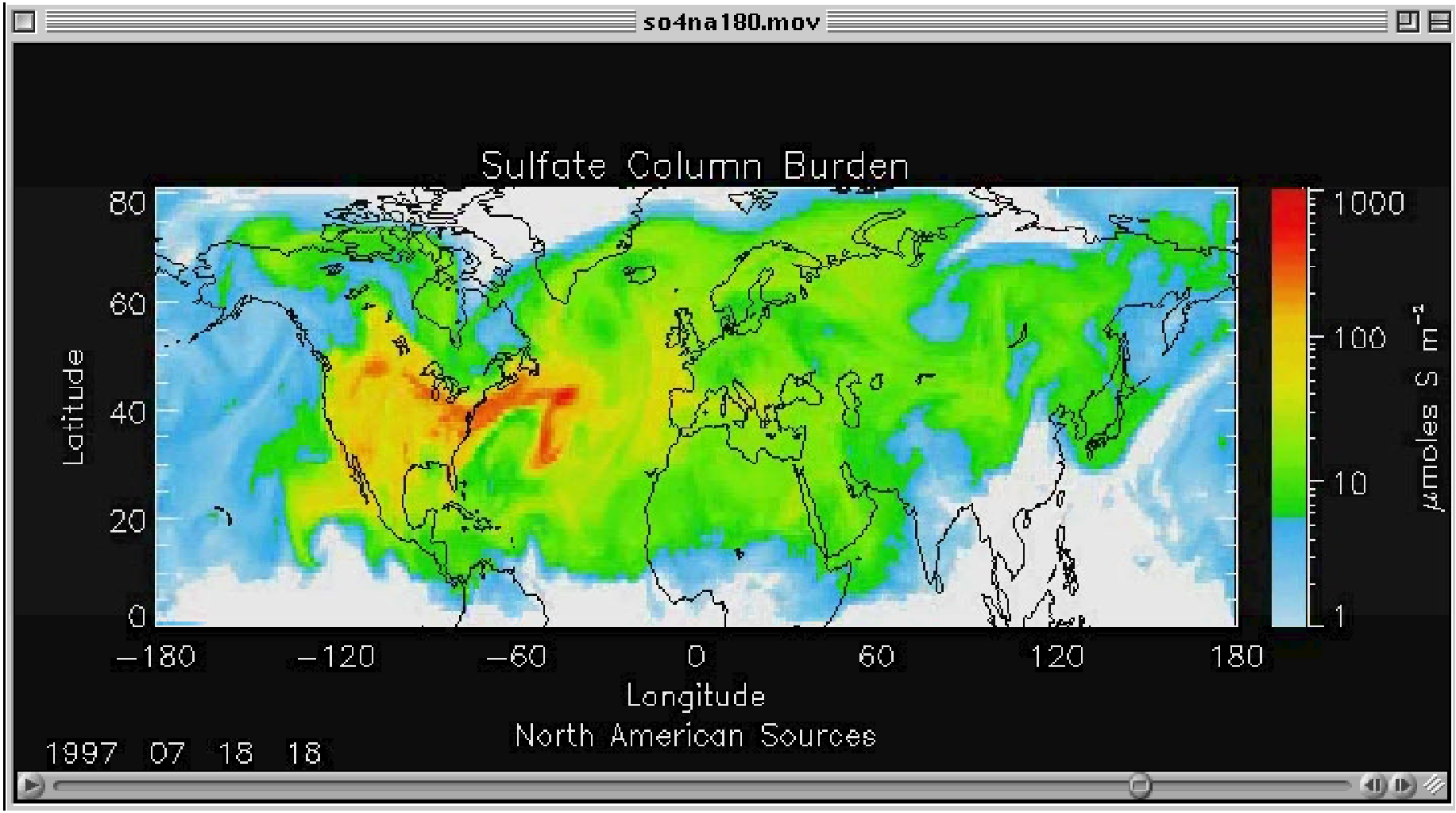
Component of Model	Number	Aggregate Number
Grid cells		
Longitude	360	360
Latitude	81	2.92×10^4
Vertical	27	7.87×10^5
Source Regions	5	3.94×10^6
Biogenic, North America, Europe, Asia, Volcanic		
Sulfur species per source region	4	1.57×10^7
SO_2, pSO_4^{2-}, gSO_4^{2-}, $aqSO_4^{2-}$		
Solutions per day		
Chemistry, Vertical transport, Precip scavenging	24	
Horizontal advection	4	
Differential equations per day	28	4.41×10^8
Days	60	2.65×10^{10}
Experiments	??	$?? \times 10^{??}$

SULFATE COLUMN BURDEN

Vertical integral of concentration

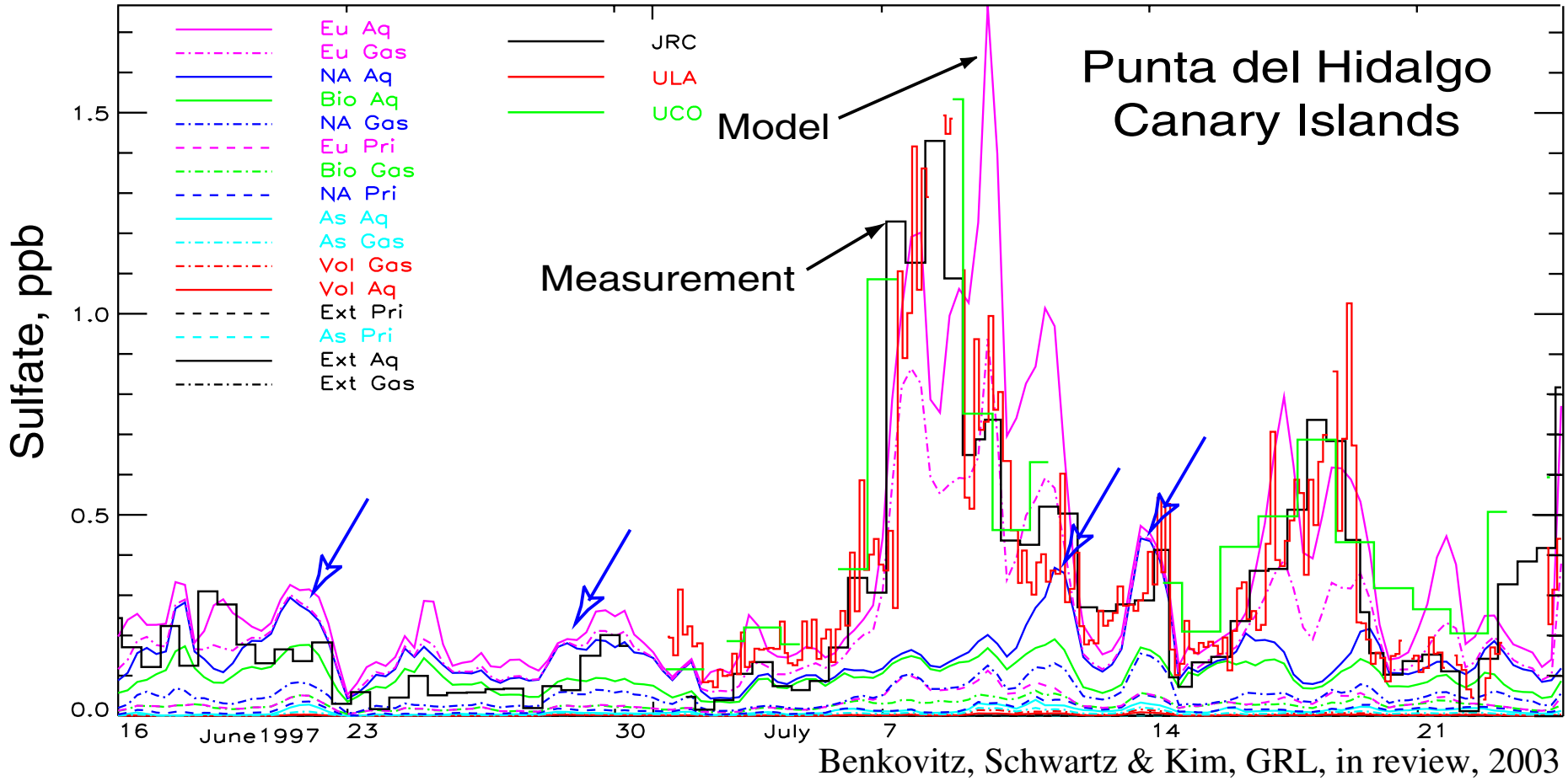
July 18, 1997, 1800 UTC - North American sources only

