12.335/12.835 EXPERIMENTAL ATMOSPHERIC CHEMISTRY, FALL 2014

TOPIC 1
ATMOSPHERIC PHOTOCHEMISTRY and AIR POLLUTION

INTRODUCTION TO THE CHEMISTRY OF AIR POLLUTION

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OZONE CYCLE & PHOTOCHEMICAL STEADY STATE APPROXIMATION (PSSA)

Ozone Cycle – *Goal is to Understand kinetics*

$$NO_2 + h\nu \xrightarrow{1} NO + O(^3P)$$

$$O(^3P) + O_2 + M \xrightarrow{2} O_3 + M$$

$$O_3 + NO \xrightarrow{3} NO_2 + O_2$$

τ ~ O(mins)

$$\frac{d[NO_2]}{dt} = -k_1[NO_2] + k_3[NO][O_3]$$

$$\frac{d[O(^3P)]}{dt} = k_1[NO_2] - k_2[O(^3P)][O_2][M]$$

$$\vdots$$

Derivation of Ozone PSSA

$$\frac{d[O(^3P)]}{dt} \cong 0 = k_1[NO_2] - k_2[O(^3P)][O_2][M]$$

$$k_1[NO_2] = k_2[O(^3P)][O_2][M]$$

$$\frac{d[O_2]}{dt} \cong 0 = -k_2[O(^3P)][O_2][M] + k_3[NO][O_3]$$

$$k_3[NO][O_3] = k_2[O(^3P)][O_2][M]$$

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]}$$

O_3 and NO_2

$$\frac{d[O_3]}{dt} = k_2[O(^3P)][O_2][M] - k_3[NO][O_3]$$

$$\frac{d[NO]}{dt} = k_1[NO_2] - k_3[NO][O_3]$$

$$\Rightarrow \frac{d([O_3]-[NO])}{dt} = 0$$

$$[O_3] - [NO] = [O_3]_0 - [NO]_0$$

Additional Conserved Quantities

$$\frac{d([O_3]+[NO_2])}{dt} = \frac{d[O_x]}{dt} = 0$$

$$[NO_2] = [NO_2]_0 + [O_3]_0 - [O_3]$$

$$k_3[O_3]\cdot([O_3] - [O_3]_0 + [NO]_0) = k_1([NO_2]_0 + [O_3]_0 - [O_3])$$

$$[O_3]^2 + ([NO]_0 - [O_3]_0 + \frac{k_1}{k_3})[O_3] - \frac{k_1}{k_3}([O_3]_0 + [NO_2]_0) = 0$$

$$a[O_3]^2 + b[O_3] + c = 0$$

Simple Quadratic Model for O_3

$$[O_3] = -\frac{1}{2}\left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right) + \frac{1}{2}\left[\left([NO]_0 - [O_3]_0 + \frac{k_1}{k_3}\right)^2 + 4\frac{k_1}{k_3}\left([O_3]_0 + [NO_2]_0\right)\right]^{\frac{1}{2}}$$

$$[NO_2] = [NO_2]_0 + [O_3]_0 - [O_3]$$

Ozone Production From Carbon Monoxide

$$CO(g) + \dot{O}H(g) \rightarrow CO_2(g) + \dot{H}(g)$$

Carbon monoxide, Hydroxyl radical → Carbon dioxide, Atomic hydrogen

$$\dot{H}(g) + O_2(g) \xrightarrow{M} H\dot{O}_2(g)$$

Atomic hydrogen, Molecular oxygen → Hydroperoxy radical

$$\dot{N}O(g) + H\dot{O}_2(g) \rightarrow \dot{N}O_2(g) + \dot{O}H(g)$$

Nitric oxide, Hydroperoxy radical → Nitrogen dioxide, Hydroxyl radical

$$\dot{N}O_2(g) + h\nu \rightarrow \dot{N}O(g) + \cdot\dot{O}(g) \qquad \lambda < 420\text{ nm}$$

Nitrogen dioxide → Nitric oxide, Atomic oxygen

$$\cdot\dot{O}(g) + O_2(g) \xrightarrow{M} O_3(g)$$

Ground-state atomic oxygen, Molecular oxygen → Ozone

Role of Reactive Organic Gases (ROG)

