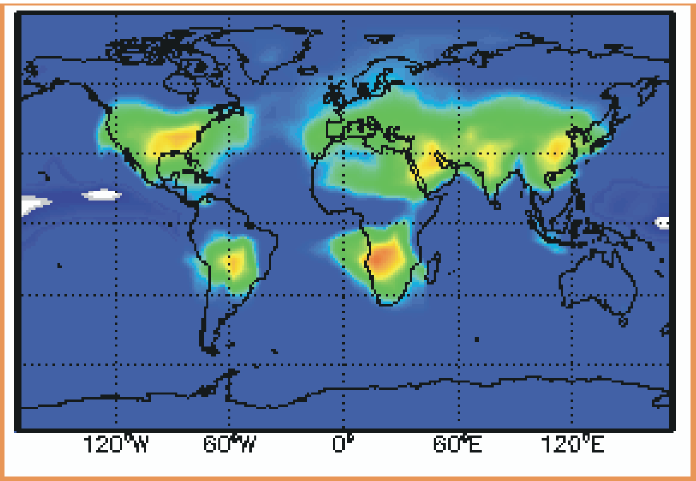

The Photochemistry of Ozone

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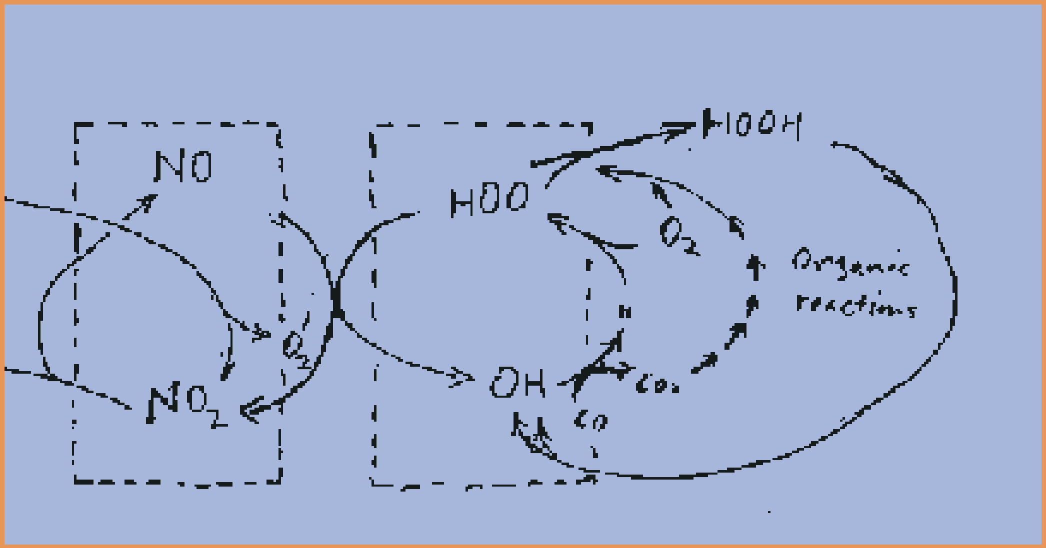
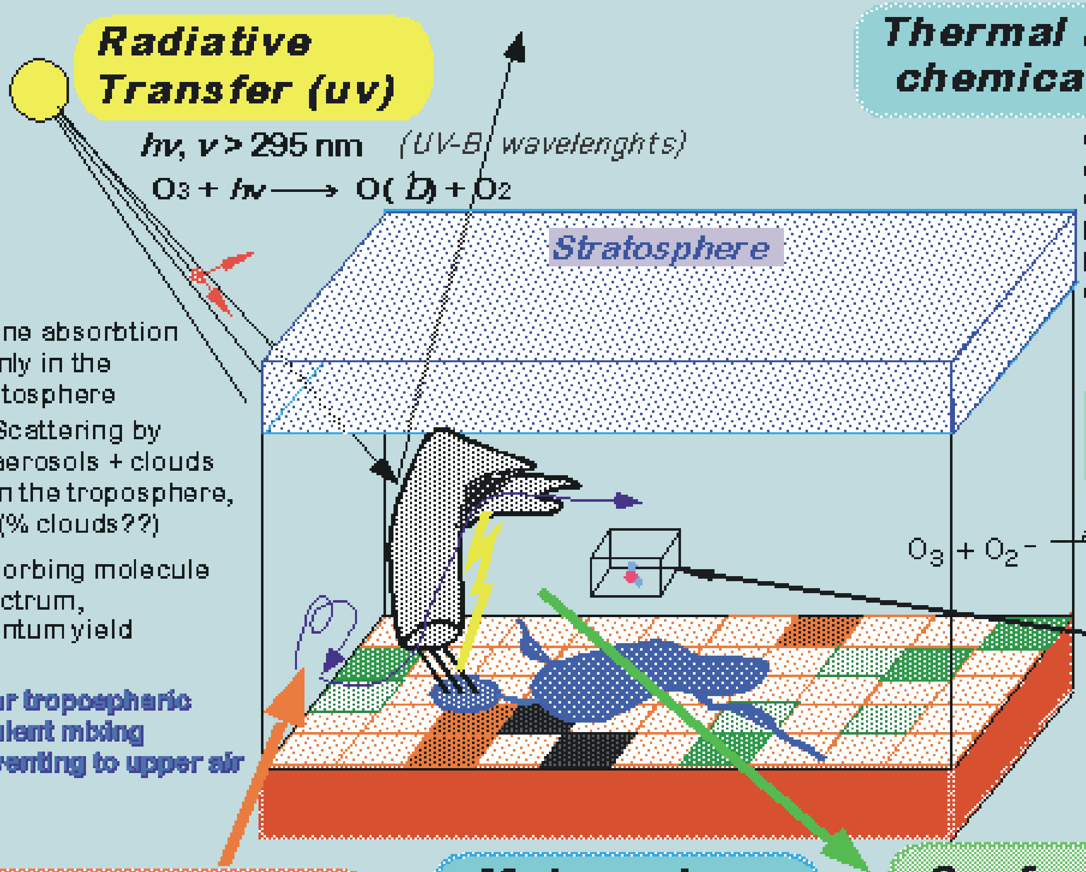


Components of a Photochemical Simulation



Radiative Transfer (uv)

$h\nu$, $\nu > 295$ nm (UV-B wavelenghts)

$O_3 + h\nu \longrightarrow O(^1D) + O_2$

Ozone absorbtion mainly in the stratosphere

Scattering by aerosols + clouds in the troposphere, (% clouds??)

Absorbing molecule spectrum, quantum yield

Lower tropospheric turbulent mixing and venting to upper air

Thermal and Photo-chemical Kinetics

$O(^1D) + H_2O \longrightarrow OH + OH$

$OH + CO \longrightarrow CO_2 + H \quad H +$

$O_2 \longrightarrow HOO$

$HOO + NO \longrightarrow NO_2$

$NO_2 + h\nu \longrightarrow O + NO$

$O + O_2 \longrightarrow O_3$

from lab data

Liquid Phase Ion + Radical Kinetics

$O_3 + O_2^- \xrightarrow{aq} OH + OH^- + 2\,O_2$.

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numerical stiffness
numerical diffusion

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Biogenic: isoprene, soil NO
Anthropogenic: internal combustion
Combined: biomass burning, CH_4

Meteorology

Competition of vertical+horizontal transport processes and transformation
Frequency, timing, and correlation of most vigorous motions

Surface Deposition

Rainout: e.g., acid rain
Dry: e.g., O_3 ox. of plants

Analysis ... understanding

Robert Chatfield NASA / Ames R.C. Earth Science

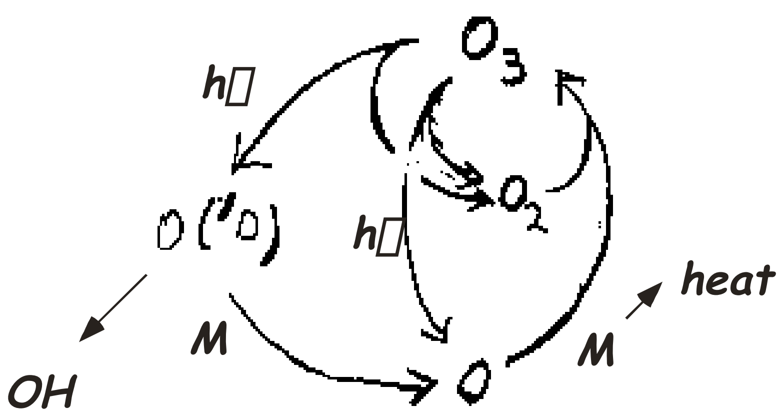
To understand O_3 production chemistry, first ways that chemically reactive oxygen may take

h□
– quantum of radiation

M — any molecule,
M carries off thermal energy

$O(^1D)$ – electronically excited oxygen
…
$O(^1D)$ +H_2O makes 2OH, taking away from the pool