Sample frame from animation



BNL Chemical Transport Model

COMPARISON OF MEASURED VS. MODELED SULFATE DURING ACE-2



Benkovitz, Schwartz & Kim, GRL, in review, 2003

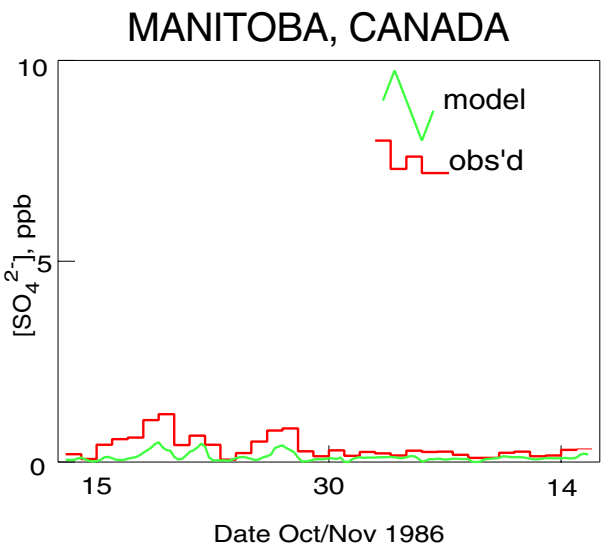
Model identifies sulfate according to geographical source and chemical formation mechanism.

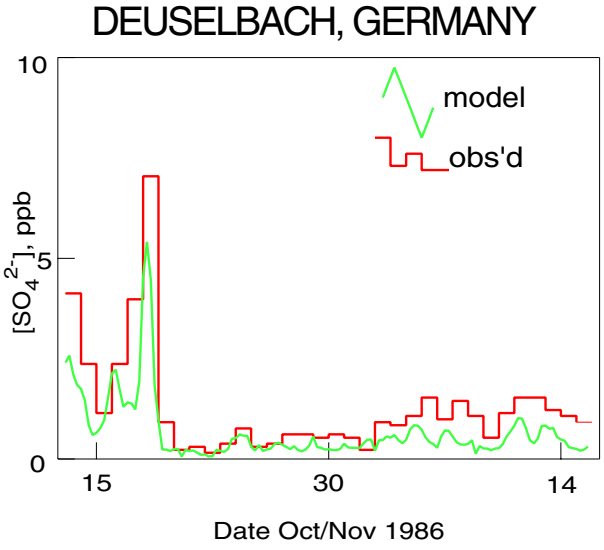
Model closely tracks observations at intensive observation stations.

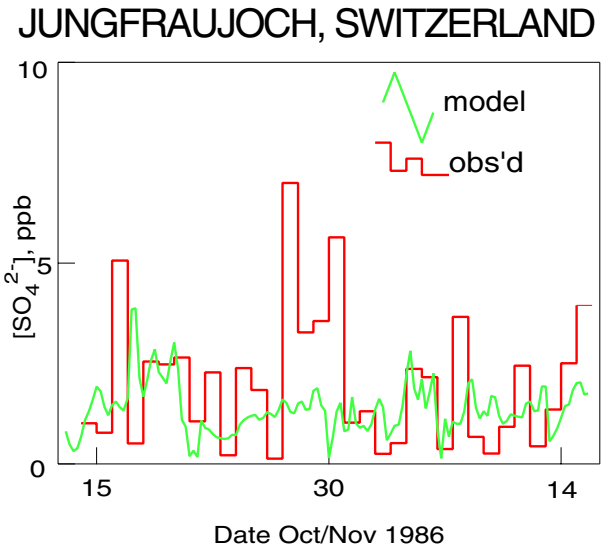
Blue arrows denote instances where sulfate was substantially from North American sources.

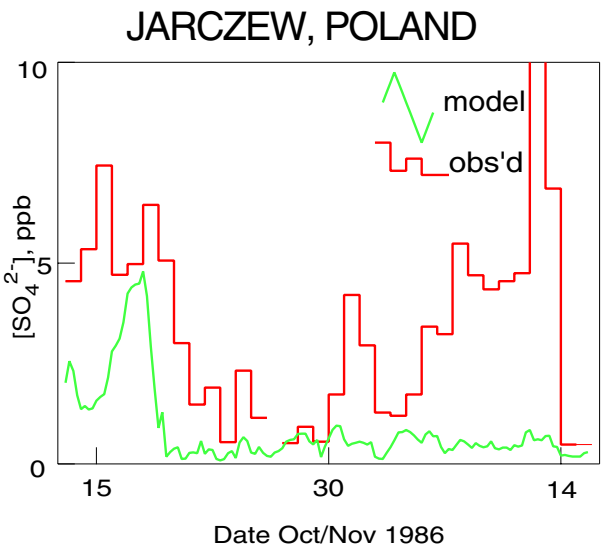
COMPARISON OF MODEL AND OBSERVATIONS

Comparisons for 24-hr sulfate mixing ratio at surface









COMPARISON OF MODEL AND OBSERVATIONS

Statistics of Comparisons

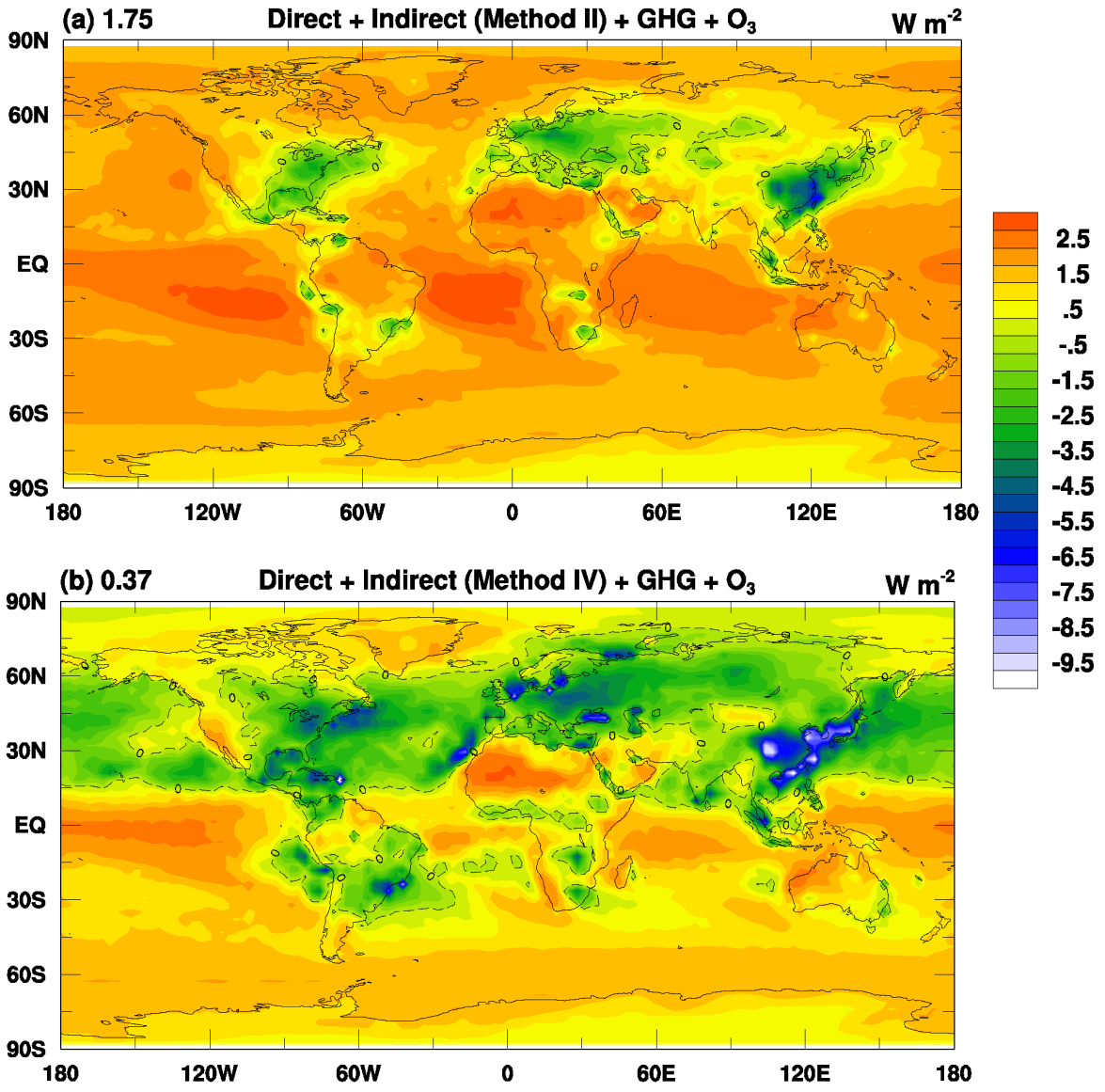
	N	Median Spread
Obs-Obs	503	1.5
Model-Obs Same locations	503	1.9
Model-Obs All locations	7907	2.3