Photoxidation of Formaldehyde (HCHO)

$$HCHO + h\nu \xrightarrow{O_2} 2HO_2 + CO$$

$$HCHO + h\nu \longrightarrow H_2 + CO$$

$$HCHO + OH \xrightarrow{O_2} HO_2 + CO + H_2O$$

$$HCHO + h\nu \rightarrow H_2 + CO$$
$$\rightarrow HCO + H$$
$$H + O_2 \rightarrow HO_2$$
$$HCO + O_2 \rightarrow HO_2 + CO$$

$$HO_2 + NO \longrightarrow NO_2 + OH$$ **x 3**

Number of NO to NO_2 conversions depends on organic

Fate of NO_x in the Atmosphere

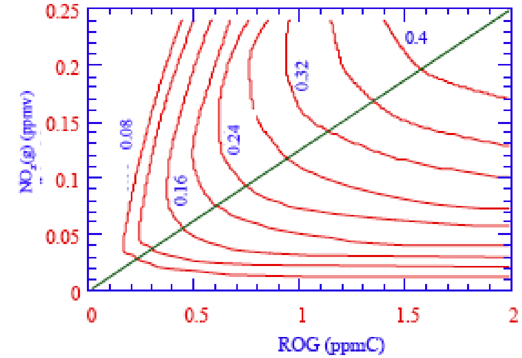
$$NO_2 + OH \longrightarrow HNO_3$$ **Acid Deposition**

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$ **Visibility, radiative transfer**

$$NO_x \longrightarrow HONO,\ CH_3C(O)OONO_2(PAN), \cdots$$

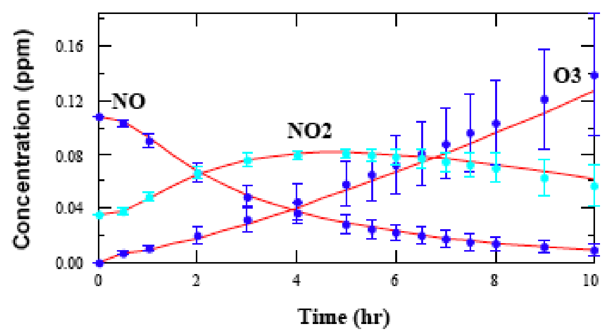
Atmospheric lifetime of NO_2 ~ 1-2 Days, PAN can travel long distances and then serve a downwind source of NO_x

Ozone Isopleth



Contours are ozone (ppmv)

Dynamics of Ozone formation



Time scale for peak NO_2 formation is ~4 hours

The hydroxyl free radical (OH) is the major oxidizing chemical in the global atmosphere

It annually removes about 3.7 billion metric tons (Pg) of trace gases (CO, CH_4, higher hydrocarbons, hydro-halocarbons, NO_x, SO_x, etc.) from the atmosphere..

With a lifetime of only about 1 second it is possible to measure locally, but not possible to measure directly at regional to global scales.

Use measurements of the industrial chemical CH_3CCl_3, whose emissions are are known and whose major sink is OH, to indirectly estimate large scale OH variations.

Oxidant Sources in the Atmosphere

Hydroxyl Radical (OH)

- Photodissociation of O_3
  - $O_3 + h\nu \rightarrow O_2 + O(^1D)$
  - $O(^1D) + H_2O \rightarrow 2\ OH\cdot$
- Photodissociation of HONO and H_2O_2
  - $HONO + h\nu \rightarrow OH\cdot + NO$
  - $H_2O_2 + h\nu \rightarrow OH\cdot + OH\cdot$
- Alkene oxidation
  - $R_1CH{=}CHR_2 + O_3 \rightarrow OH\cdot +$ prod.
- From $HO_2\cdot$
  - $NO + HO_2\cdot \rightarrow NO_2 + OH\cdot$

Hydroperoxyl Radical (HO_2)

- Photodissociation of CH_2O
  - $CH_2O + h\nu \rightarrow H\cdot + HCO\cdot$
  - $H\cdot + O_2 + M \rightarrow HO_2\cdot + M$
  - $HCO\cdot + O_2 \rightarrow HO_2\cdot + CO$
- From alkoxy radical reactions
  - $RCH_2O\cdot + O_2 \rightarrow RCHO + HO_2$
  - Byproduct of oxidation of organics

MIT Chemical Engineering 10.391J Spring 2004

OH Production Steady State

Production of OH is by reaction of water vapor with $O(^1D)$

$$\begin{aligned}
&(R1)\quad O_3 + h\nu \rightarrow O_2 + O(^1D)\\
&(R2)\quad O(^1D) + M \rightarrow M + O(^3P)\\
&(R3)\quad O(^1D) + H_2O \rightarrow 2OH
\end{aligned}$$