Ox



e.g., heating of stratosphere

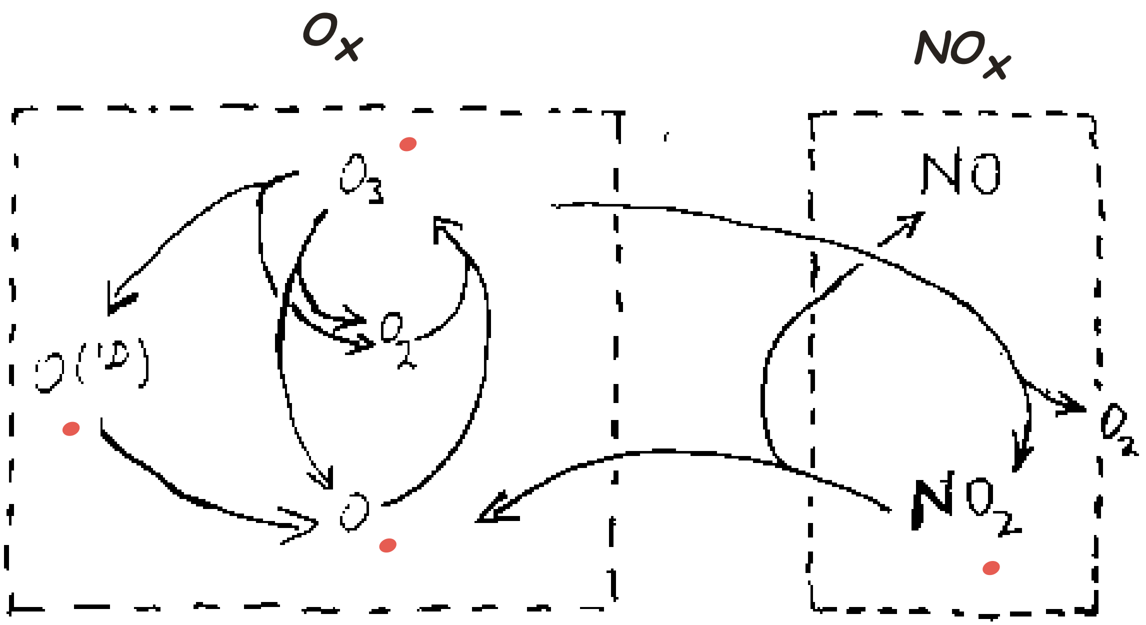
$O_3 \xrightarrow{h\nu} O_2 + O(^1D)$ ~1 da^{-1}

↓ M every few collisions

$O_3 \xrightarrow{h\nu} O_2 + O$ ~0.5 hr^{-1}

$O + O_2 \xrightarrow{M} O_3$ $\overset{<}{\text{fw}}$ 1 sec

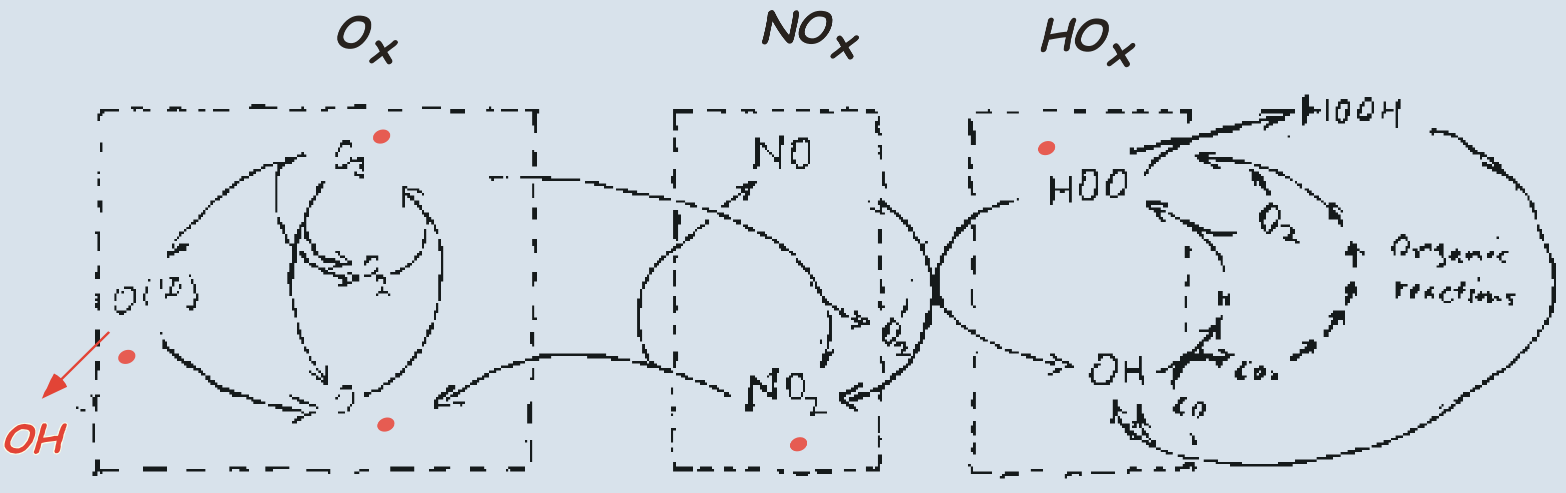
Ox and NOx fields can trade the extra energy



- ● traces the odd oxygen, extra oxidizing power

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$NO_2 \xrightarrow{h\nu} NO + O \qquad \sim 10^3 s$$



● traces the odd oxygen, extra oxidizing power

Note the correspondence between Ozone and OH, the major oxidants, Ozone makes OH locally, OH can add to Ozone over time.

$$\begin{cases} OH + CO \rightarrow H \\ H + O_2 \rightarrow HO_2 \end{cases}$$

fixes new O

$HOO + NO \rightarrow OH + NO_2$

splits the O making [illegible] "odd oxygen"

$HOO + HOO \rightarrow HOOH + O_2$

lower trops: HOOH → [illegible] removed to rain and surface

upper trop: $HOOH \xrightarrow{h\nu} OH + OH$

Summarizing, ...

Tropospheric ozone production depends on two sorts of energy:

Thermal reactions (slow burning or smog reactions) to convert OH to HOO, releasing thermal energy,

and

Photochemical energy, which mostly just keeps the NOx cycle turning and plenty of NO available for HOO ... but doesn't add the vital chemically excited "odd oxygen" as in the stratosphere

Question:

- *Where should ozone production maximize:*

Argue for • lower troposphere ... lots of smog and other organic species emissions.

or

Argue for • upper troposphere, where photolysis is very strong, and many N compounds break down to NO:
$HNO_3 \Rightarrow NO_2 \Rightarrow NO$ *(but some NO is locked away as PAN)*

Kinetic equations for Ozone Production

The analysis begins by considering the production of ozone. In a given well-mixed parcel of air, each additional NO_x molecule from any source produces ozone by speeding these reactions;

(R1) $$HOO^{\bullet} + NO \longrightarrow NO_2 + OH^{\bullet}$$

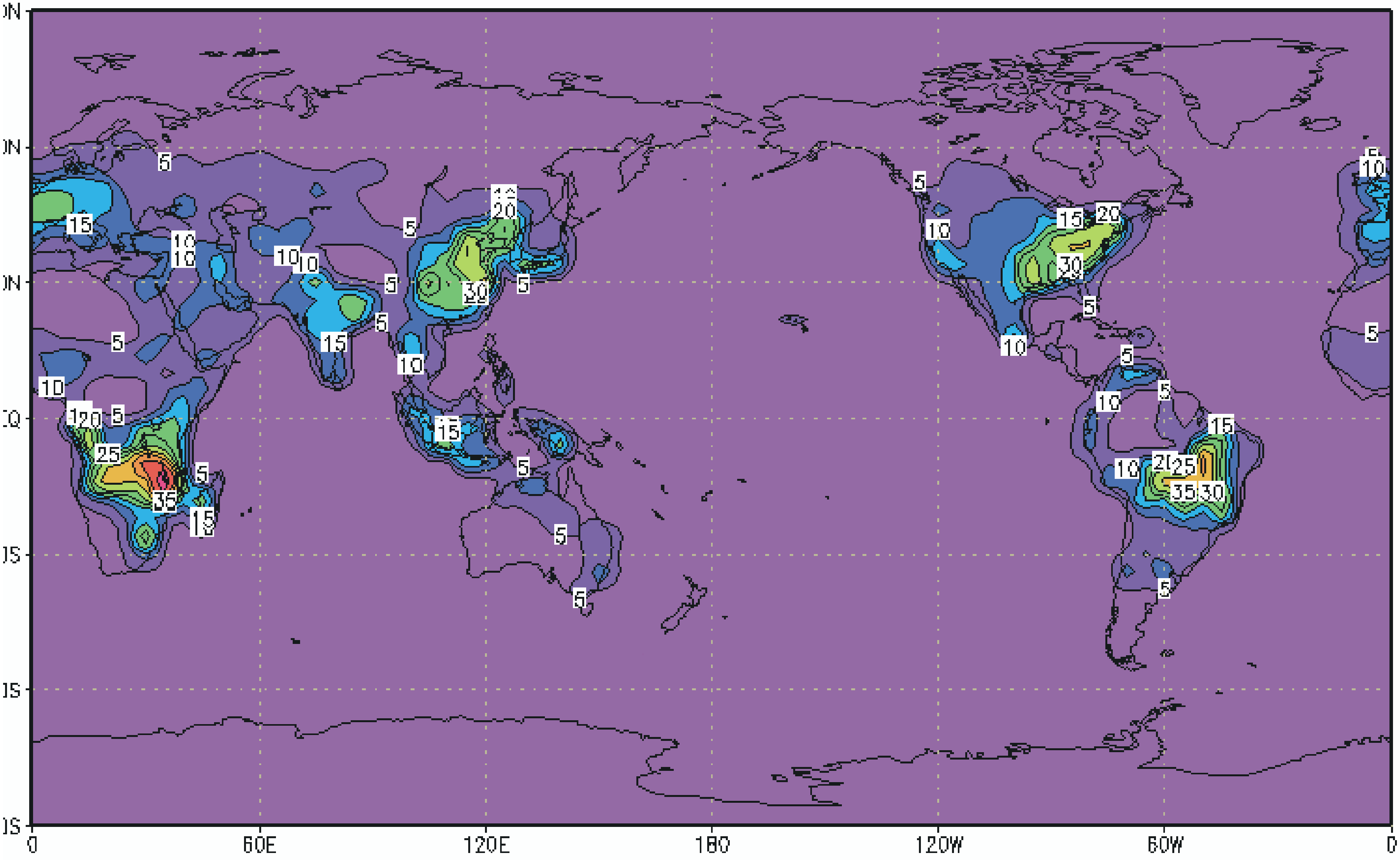
(R2) $$ROO^{\bullet} + NO \longrightarrow NO_2 + \text{various products}$$