Benkovitz and Schwartz, *JGR*, 1997

SHORTWAVE FORCING, ANNUAL AVERAGE

GHG's + O_3 + Sulfate (Direct and Indirect)

Two Formulations of Cloud Droplet Concentration

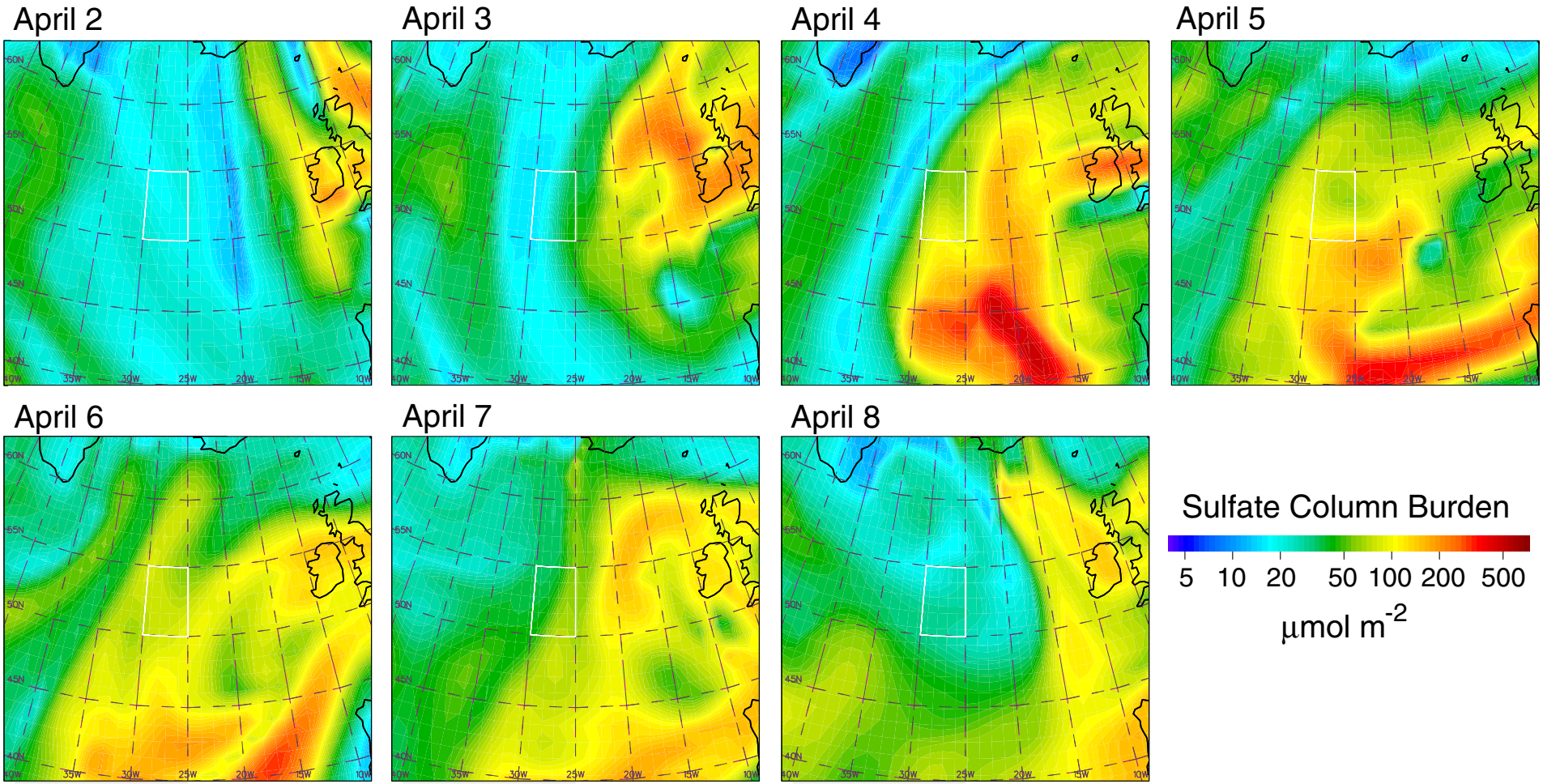


Kiehl et al., JGR, 2000

MODELED SULFATE COLUMN BURDEN

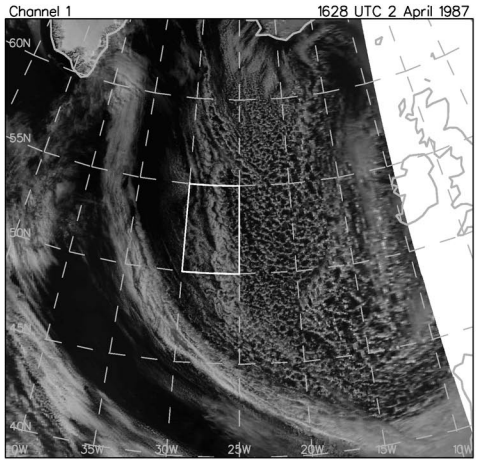
$$\int [SO_4^{2-}] dz$$

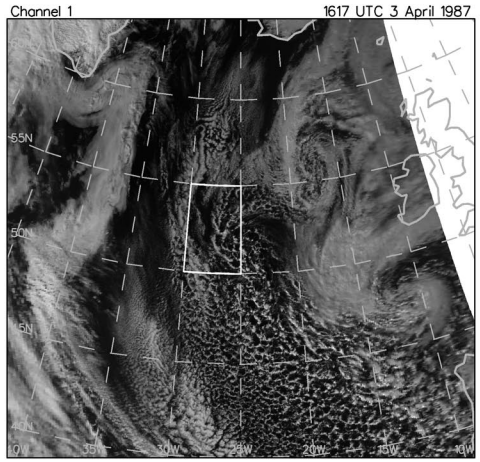
April 2-8, 1987