Assuming steady state for $O(^1D)$ (since R2>>R3)

$$P_{OH} = 2k_3[O(^1D)][H_2O] = \frac{2k_1k_3}{k_2[M] + k_3[H_2O]}[O_3][H_2O]$$

$$\approx \frac{2k_1k_3}{k_2[M]}[O_3][H_2O]$$

MIT Chemical Engineering 10.571 Spring 2007

HOWEVER, IN POLLUTED AIR THERE ARE MULTIPLE SOURCES OF OH DEPENDING ON TIME OF DAY

Early Morning Source of OH in Polluted Air

$$HONO(g) + h\nu \rightarrow \dot{O}H(g) + \dot{N}O(g) \qquad \lambda < 400\ nm$$

Nitrous acid → Hydroxyl radical + Nitric oxide

Mid-Morning Source of OH in Polluted Air

$$HCHO(g) + h\nu \rightarrow H\dot{C}O(g) + \dot{H}(g) \qquad \lambda < 334\ nm$$

Formaldehyde → Formyl radical + Atomic hydrogen

$$\dot{H}(g) + O_2(g) \xrightarrow{M} H\dot{O}_2(g)$$

Atomic hydrogen + Molecular oxygen → Hydroperoxy radical

$$H\dot{C}O(g) + O_2(g) \rightarrow CO(g) + H\dot{O}_2(g)$$

Formyl radical + Molecular oxygen → Carbon monoxide + Hydroperoxy radical

$$\dot{N}O(g) + H\dot{O}_2(g) \rightarrow \dot{N}O_2(g) + \dot{O}H(g)$$

Nitric oxide + Hydroperoxy radical → Nitrogen dioxide + Hydroxyl radical

Afternoon Source of OH in Polluted Air

$$O_3(g) + h\nu \rightarrow O_2(g) + \cdot\dot{O}(^1D)(g) \qquad \lambda < 310\ nm$$

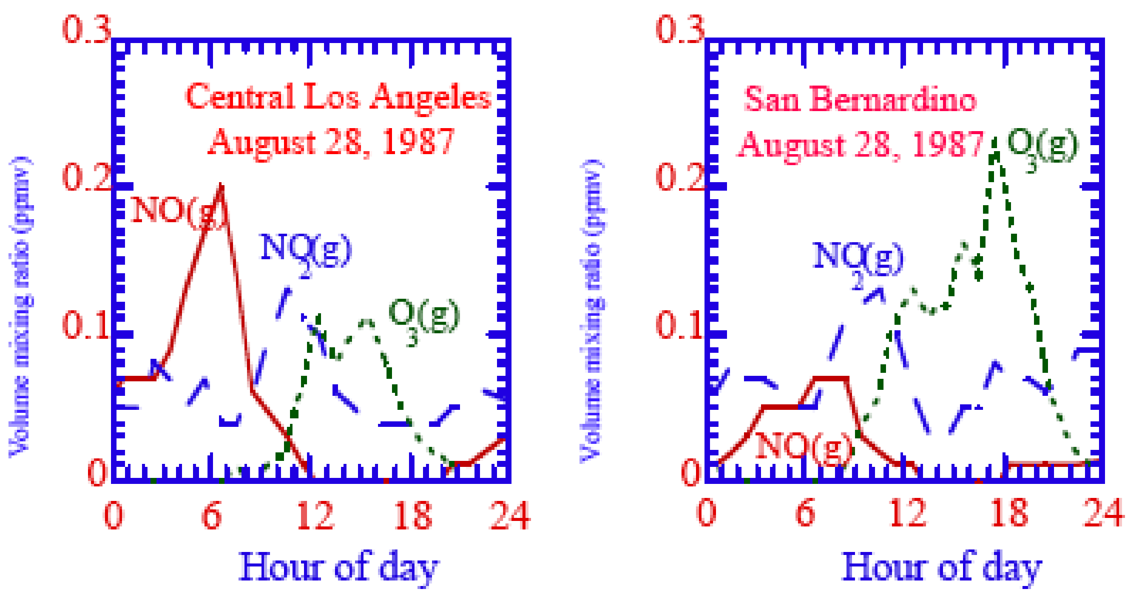
Ozone → Molecular oxygen + Excited atomic oxygen

$$\cdot\dot{O}(^1D)(g) + H_2O(g) \rightarrow 2\dot{O}H(g)$$

Excited atomic oxygen + Water vapor → Hydroxyl radical

BECAUSE OZONE PRODUCTION TAKES TIME, TRANSPORT PLAYS AN IMPORTANT ROLE IN DETERMINING EXPOSURE LEVELS

Pollutant Dynamics in Los Angeles



Can we explain the dynamics?