(R3) $$NO_2 \xrightarrow{h\nu} NO + O \xrightarrow{O_2} O_3 \,.$$

Since the latter reaction is fast, ozone production is to a very close approximation given as

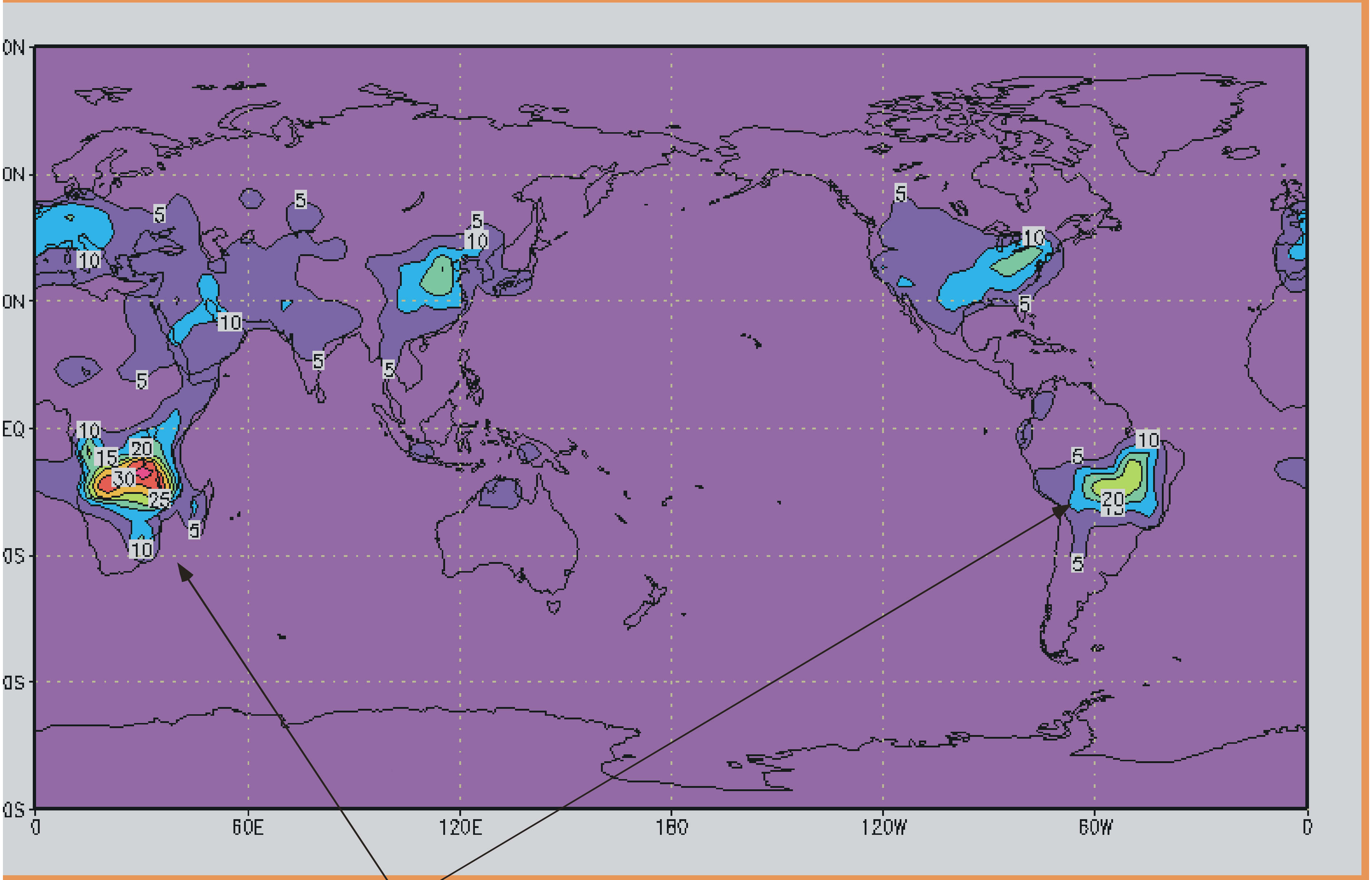
$$k_{HOO,\,NO}[HOO^{\bullet}][NO] + \sum_{R_i} k_{R_iOO,\,NO}[R_i^{\bullet}OO][NO] \,,$$

Production of Ozone, 930 mb, October mean, GEOS-CHEM model



Harvard GEOS-Chem Web pages

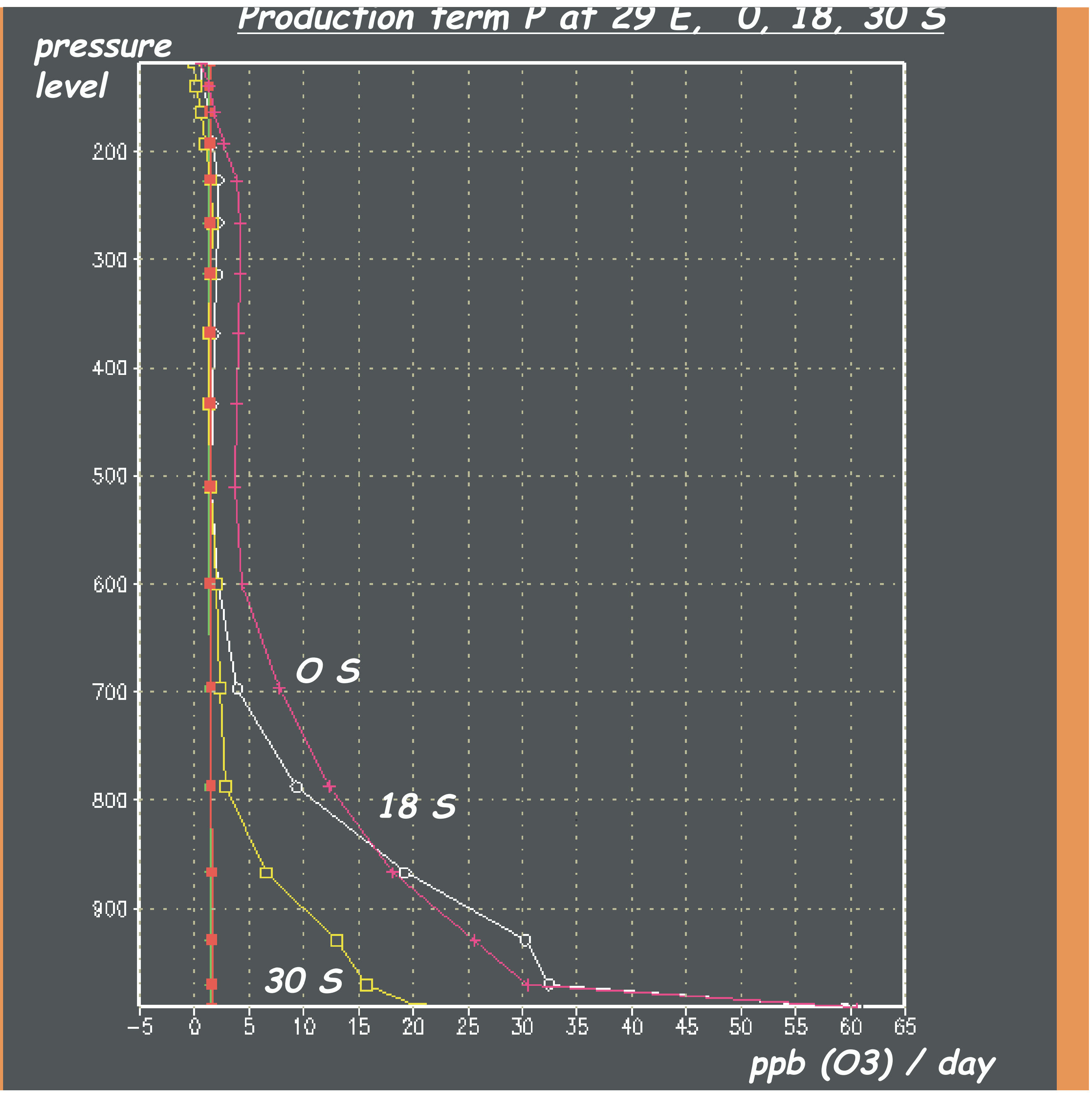
Production of Ozone, 867 mb, October mean, GEOS-CHEM model



Areas with high mixing layers and (burning) pollution

Biomass Pollution
in a deeper
layer

Industrial Pollution
near surface



Ozone Loss:

Total loss rates tend to maximize where O_3 is high:

for O_3 + HOO this is obvious, loss ~ k $[HOO][O_3]$

for $O(^1D) + H_2O$, recall that $O(^1D) \sim O_3$, so

loss ~ k $[H_2O]$ {factor ~O_3}

Both production and loss depend strongly on UV light levels

So we write, total loss ~ $L[O_3]$ and we write a linearized equation

$$d [O_3] / dt = P - L[O_3]$$

and we call L a first-order loss rate coefficient

and L^{-1} a loss time-scale

L tends to be high in two kinds of areas, those areas with

- high light and H_2O

and

- high general smog activity (high HOO <=> OH cycling)

Efficiency at dilution. Beyond this linear influence, an important process is the relatively efficient production of tropospheric ozone per NO_x molecule that occurs at low NO_x concentrations [see *Liu et al.*, 1987; *Lin et al.*, 1988]. As NO_x is added to the system, the ozone-producing channel for $HOO^\bullet$ and $ROO^\bullet$ is progressively favored with with respect to these reactions

(R4) $HOO^\bullet + O_3 \longrightarrow OH^\bullet + O_2$

(R5) $HOO^\bullet + HOO^\bullet \longrightarrow HOOH$

(R6) $ROO^\bullet + HOO^\bullet \longrightarrow ROOH + \text{other products}$

which produce no ozone and may destroy it. In fact, the reactions

$$HOO^\bullet + O_3 \longrightarrow OH^\bullet + O_2$$

and

(R7) $O_3 \xrightarrow{h\nu} O(^1D) + O_2$

(R8) $O(^1D) + H_2O \longrightarrow 2\,OH^\bullet$

play almost equal roles in the destruction of ozone in these simulations. Each added molecule of NO_x tends to increase the rates (R1,R2 above in a linear manner with the increase of NO. At the same time, however, each additional NO_x molecule has three other effects. It may tend to decrease the factor $[HOO^\bullet]$ as the increasing $HOO^\bullet$ + NO rate provides a sink for $HOO^\bullet$ in addition to the sink provide by O_3. (The same occurs for the organic peroxy radicals.) In fact, for the conditions of CO, hydrocarbons, and photolysis we describe, this does occur in the range from 0.3 to 3 ppb.

Duties of a good photochemical reaction mechanism, for urban/fire-plume smog and free troposphere applications:

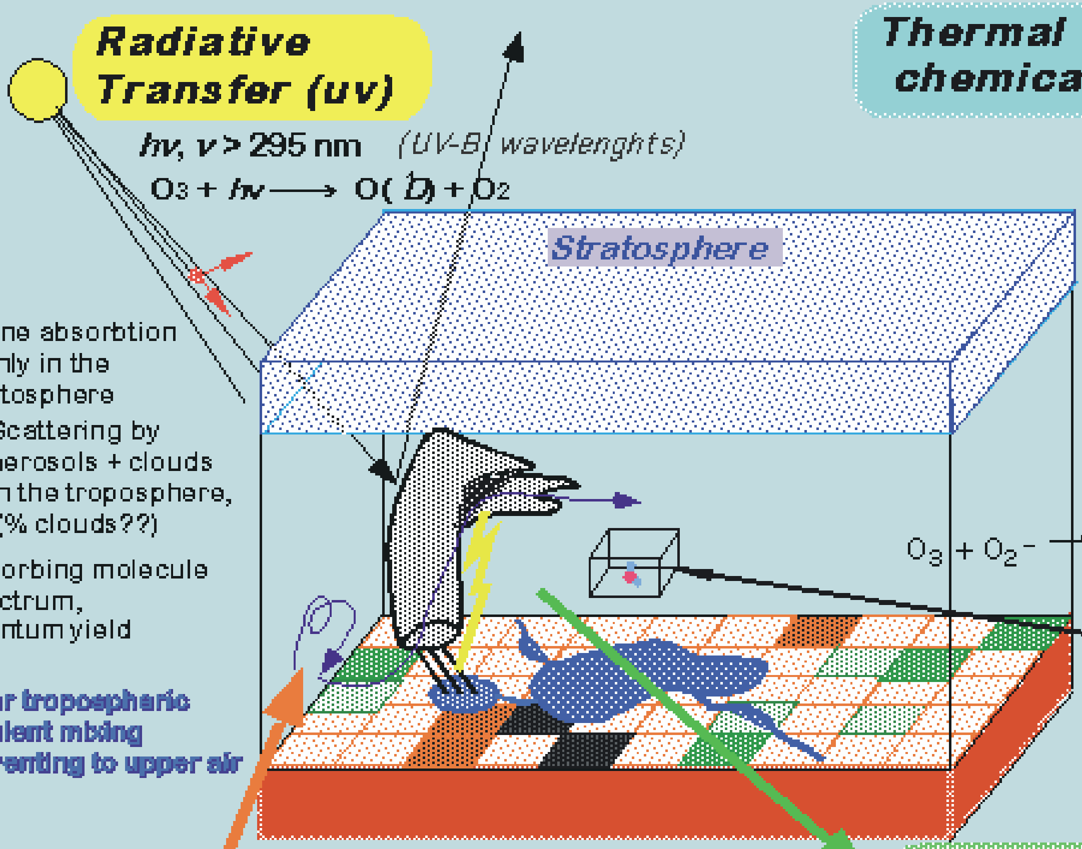
- Supply conversion reactions of OH => HOO and ROO
  at a correct rate through hours and days after emission
  so that HOO + NO are making ozone at the right time
  - Convert the large carbon chains of emitted compounds into
    simpler compounds so that both the mass of carbon "fuel"
    and the production of HOO, ROO are approximately correct

- Have the correct amount of NO_x available and NO, so that
  HOO+NO, ROO+NO are correct
  - Compounds which store and then release NO, such as PAN, i.e.,
    $CH_3(C=O)OONO_2$, should do their job
  - $OH+NO_2$ and other reactions that tend to take NO_x out of the
    system should occur in time with HOO+NO (O_3 production) reactions

- HOO + ROO and ROO + ROO self reactions should be correct
  at all temperatures and pressures (not just surface conditions)

Favorite mechanisms: SAPRAC (smog), RACM 2/Stockwell, Harvard / Bey etc.

Components of a Photochemical Simulation



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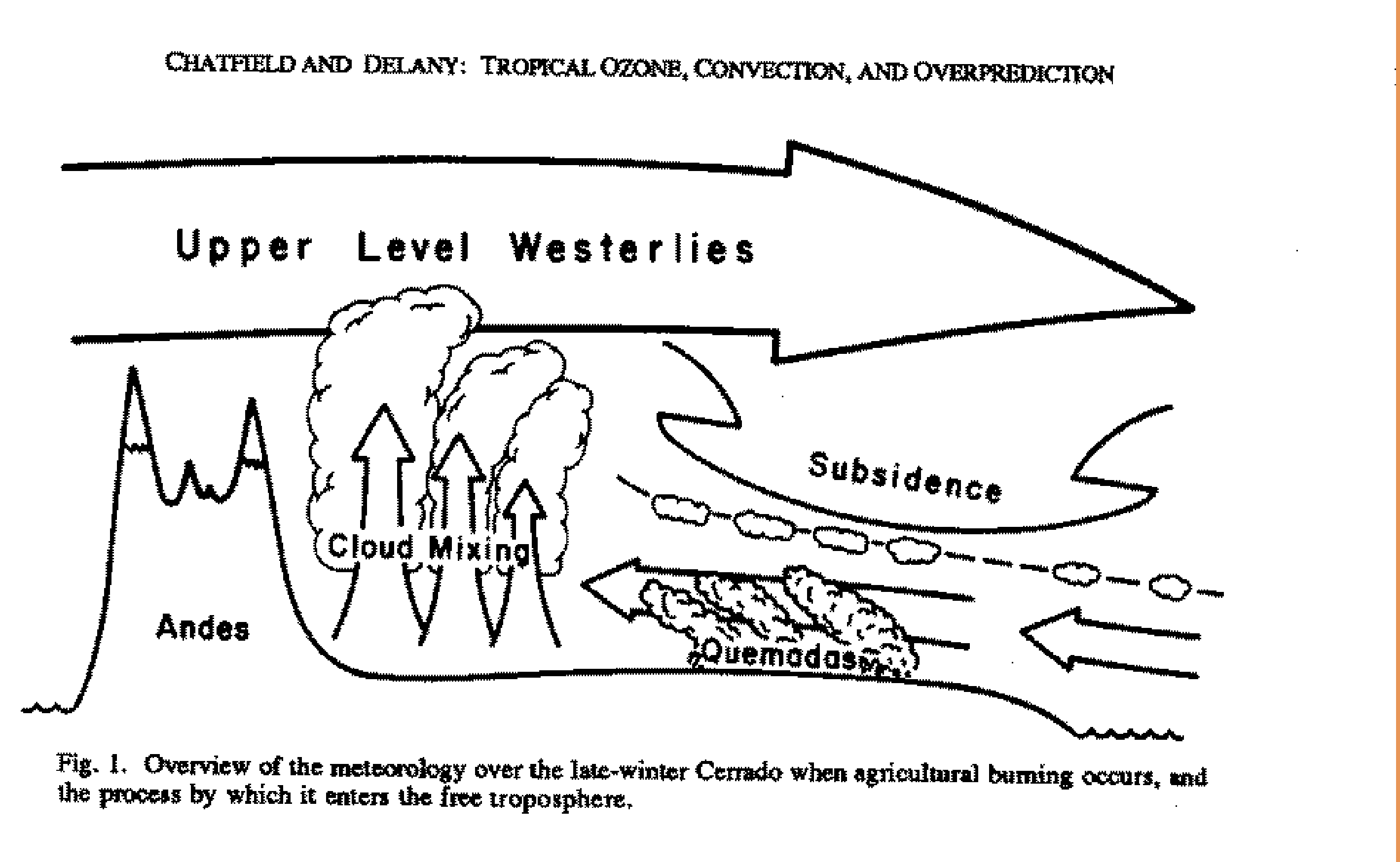
Analysis ... understanding