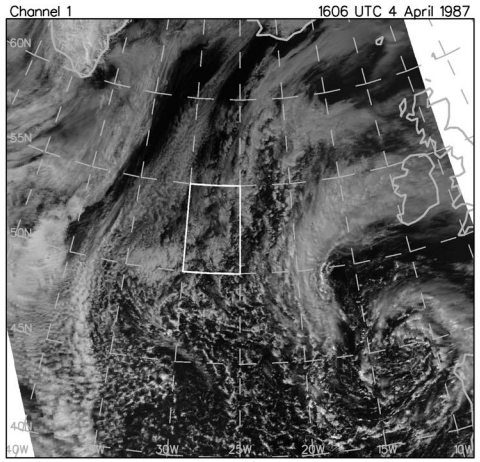


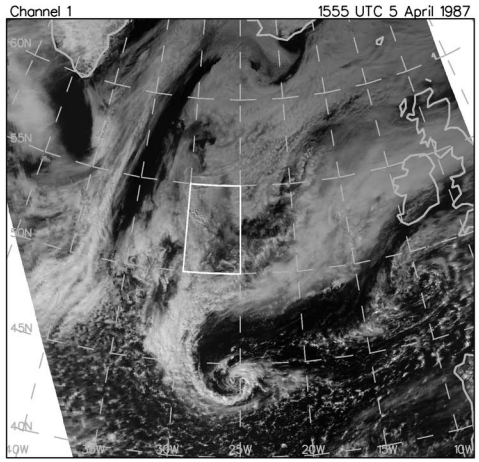
AVHRR IMAGES APRIL 2-8, 1987

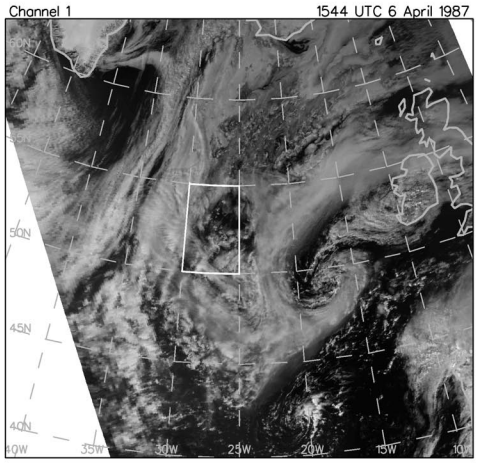
Channel 1, Visible, 0.58-0.68 µm

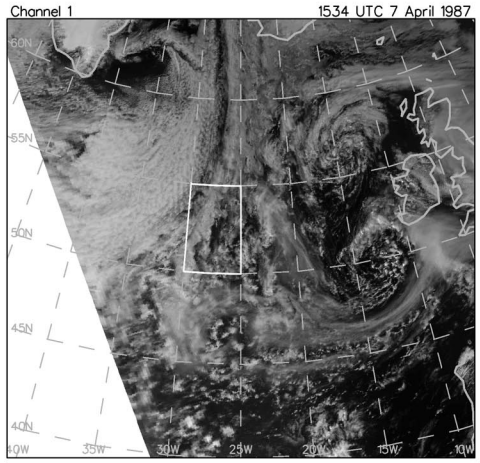


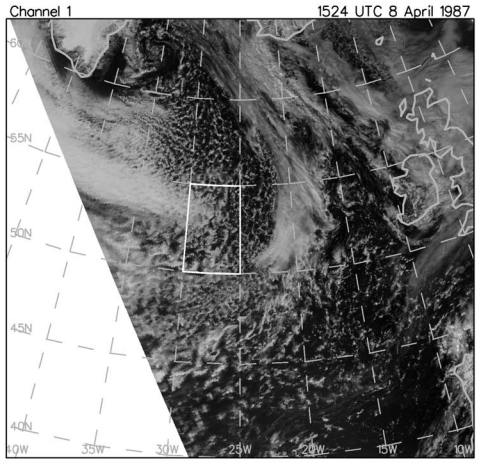


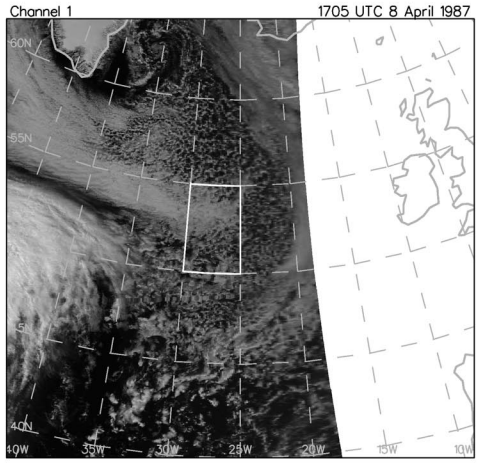








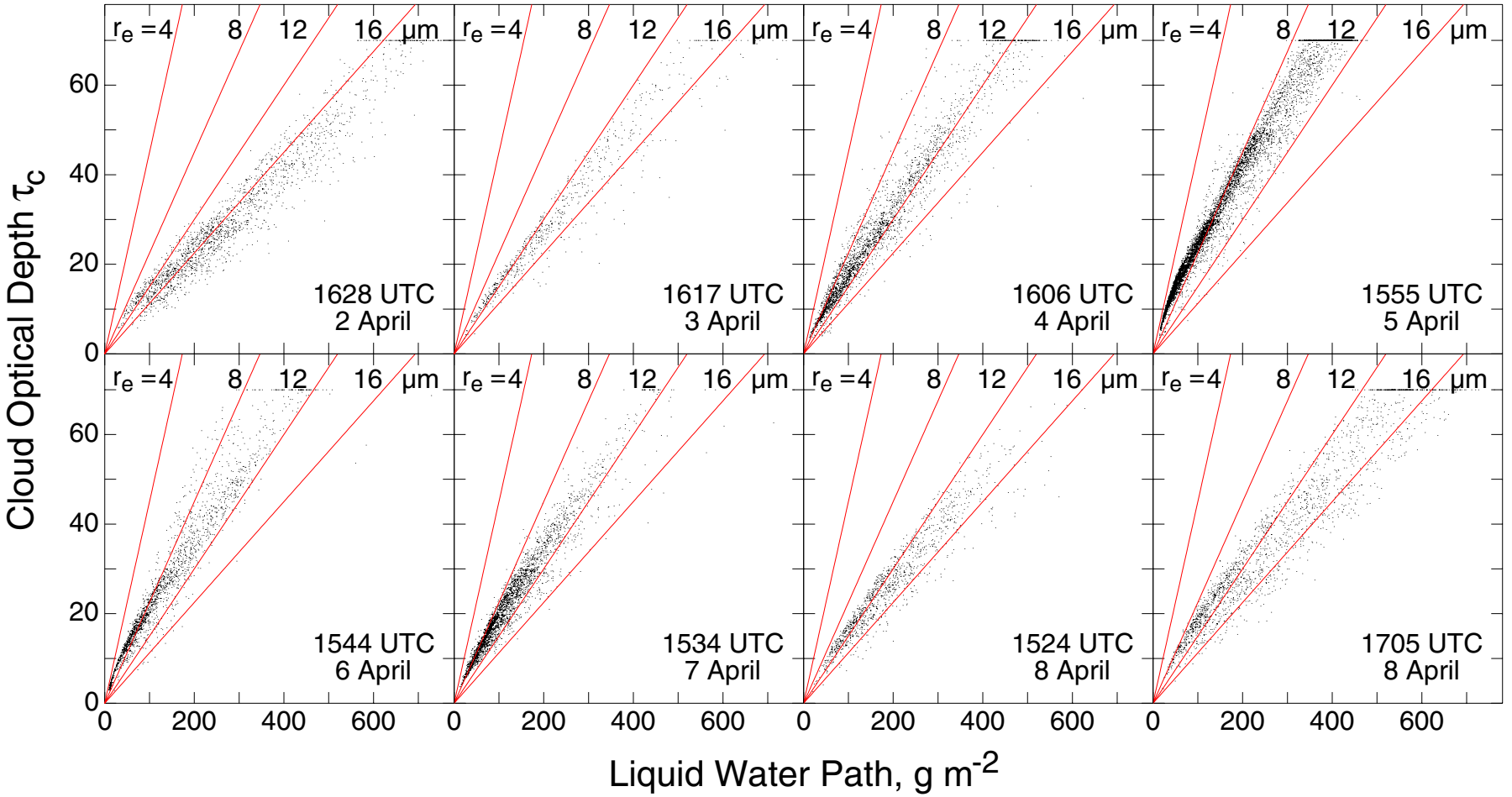