USA TROPOSPHERIC COLUMN OZONE BY SEASON

(Satellite observations in DOBSON UNITS = 2.7×10^{16} molecules/cm^2)

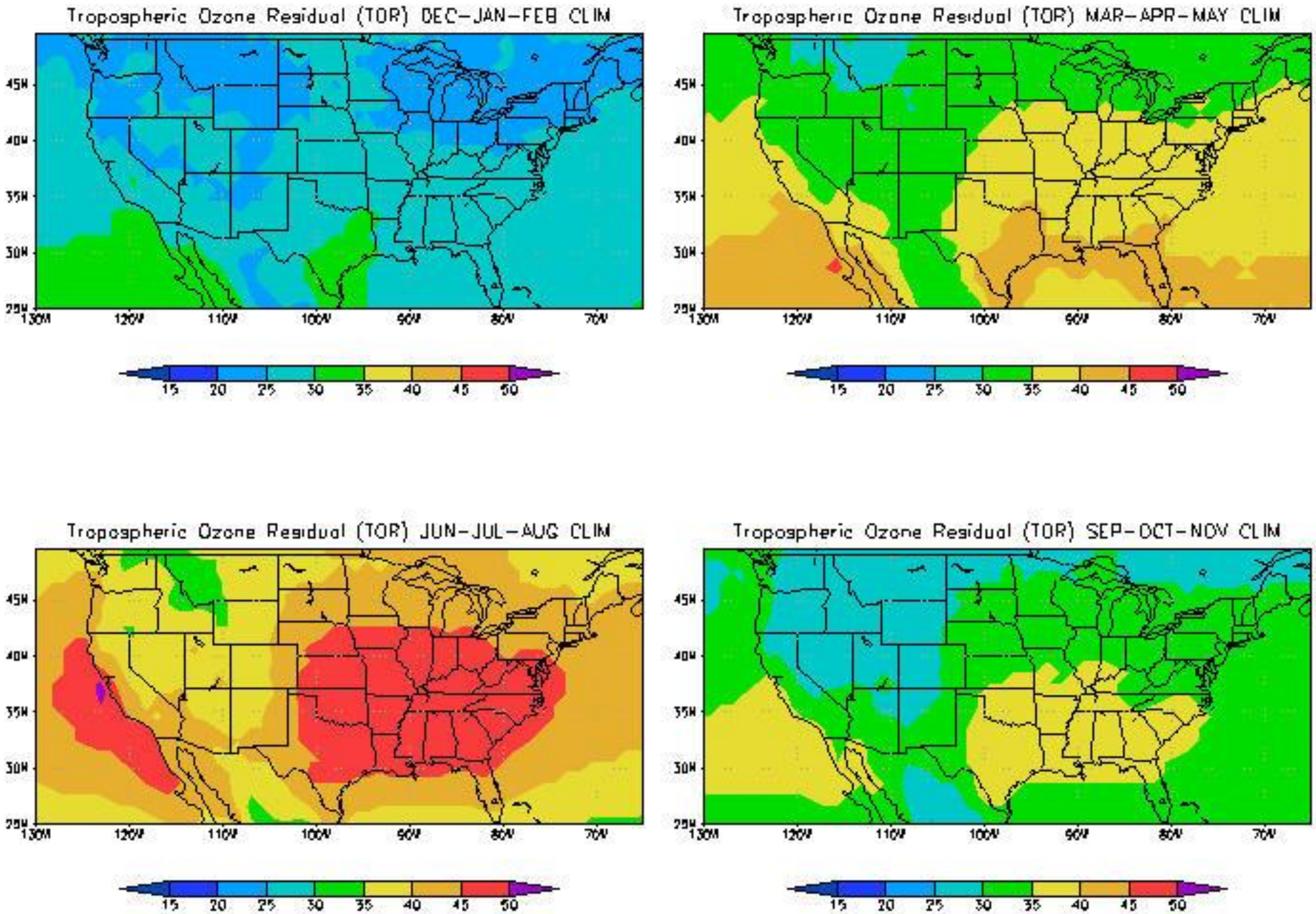