Robert Chatfield NASA / Ames R.C. Earth Science

An example of tropospheric chemistry



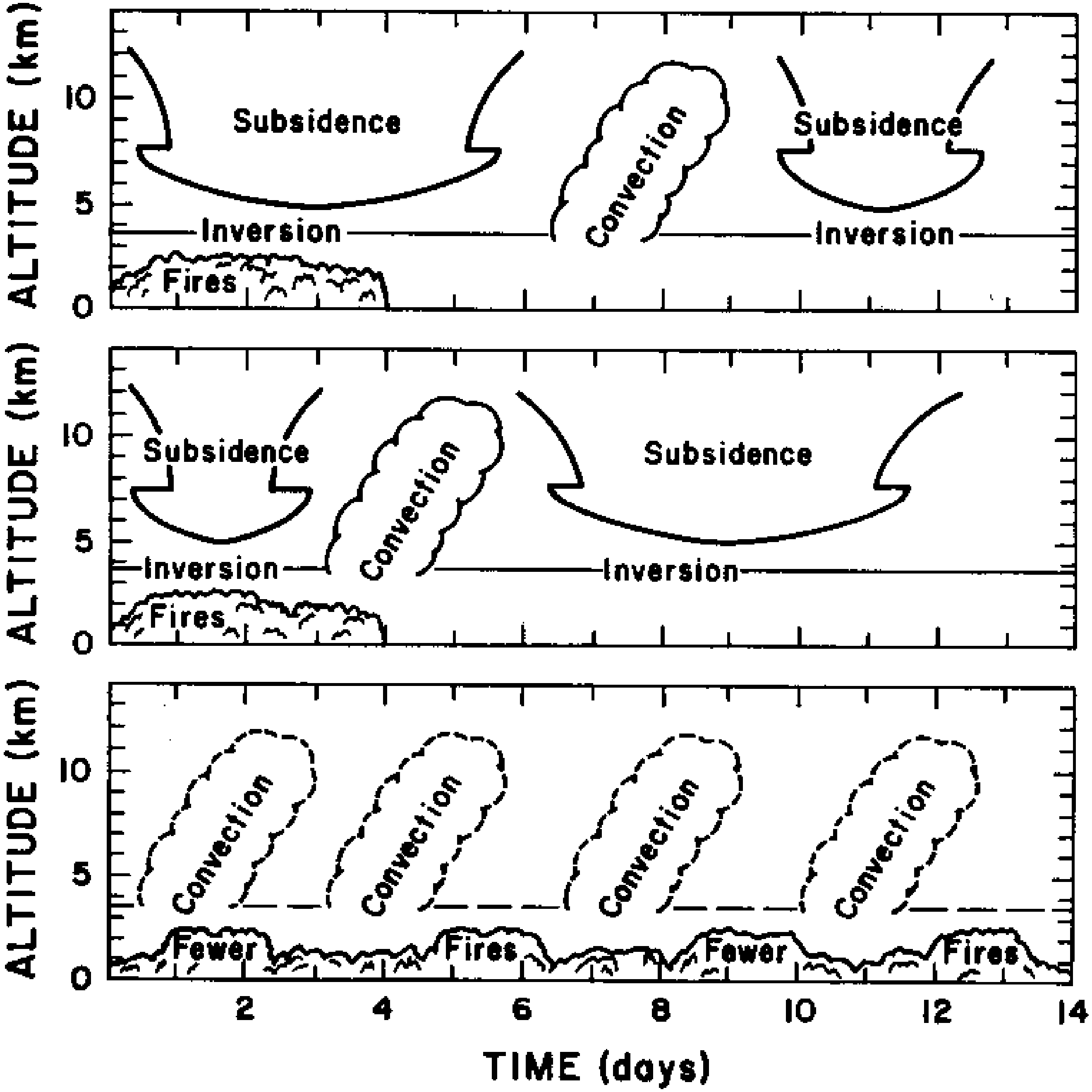
CHATFIELD AND DELANY: TROPICAL OZONE, CONVECTION, AND OVERPREDICTION

Fig. 1. Overview of the meteorology over the late-winter Cerrado when agricultural burning occurs, and the process by which it enters the free troposphere.

Cook, then Mix

Mix, then Cook

The Stir-Fry Error



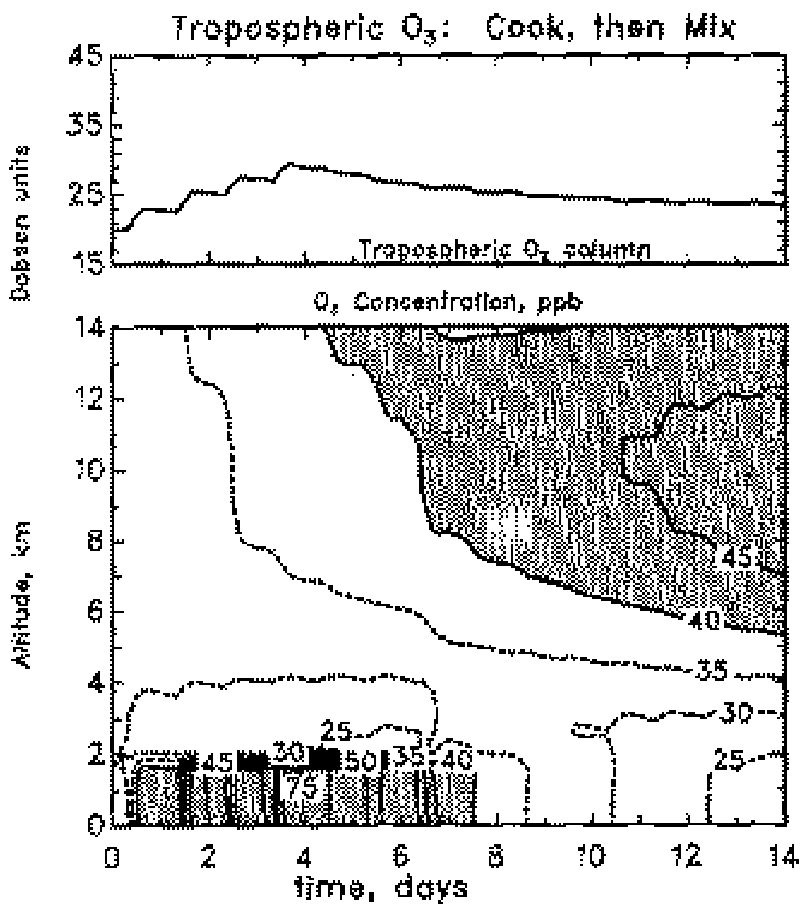


Fig. 4. Vertical distribution of ozone (ppbv) and ozone column (Dobson units) for the troposphere in the cook-then-mix simulation . Note that the most common process for the tropospheric ozone column is slow decay except when fresh nitrogen oxides, mostly HNO_3 which is not rained out, enter the system, at day 7. Relatively little ozone is made.

Cook, then Mix

Mix, then Cook

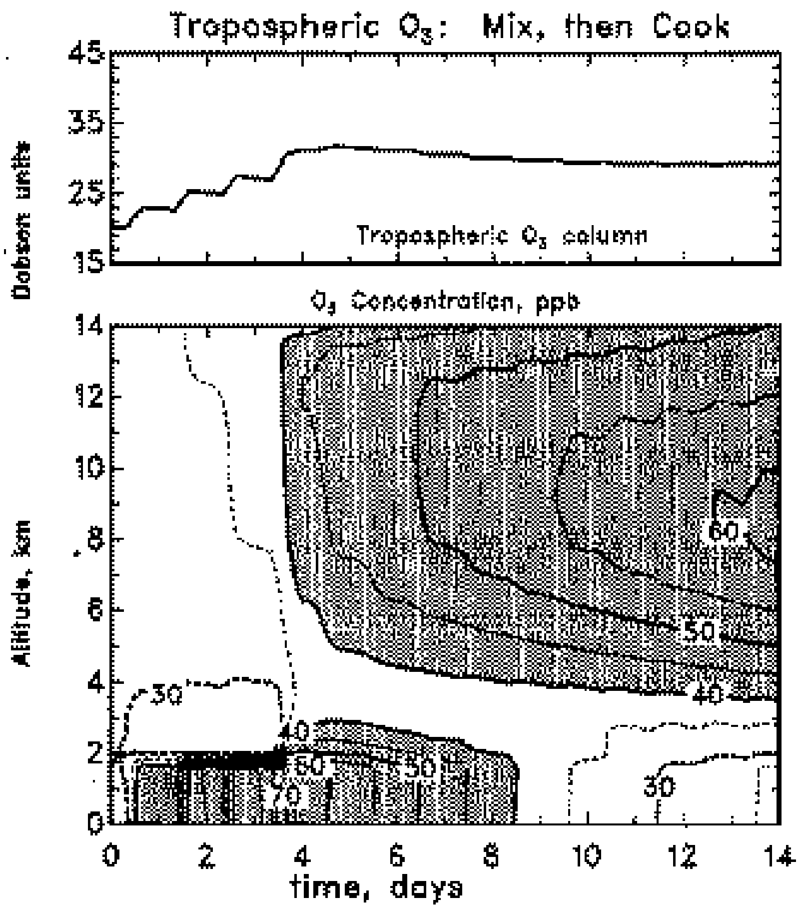


Fig. 5. Vertical distribution of ozone and ozone column for the troposphere in the mix-then-cook simulation. Note that the ozone column does not change during mixing, but does increase rapidly for one or two days, as the injected NO_x is converted to HNO_3. Tropospheric ozone then continues to be produced at a slower rate in the middle and upper troposphere, as HNO_3 reconverts to NO_x, again catalyzing ozone production. The same behavior is recognizable to some extent in Figure 4, but there midtropospheric ozone production is overwhelmed by lower tropospheric destruction in determining the column. In this case, there is net column ozone increase to values as high or higher than observed in the mean over the burning-influenced tropics.