CLOUD OPTICAL DEPTH

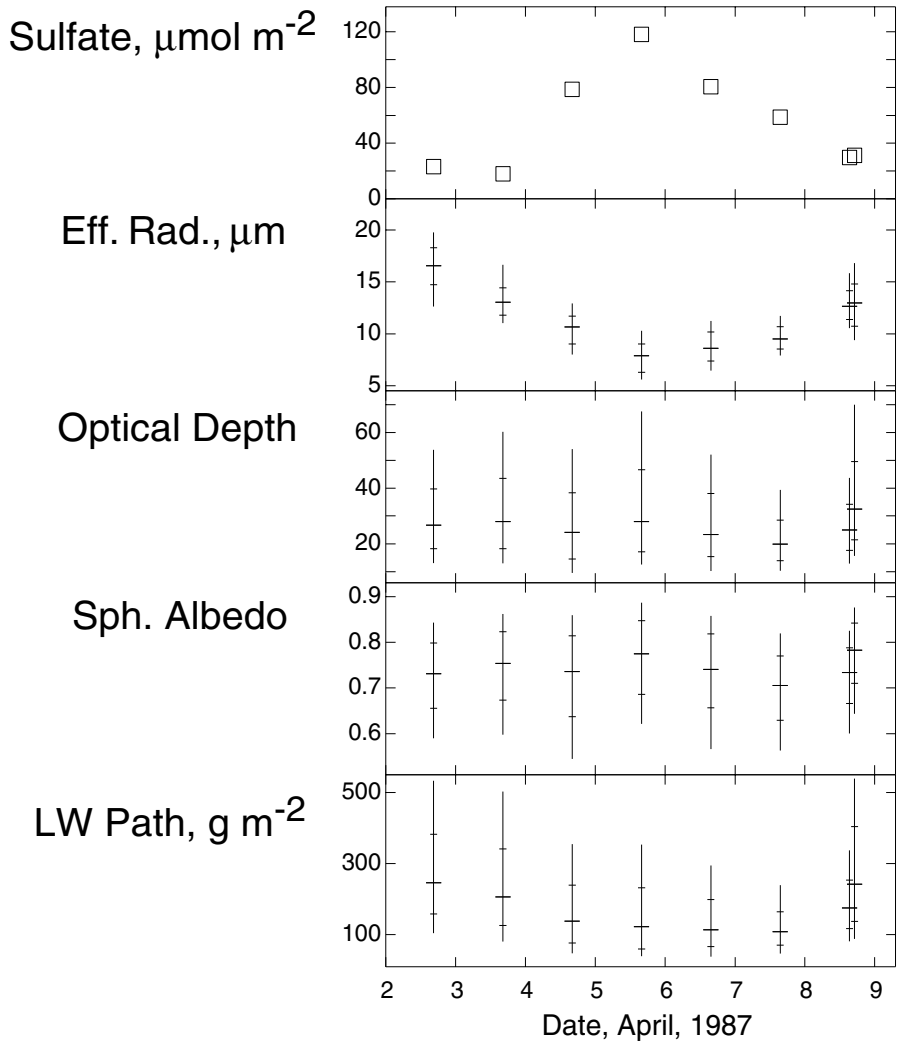
Dependence on Liquid Water Path

25°-30°W, 50°-55°N April 2-8, 1987



CLOUD PROPERTIES AND SULFATE COLUMN BURDEN

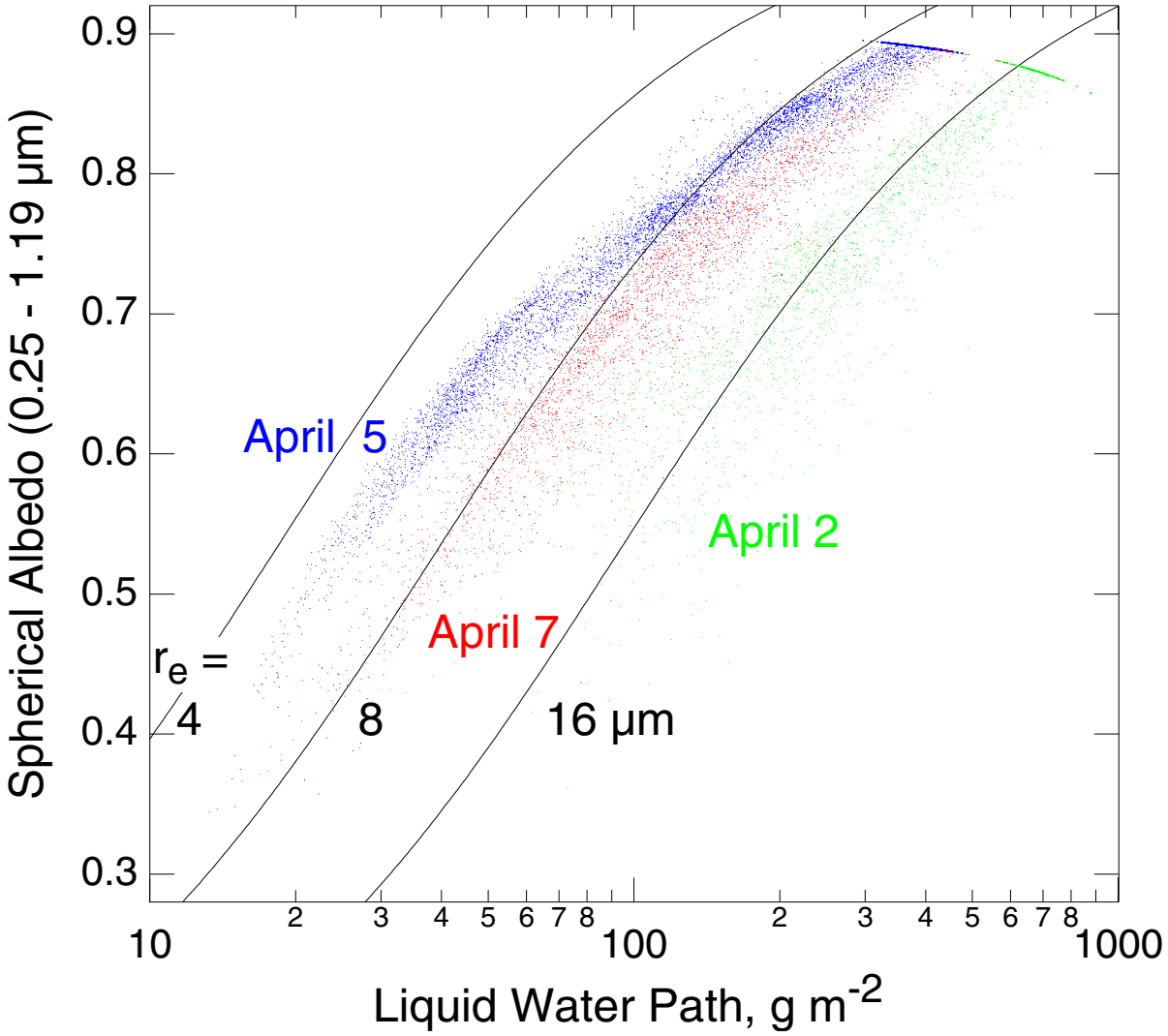
25°-30°W, 50°-55°N, April 2-8, 1987



CLOUD-TOP ALBEDO

Dependence on Liquid Water Path

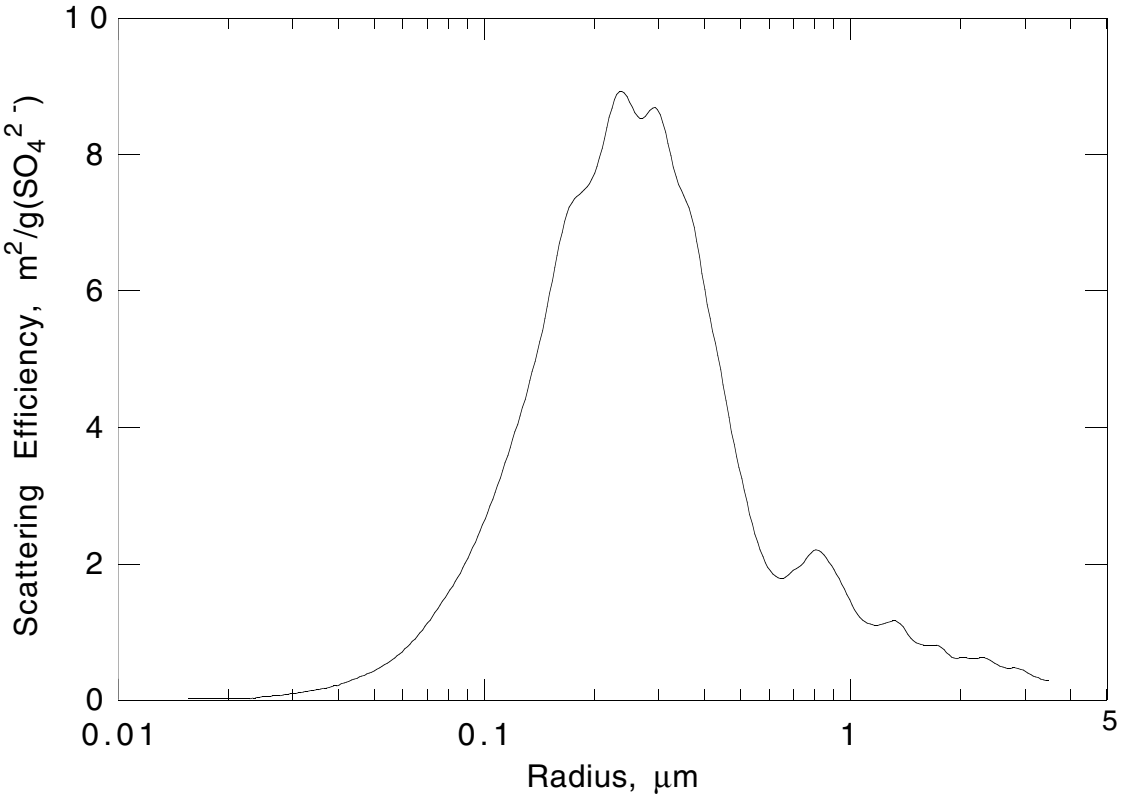
25°-30°W, 50°-55°N April 2, 5 and 7,1987