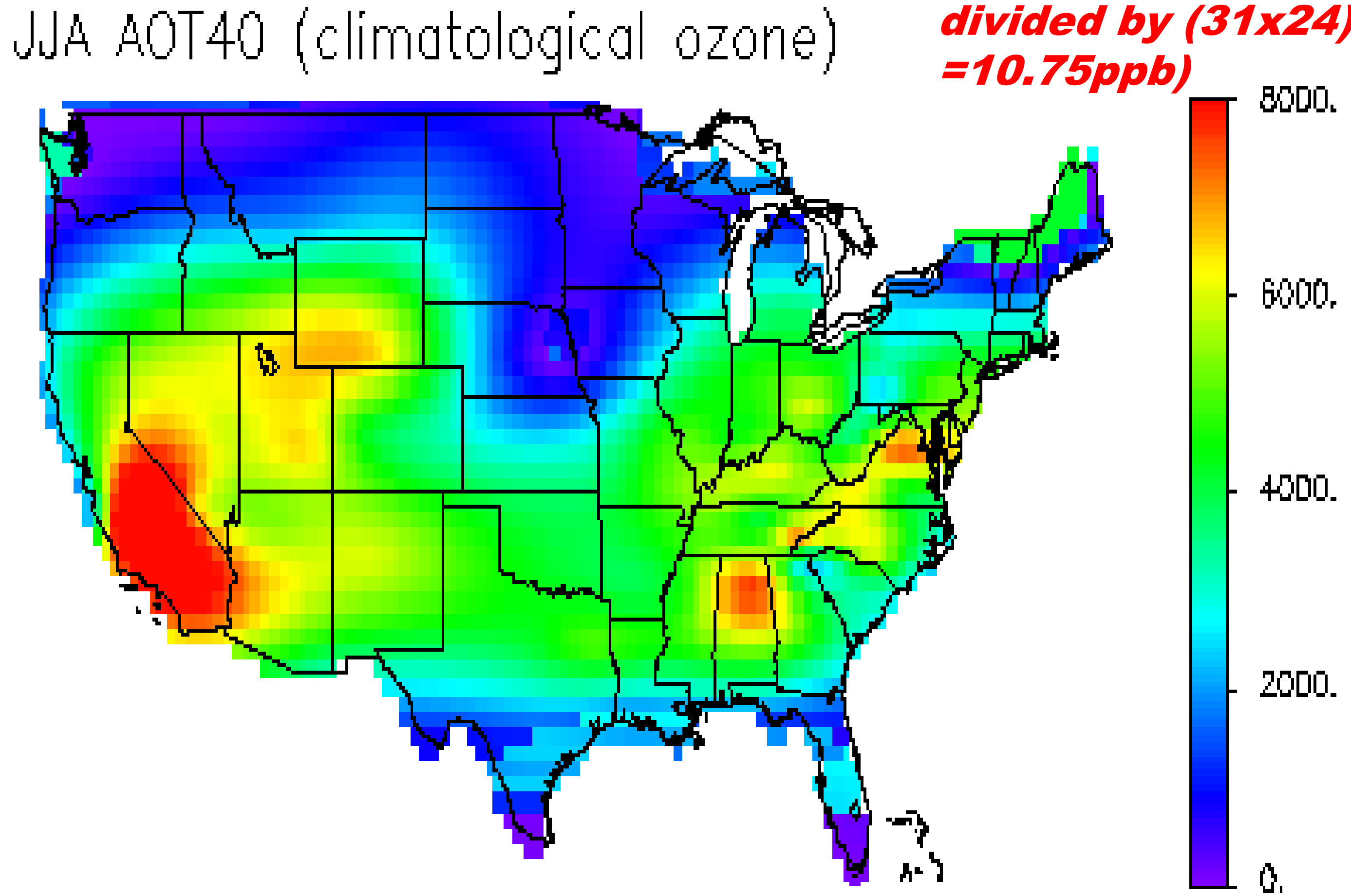
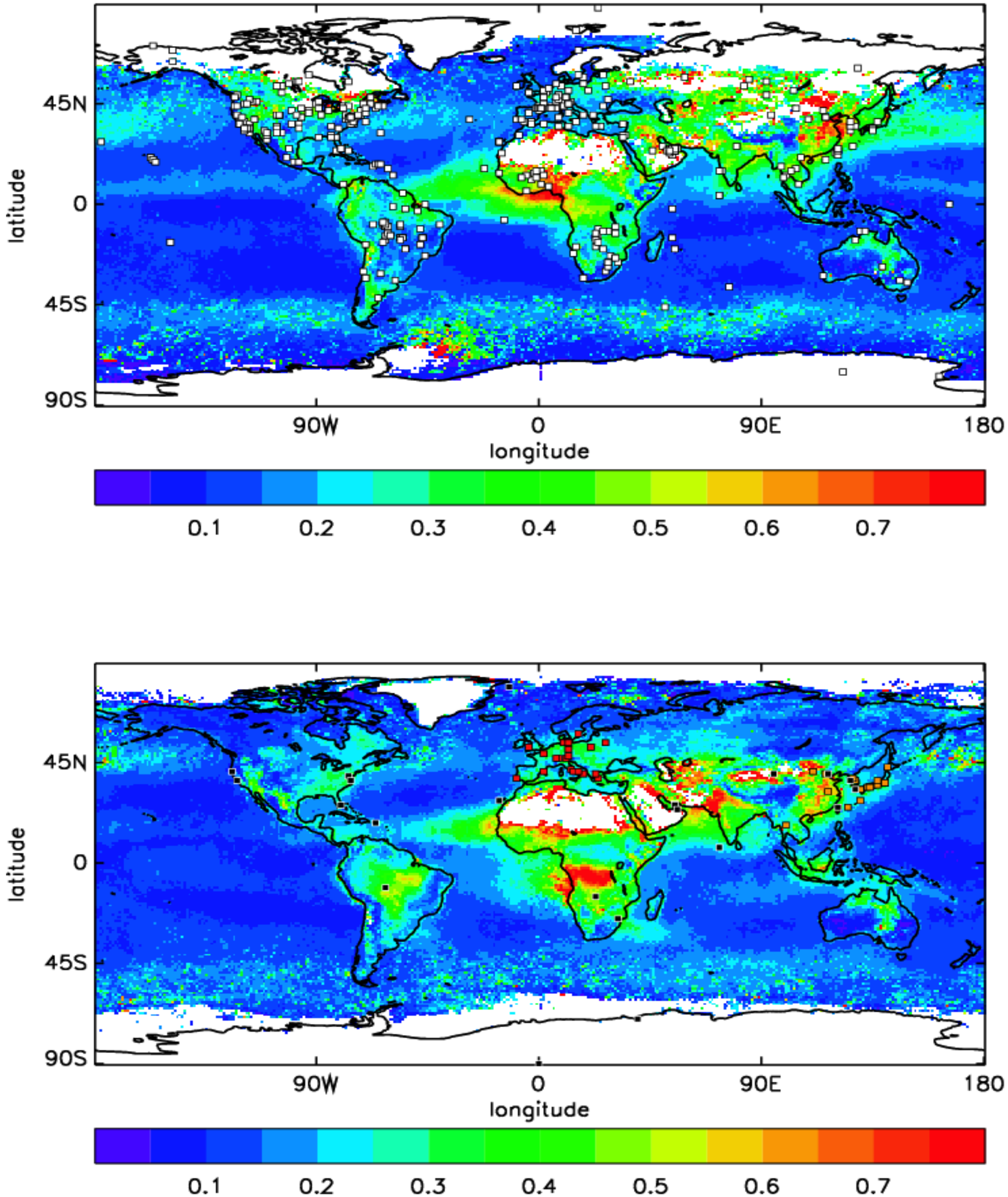