- Reasons why Mix-then-Cook makes more ozone:

Vertical mixing: NO is favored away from the surface:

- NO_2, HNO_3 are strongly removed at Earth's surfaces, ~1 cm/s
- removing these favors a system with more N compounds including NO
- HNO_3 also tends to break down by photolysis to NO_2 and NO,
  and to be harder to re-form
- NO_2 also breaks down to make NO and is harder to re-form

Horizontal Mixing: "Efficiency at Dilution"

The toal no. of O_3 molecules also increases if not O_3 highest concentration

- Mixing out NO into a larger volume allows several "non-linear" chemical effects:

recall $HOO + NO \Rightarrow OH + NO_2$

makes both ozone and OH

(a) more NO => less HOO by the HOO+NO reaction itself
(Le Chatelier effect)

(b) more NO => more OH, but $OH + NO_2$ destroys the NO_x (and NO)

(c) more O_3 can drive N species to more oxidized states, making it more likely that they are removed to nitric acid, HNO_3 or to HNO_4:

$NO \Rightarrow NO_2 \Rightarrow NO_3 \Rightarrow\Rightarrow N_2O_5 \Rightarrow HNO_3 \Rightarrow$ particles, rain

The Stir-Fry Error

probably has both

vertical mixing

and

efficiency at dilution

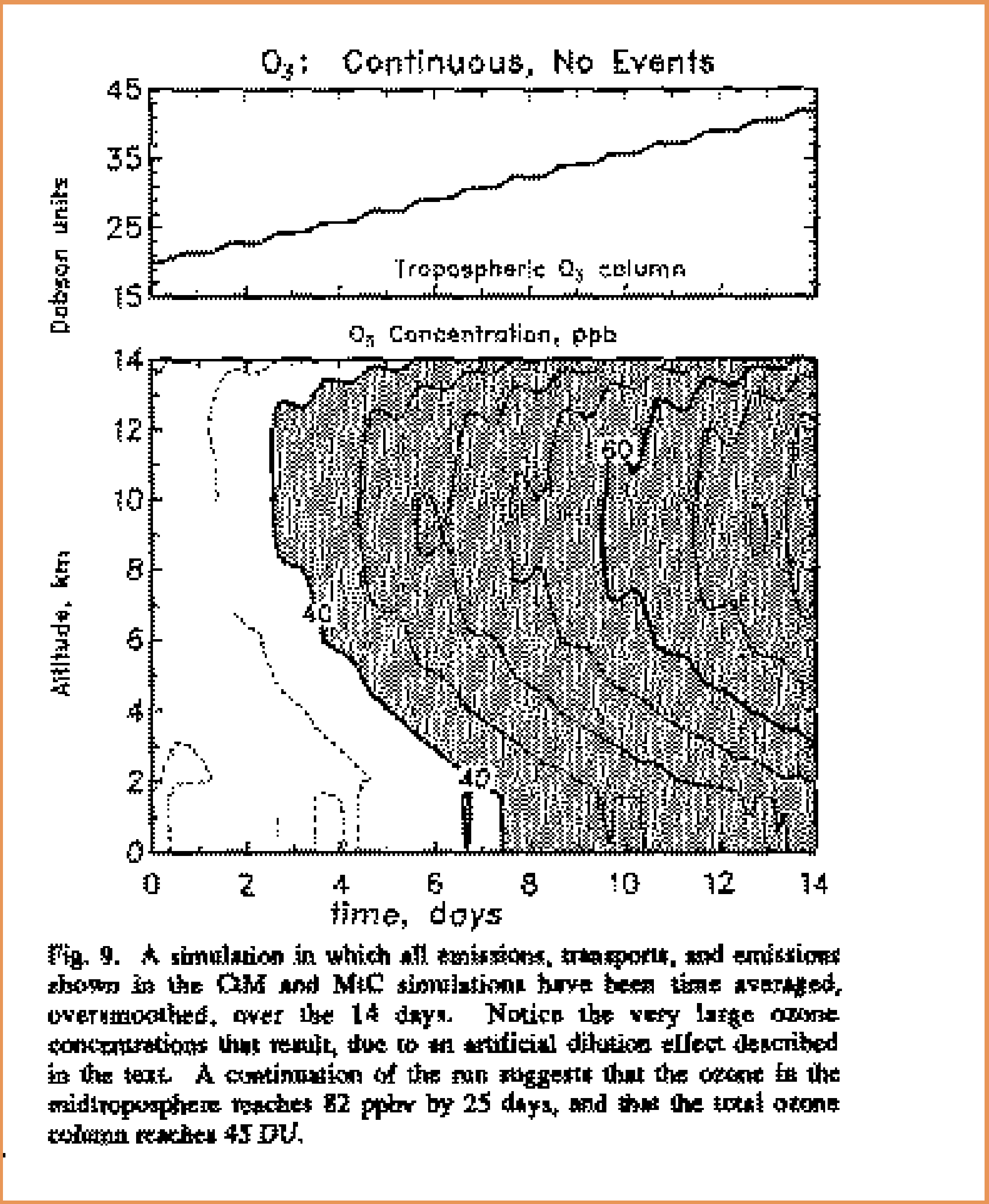
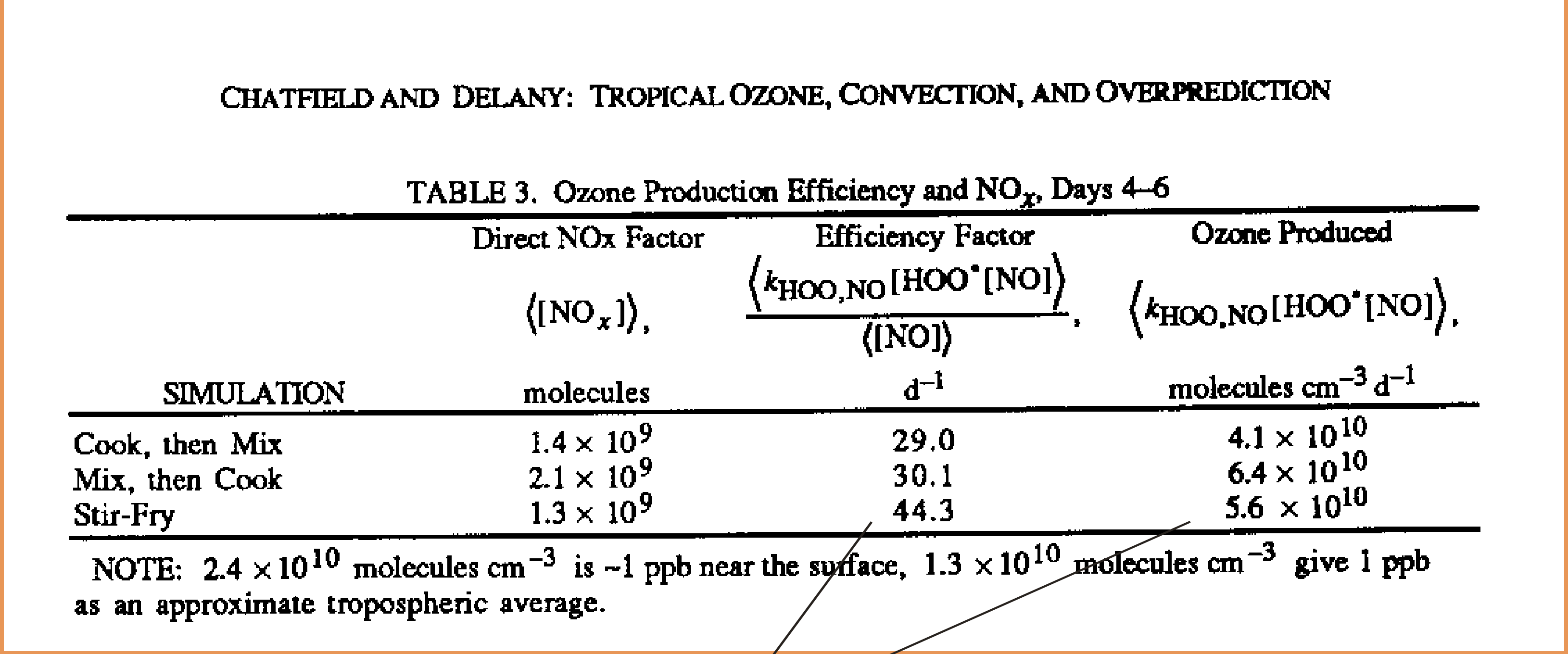


Fig. 9. A simulation in which all emissions, transports, and emissions shown in the CtM and MtC simulations have been time averaged, oversmoothed, over the 14 days. Notice the very large ozone concentrations that result, due to an artificial dilution effect described in the text. A continuation of the run suggests that the ozone in the midtroposphere reaches 82 ppbv by 25 days, and that the total ozone column reaches 45 DU.