Schwartz, Harshvardhan & Benkovitz, PNAS, 2002

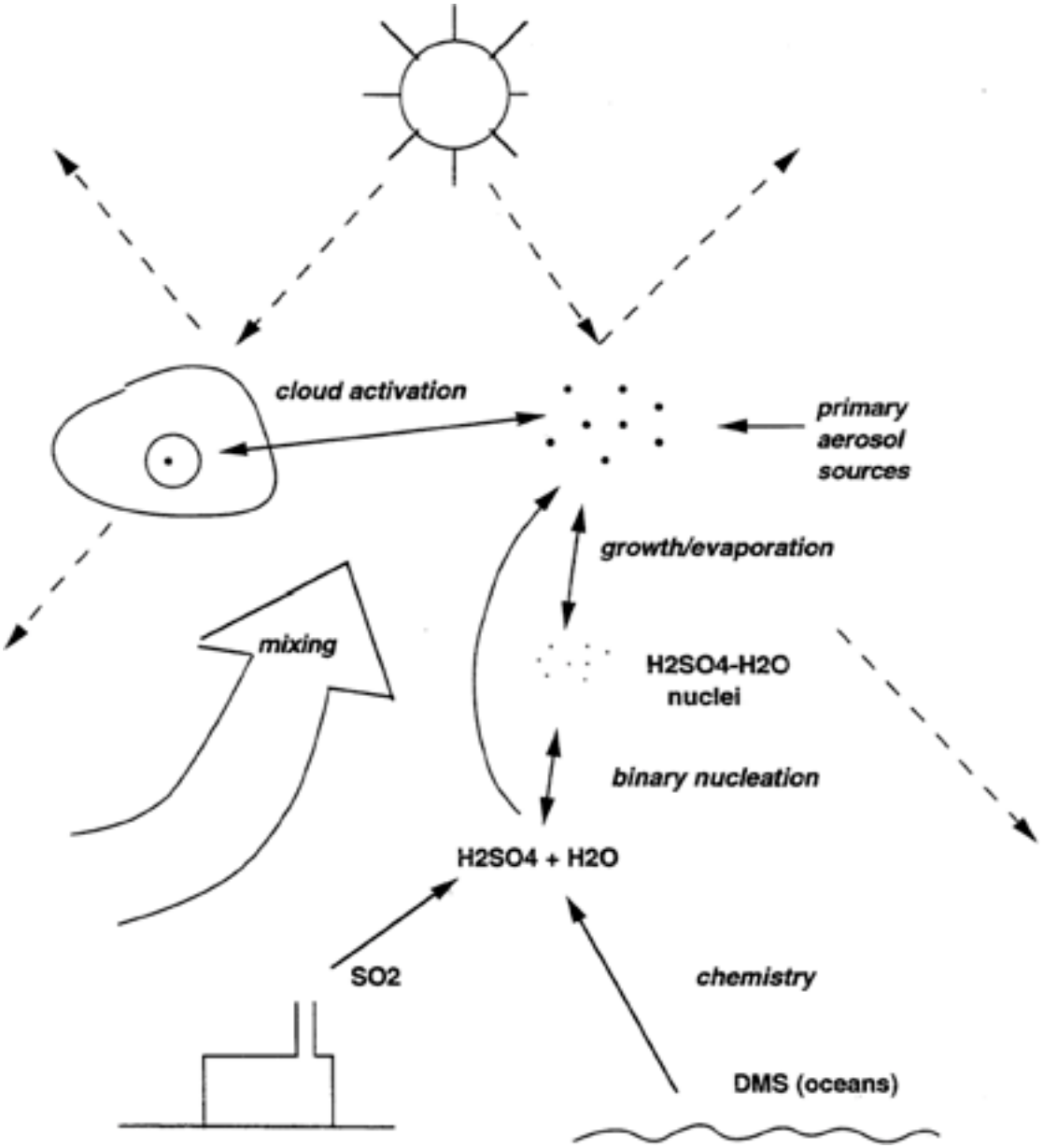
SIZE MATTERS

Light scattering efficiency of ammonium sulfate vs. radius



Data of Ouimette and Flagan, *Atmos. Environ.*, 1982

NUCLEATION AND GROWTH PROCESSES OF ATMOSPHERIC AEROSOLS AND CLOUDS



DO YOU HAVE A FEW MOMENTS?

The Problem

How to represent the size-distribution of atmospheric aerosols and its evolution in chemical transport models

The Solution

Represent the size distribution in terms of its low-order moments

$$\mu_k \equiv \int_0^\infty r^k \left(\frac{dN}{dr}\right) dr$$

PHYSICAL INTERPRETATION OF MOMENTS

Moment	Physical Interpretation	Unit
μ_0	Particle number concentration	cm^{-3}
μ_1	Total radius per unit volume	$cm\ cm^{-3}$
μ_2	$(4\pi)^{-1} \times$ Area per unit volume	$cm^2\ cm^{-3}$
μ_3	$(\frac{4\pi}{3})^{-1} \times$ Volume per unit volume	$cm^3\ cm^{-3}$

EVALUATING AEROSOL PROPERTIES AND EVOLUTION FROM THE MOMENTS OF THE PSD

McGraw, Schwartz, *et al*.

An aerosol physical or optical property or growth rate is an integral over the size distribution, requiring integrals of the form

$$P = \int_0^\infty \sigma(r) f(r) dr$$

where the kernel function $\sigma(r)$ describes the property of interest.

***Problem*:** *How to evaluate integrals over the aerosol size distribution when only the lower-order moments of the distribution are known???*

Solution: *Gaussian quadrature* $\int_0^\infty \sigma(r) f(r) dr \approx \sum_{i=1}^{N} \sigma(r_i) w_i$

Here $\sigma(r)$ *is the known kernel function and* $f(r)$ *is the unknown size distribution.*

The N abcissas $\{ r_i \}$ and N weights $\{ w_i \}$ are determined from $2N$ moments of $f(r)$ by inversion of

$$\mu_k \equiv \int_0^\infty r^k f(r) dr = \sum_{i=1}^{N} r_i^k w_i \qquad k = 0, 1, \ldots, 2N\text{-}1 \; .$$

Aerosol ***properties*** (e.g., light scattering coefficient) evaluated ***from the lowest six moments*** are accurate typically to a few percent.

APPLICATION TO SULFATE IN EASTERN NORTH AMERICA

Simulations: 40 days, 19 July to 28 August 1995.

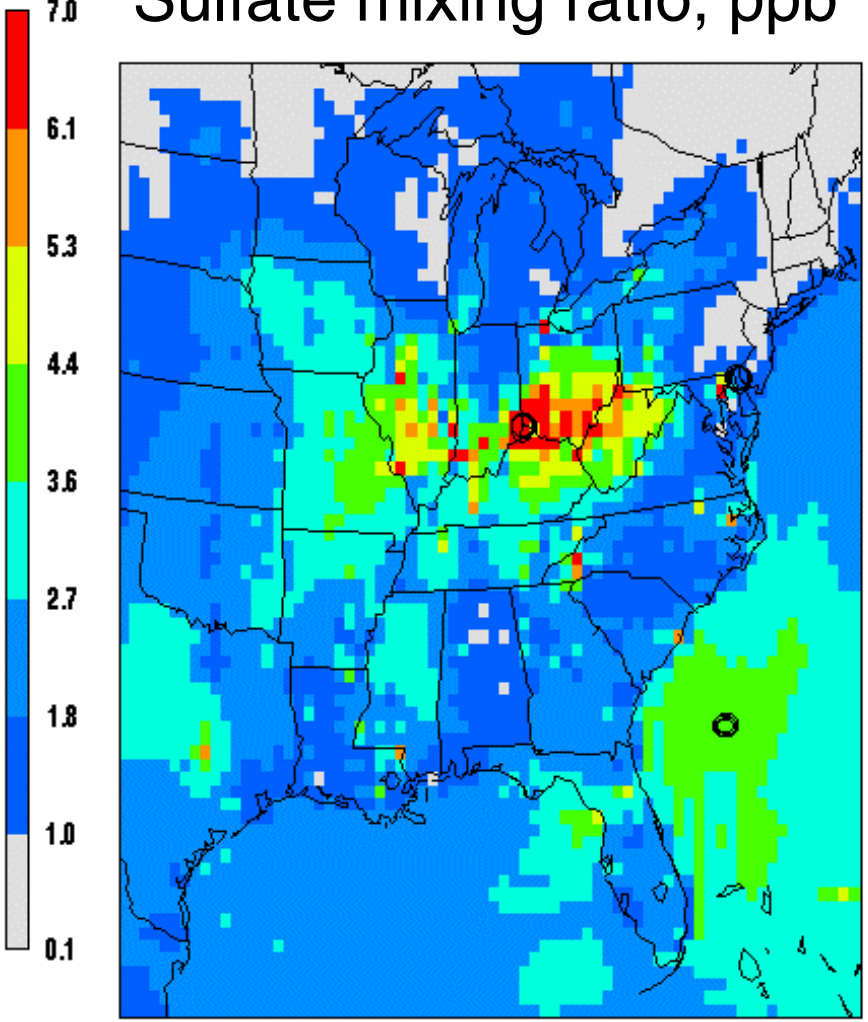
Comparison with observations: Sulfate mass concentration, aerosol number concentration and size distributions at the Great Smoky Mountains National Park during Southeastern Aerosol and Visibility Study.