Image courtesy of Fishman, J., A. E. Wozniak, and J. K. Creilson.
From *Atmospheric Chemistry and Physics* 3 (2003): 893–907.

As we will discuss in a later lecture, human health is affected by exposure to ozone expressed here as a function of the AOT40 Index (AOT40 = hourly ozone exposure above 40 ppb in units of ppb.hr/mo.)

NOTE: (8000 ppb.hr/mo divided by (31x24)hr/mo =10.75ppb)





ATMOSPHERIC AEROSOLS

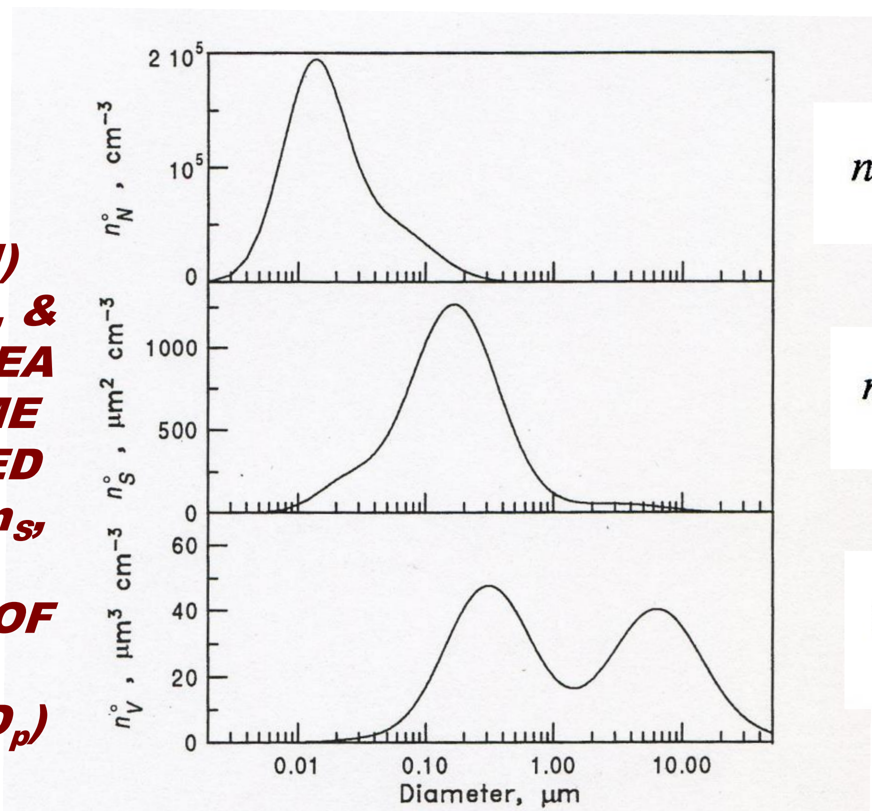
DEFINITION: ALL SUSPENDED LIQUID, SOLID & MIXED LIQUID-SOLID PARTICLES IN AIR EXCEPT WATER DROPLETS & ICE CRYSTALS e.g. BLACK CARBON, SULFATE, ETC.

FIGURES: Aerosol optical depth, τ_{aer}, at 0.55 μm (color bar) as determined by the MODIS satellite instrument for the January to March 2001 mean (top panel) and for August to October 2001 mean (bottom panel). The top panel also shows the location of AERONET sites (white squares) that have been operated (not necessary continuously) since 1996. The bottom panel also shows the location of different aerosol lidar networks (red = EARLINET, orange = ADNET, black = MPLNET). (Ref: IPCC AR4 WG1, Chap. 2, Fig. 2.11, 2007)

TYPICAL URBAN AEROSOL COMPOSITION, ORIGIN (primary, secondary, either) & SHAPE

- Sulfates [H_2SO_4 (aq), $NH_4)_2SO_4$ (aq, s)]
- Black Carbon [C) (s)]
- Organic Carbon [$C_xH_yO_z$ (l, s)]
- Dust [Silicates (s), Clays (s), Pollens (s)]
- Nitrates [HNO_3 (aq), NH_4NO_3) (aq, s)]
- Chlorides [NaCl (aq, s)]
- Mixtures[(H_2SO_4 on BC, OC, dust]
- Spheres (liquids)
- Crystals (ice, salts, minerals)
- Dendriform (snow, soot)

TYPICAL URBAN AEROSOL NUMBER (N) DENSITY (n_n), & SURFACE AREA (S) & VOLUME (V) WEIGHTED DENSITIES (n_S, n_V), AS FUNCTIONS OF PARTICLE DIAMETER (D_p)



$$n_N(D_p) = \frac{dN}{dD_p}$$

$$n_S(D_p) = \pi D_p^2 n_N(D_p)$$

$$n_V(D_p) = \frac{\pi}{6} D_p^3 n_N(D_p)$$

Examining the chemistry and physics of air pollution, we see that air pollution regulations affect climate by increasing CH_4 (warming), decreasing H_2SO_4 aerosols (warming), decreasing O_3 (cooling) and decreasing black carbon aerosols (cooling).