CHATFIELD AND DELANY: TROPICAL OZONE, CONVECTION, AND OVERPREDICTION

TABLE 3. Ozone Production Efficiency and NO_x, Days 4–6

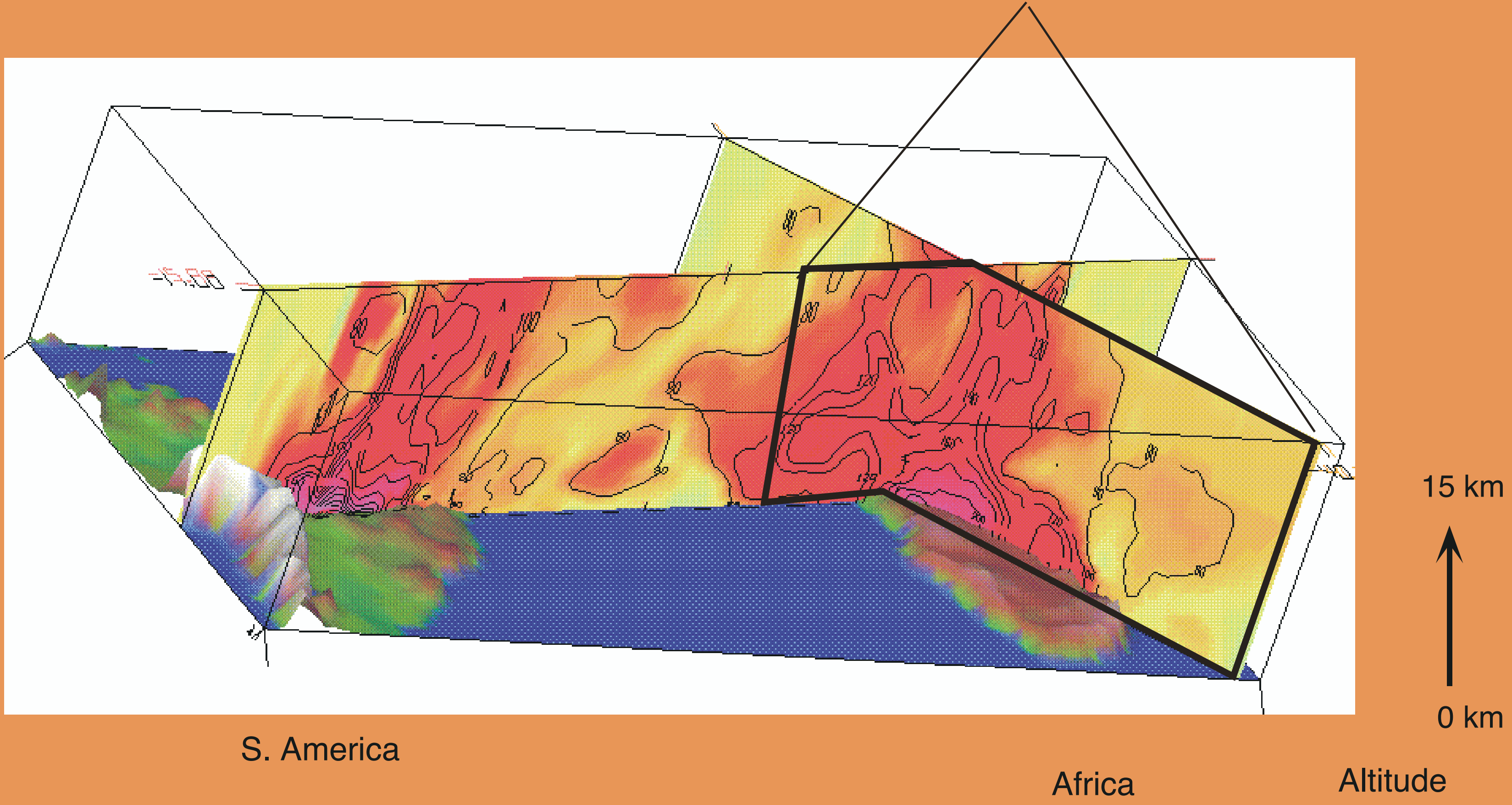
SIMULATION	Direct NOx Factor $\langle [NO_x] \rangle$, molecules	Efficiency Factor $\frac{\langle k_{HOO,NO}[HOO^\bullet][NO] \rangle}{\langle [NO] \rangle}$, d^{-1}	Ozone Produced $\langle k_{HOO,NO}[HOO^\bullet][NO] \rangle$, molecules cm^{-3} d^{-1}
Cook, then Mix	1.4×10^9	29.0	4.1×10^{10}
Mix, then Cook	2.1×10^9	30.1	6.4×10^{10}
Stir-Fry	1.3×10^9	44.3	5.6×10^{10}

NOTE: 2.4×10^{10} molecules cm^{-3} is ~1 ppb near the surface, 1.3×10^{10} molecules cm^{-3} give 1 ppb as an approximate tropospheric average.

The Stir-Fry Error budget

Note that broadly dispersed NO sources, e.g., soil emission, lightning can add to ozone beyond what their simple source strength would suggest, 3 Tg (N) / year can be quite significant

Note that it is easy to make modeling errors which put N where it's not really present. This can make for large simulation errors.



Make an idealized model of this flow in detail

Figure 2

- *A simplified conceptual model useful to explain vertical mixing and transport*

Chatfield et al., 1996
NASA program 579-24-13-10

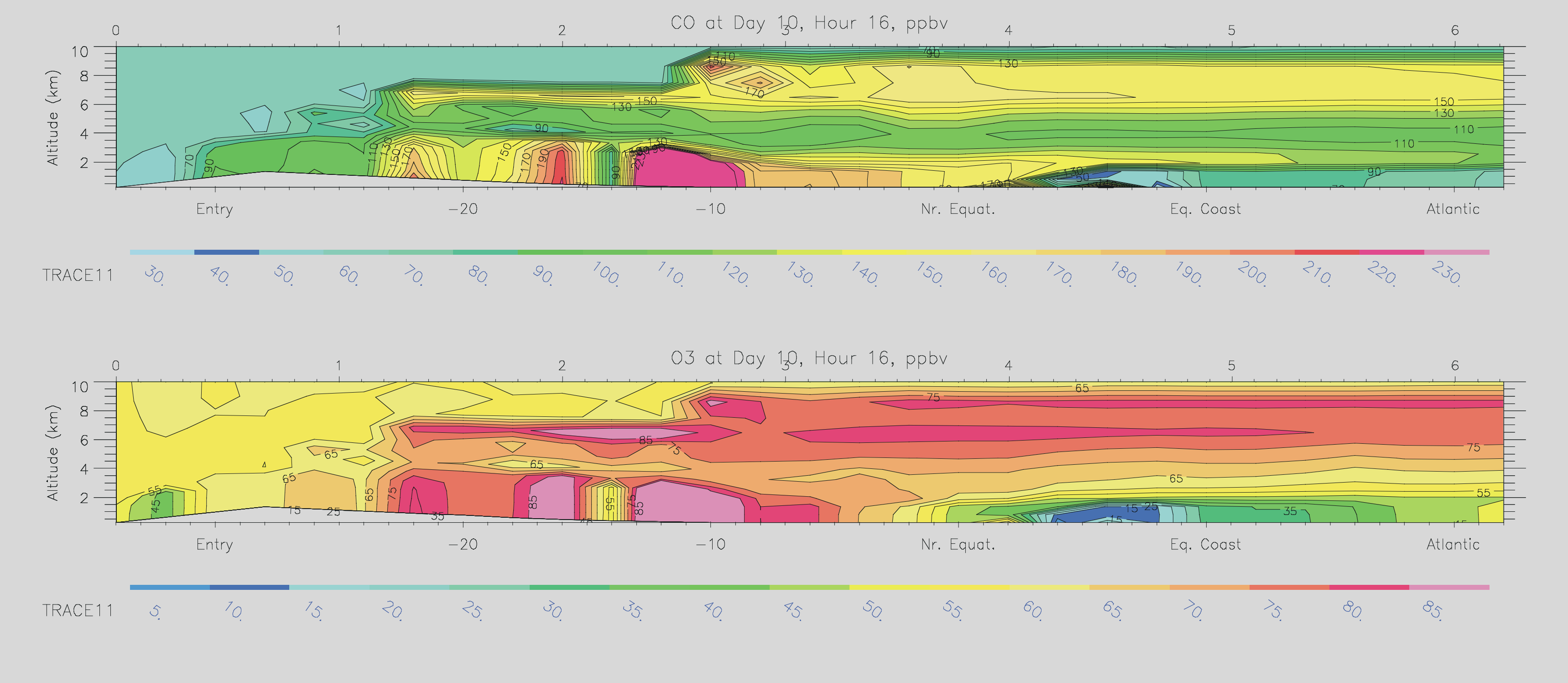
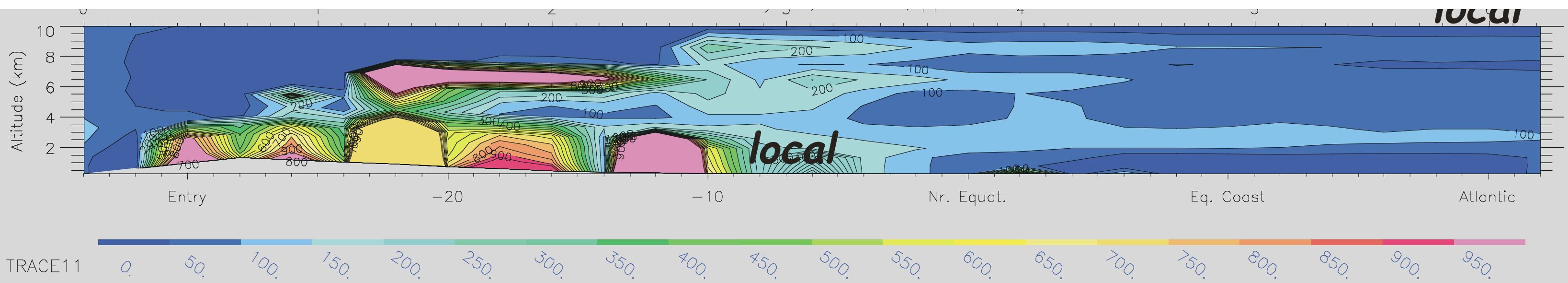