Limitation: Model is for sulfate only; size measurements are for entire aerosol, not just sulfate.

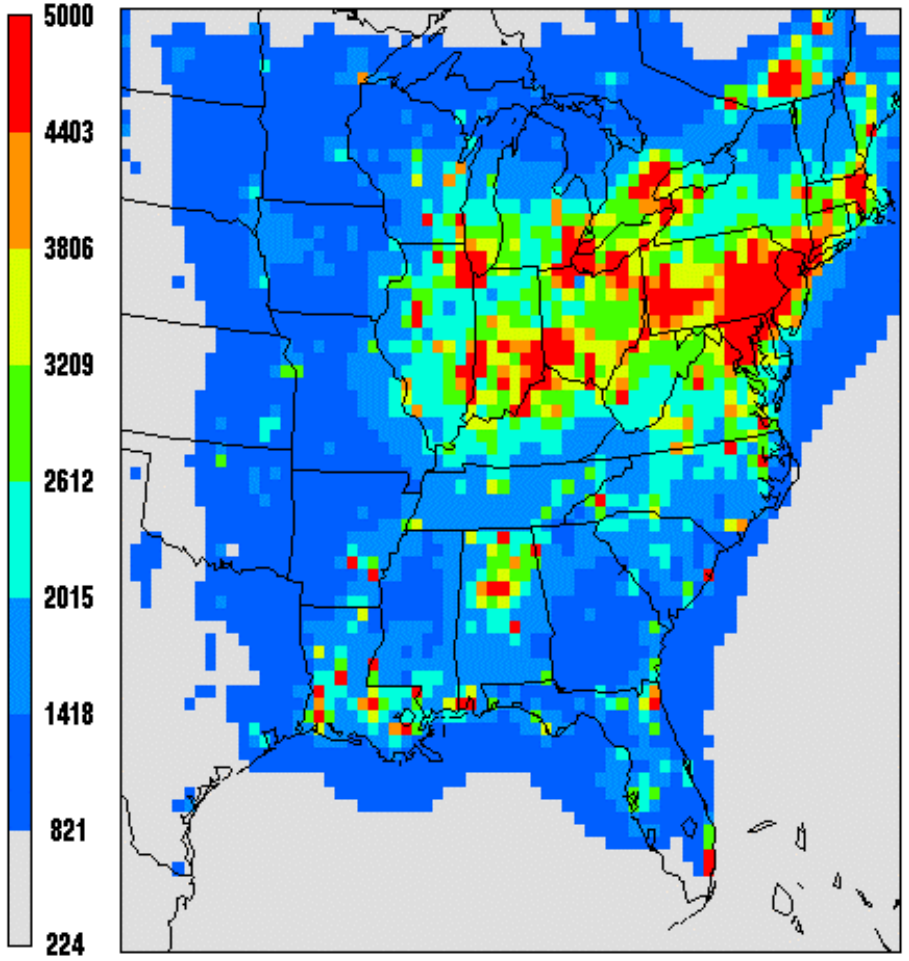
RESULTS

40-day averages at lowest model layer.