Figure 7

The vertical expression of the tropospheric plume depends on the compound described:

- ***some compounds follow emission nearly molecule-for-molecule***
- ***some compounds are removed by upward transport in raining clouds***
- ***some compounds are preferentially produced or preserved in the upper troposphere***

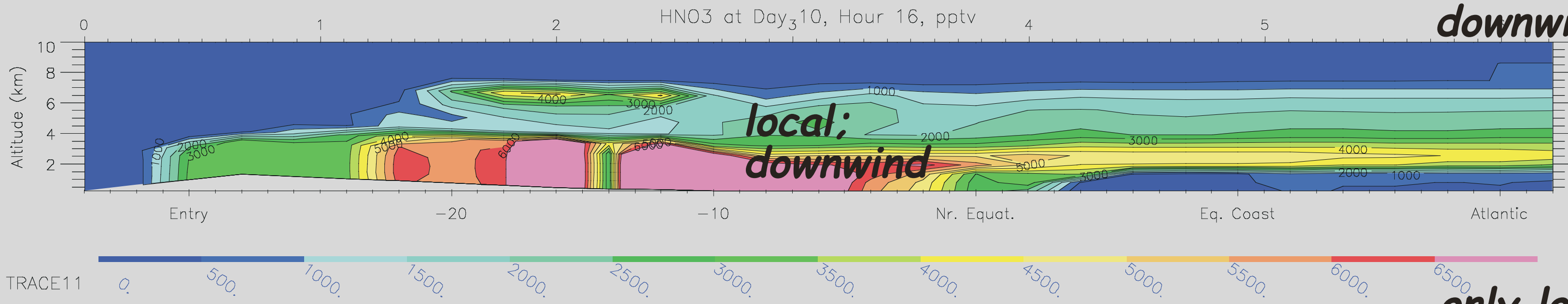


local

local

local;
downwind

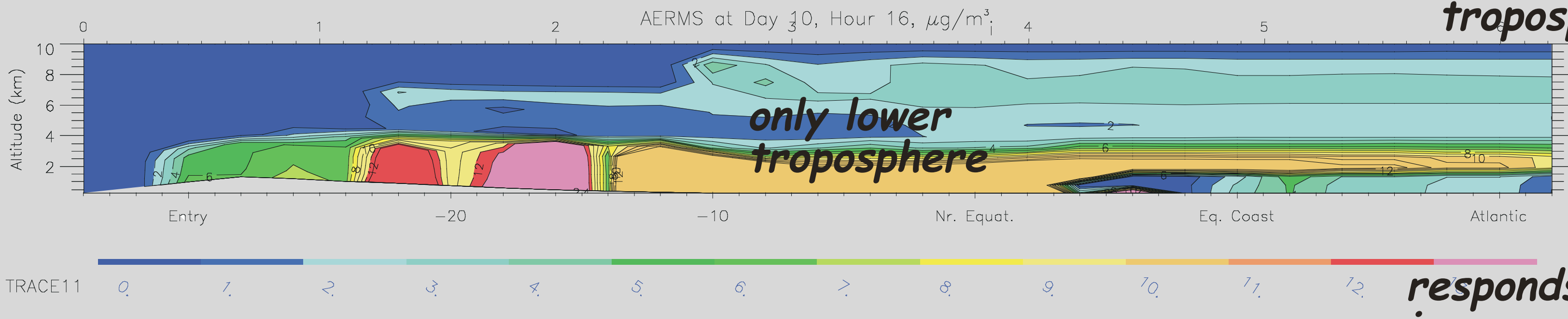
HNO3 at Day 10, Hour 16, pptv



local;
downwind

only lower
troposphere

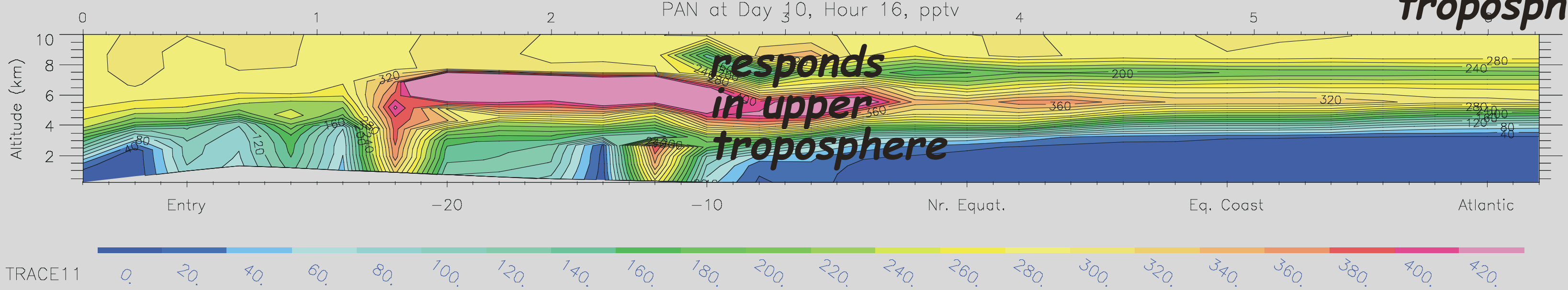
AERMS at Day 10, Hour 16, $\mu g/m^3$



only lower
troposphere

responds
in upper
troposphere

PAN at Day 10, Hour 16, pptv



responds
in upper
troposphere

Questions remaining about O_3 chemistry:

- The NOx goes away quickly and net production stops, or does it
- Aerosol and cloud removal of ozone is not very significant;

  ...why does O_3 disappear so rapidly below Stratocumulus base?
- Why does not South Asia produce more O_3?

  ... Indonesia in big burning years...

  Why not North Africa in burning season

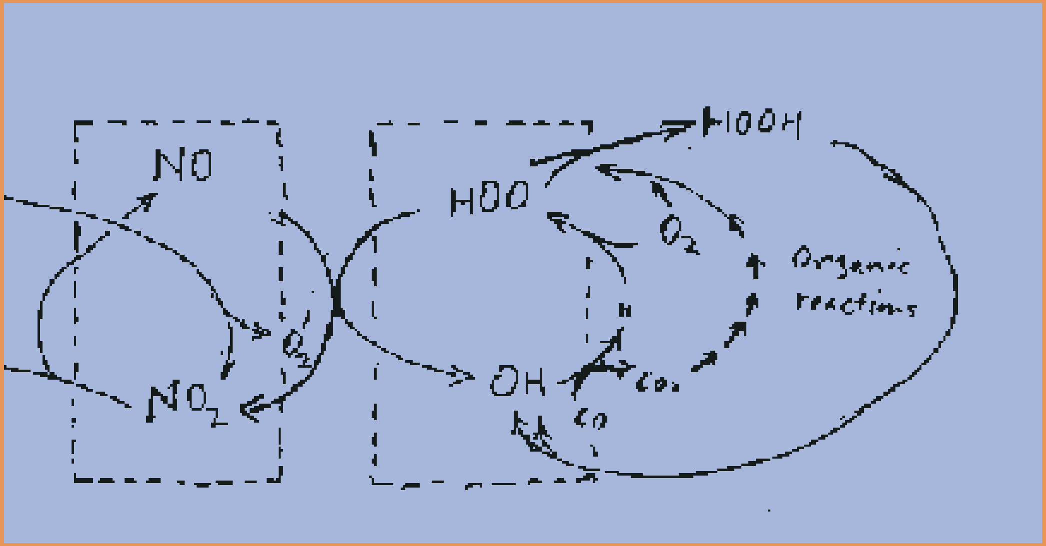
  (North Africa does? ... aircraft measurements, Martin)

NOx -> dust and smoke aerosol? (Carmichael and colleagues)

- How can we tell lightning-induced ozone from stratospheric ozone?

- Slow & potent chemistry of the upper troposphere:
  more questions about fate of NOx
  (NOx -> ice? HO_2NO_2=> aerosol? PEM-West Mission papers)
- Source of HOO and ROO radicals? SONEX data analysis
  in N. Atlantic had to posit “unknown organic sources” of radicals
  (Jaegle and Jacob, Faloona et al. studies). Measurements of OH
  and HOO self consistent, but too low.

  One favorite idea: certain organic compounds are frequent
  in the upper troposphere, but difficult to measure.



Summary:

- Ozone is just one member of several families of “odd oxygen” with extra chemical energy
- In the troposphere, thermal reactions (slow burning) creates new odd oxygen, but photolysis reactions, and NO, are needed to make the creation process work.

- Production and Loss of ozone are strongly connected in space
- The upper troposphere has slow ozone production rates, but over time can reach very high levels

- Questions: is there continuing plume production of ozone?
  what happens to NOx near sources (dust?)?
  where does it come from further away?

Do we understand O_3 destruction beneath stratocumulus decks