Sulfate mixing ratio, ppb



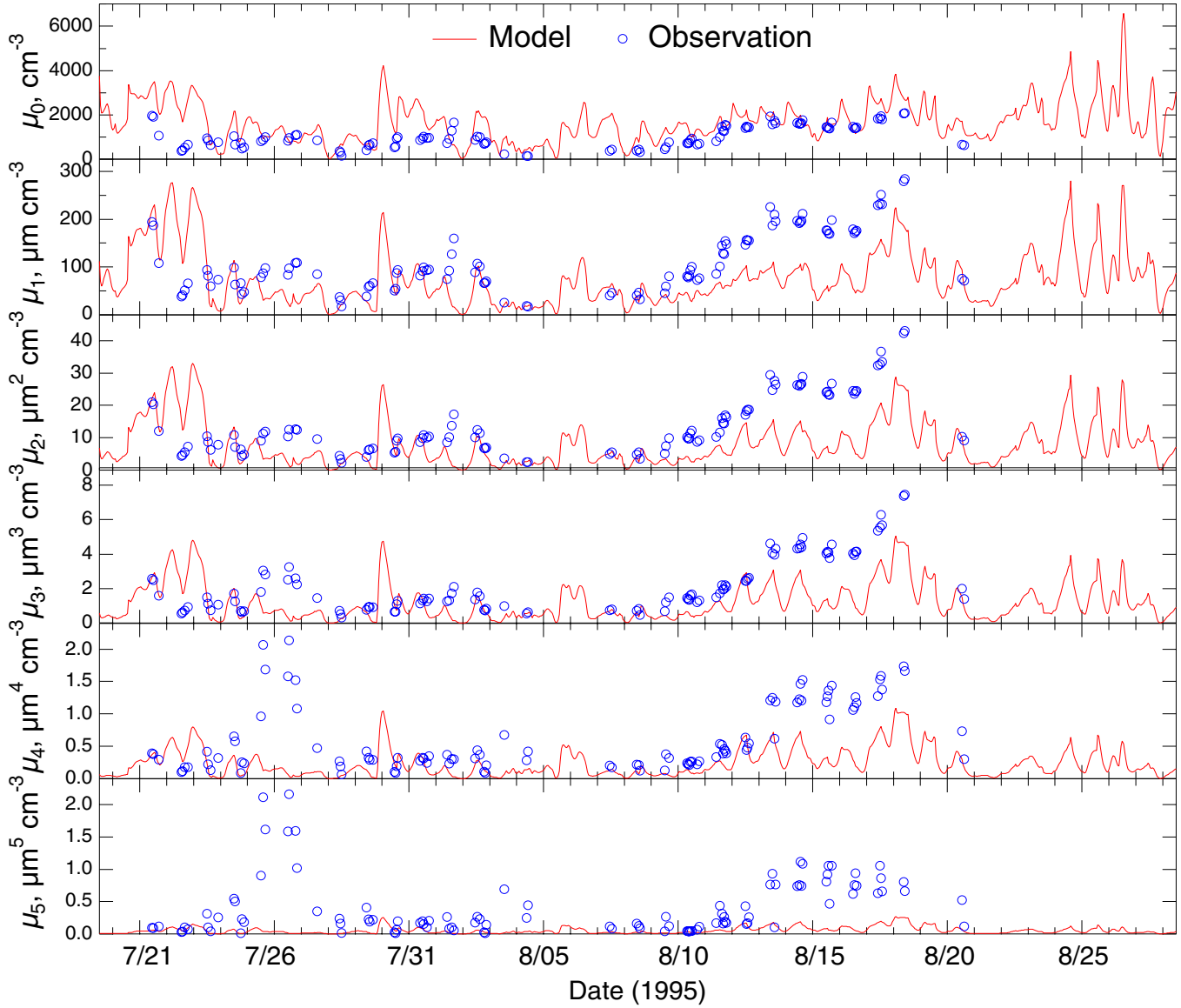
Number concentration, cm^{-3}



Yu, Kasibhatla, Wright, Schwartz, McGraw & Deng, *JGR*, in press, 2003

TIME SERIES COMPARISON FOR AEROSOL MOMENTS

Look Ridge, Great Smoky Mountains TN (84° W, 36° N; 900 m) during SEAVS



Yu, Kasibhatla, Wright, Schwartz, McGraw & Deng, *JGR*, in press, 2003

TIME SERIES COMPARISON FOR AEROSOL INTENSIVE PROPERTIES EVALUATED FROM MOMENTS

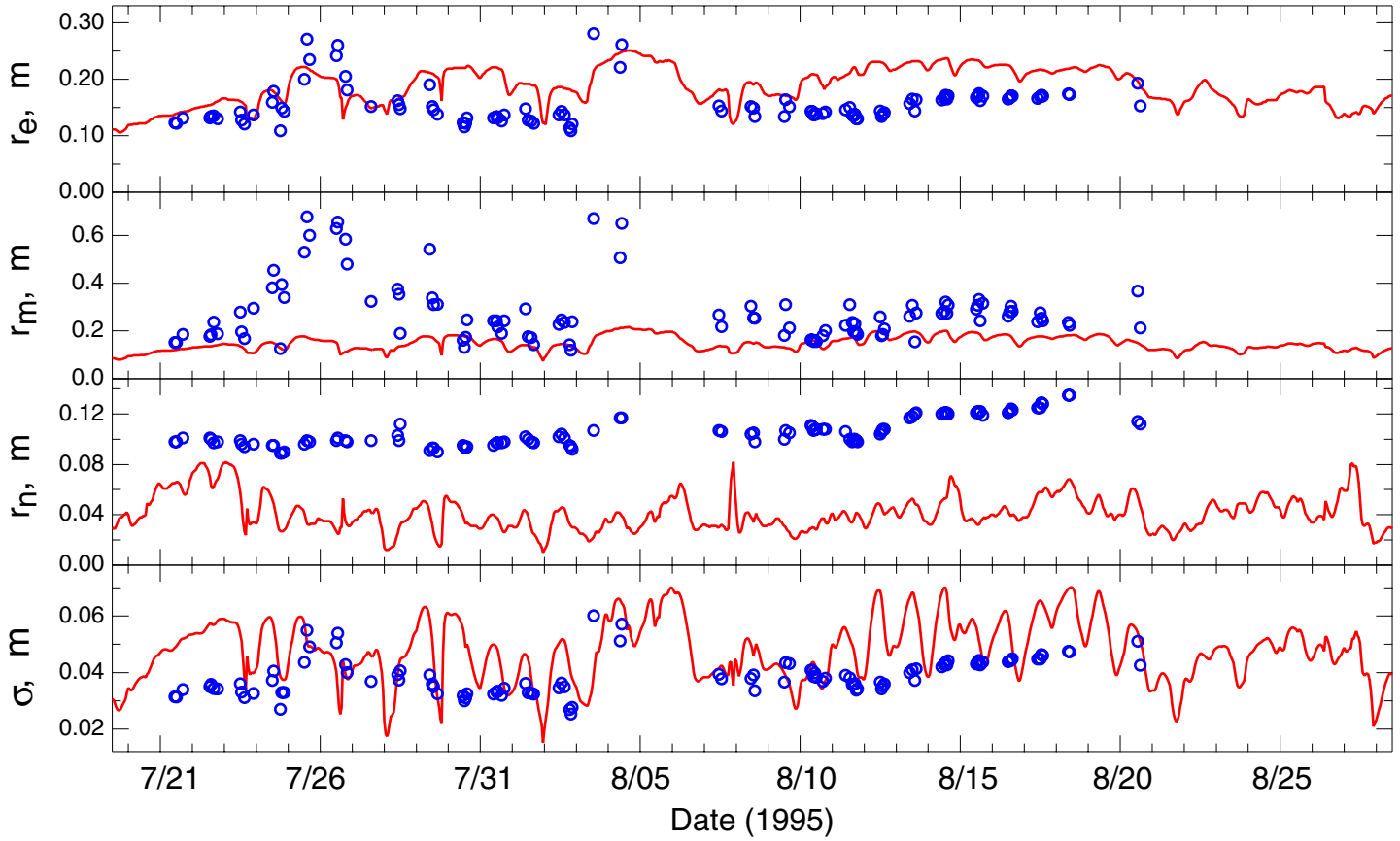
Look Ridge, Great Smoky Mountains TN (84° W, 36° N; 900 m) during SEAVS

Equivalent radius $r_e = \mu_3/\mu_2$

Mass-mean radius $r_m = \mu_3/\mu_0$

Mass-mean radius $r_n = \mu_3/\mu_0$

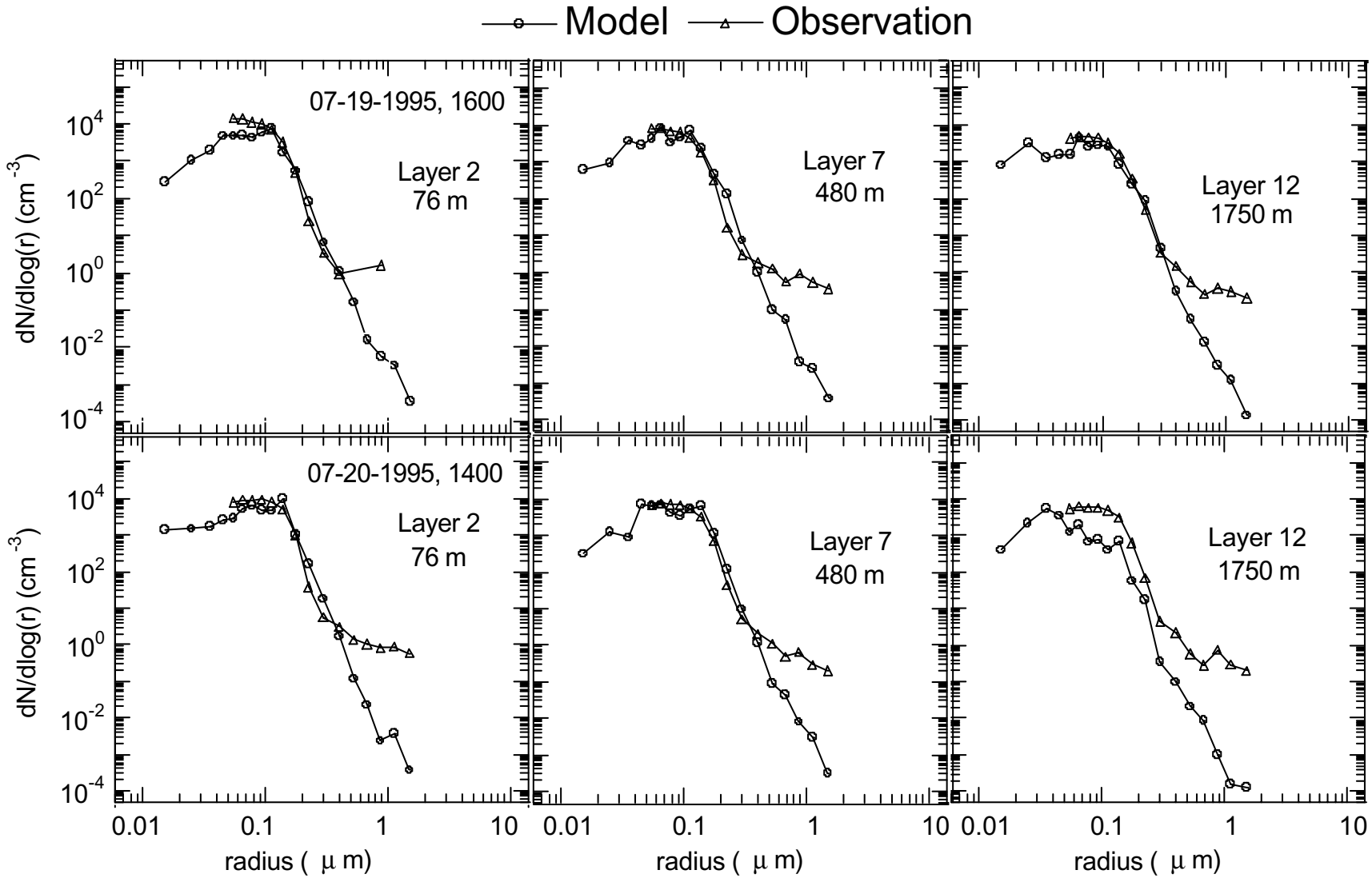
Standard deviation $\sigma = (\mu_2\mu_0 - \mu_1^2)^{1/2} / \mu_0^2$



Yu, Kasibhatla, Wright, Schwartz, McGraw & Deng, *JGR*, in press, 2003

SIZE DISTRIBUTIONS

Comparison of Measurement and Retrieval from Model At 3 Altitudes near Nashville TN



Yu, Kasibhatla, Wright, Schwartz, McGraw & Deng, *JGR*, in press, 2003

SUMMARY

Aerosol forcing is the ***greatest source of uncertainty*** in radiative forcing of climate change over the industrial period.

Knowledge of this forcing is required to build confidence in climate models or to empirically infer climate sensitivity.

Representing aerosol forcing in climate models requires accurate representation of the distribution and properties of anthropogenic aerosols.

Sulfate is a major aerosol constituent and a major test-bed for ability to represent aerosols in models.

Present model does a ***"pretty good job"*** of representing sulfate mass concentration on subhemispheric to hemispheric scales but not good enough.

Representing aerosol microphysical properties and evolution in chemical transport models is necessary but still in its infancy.