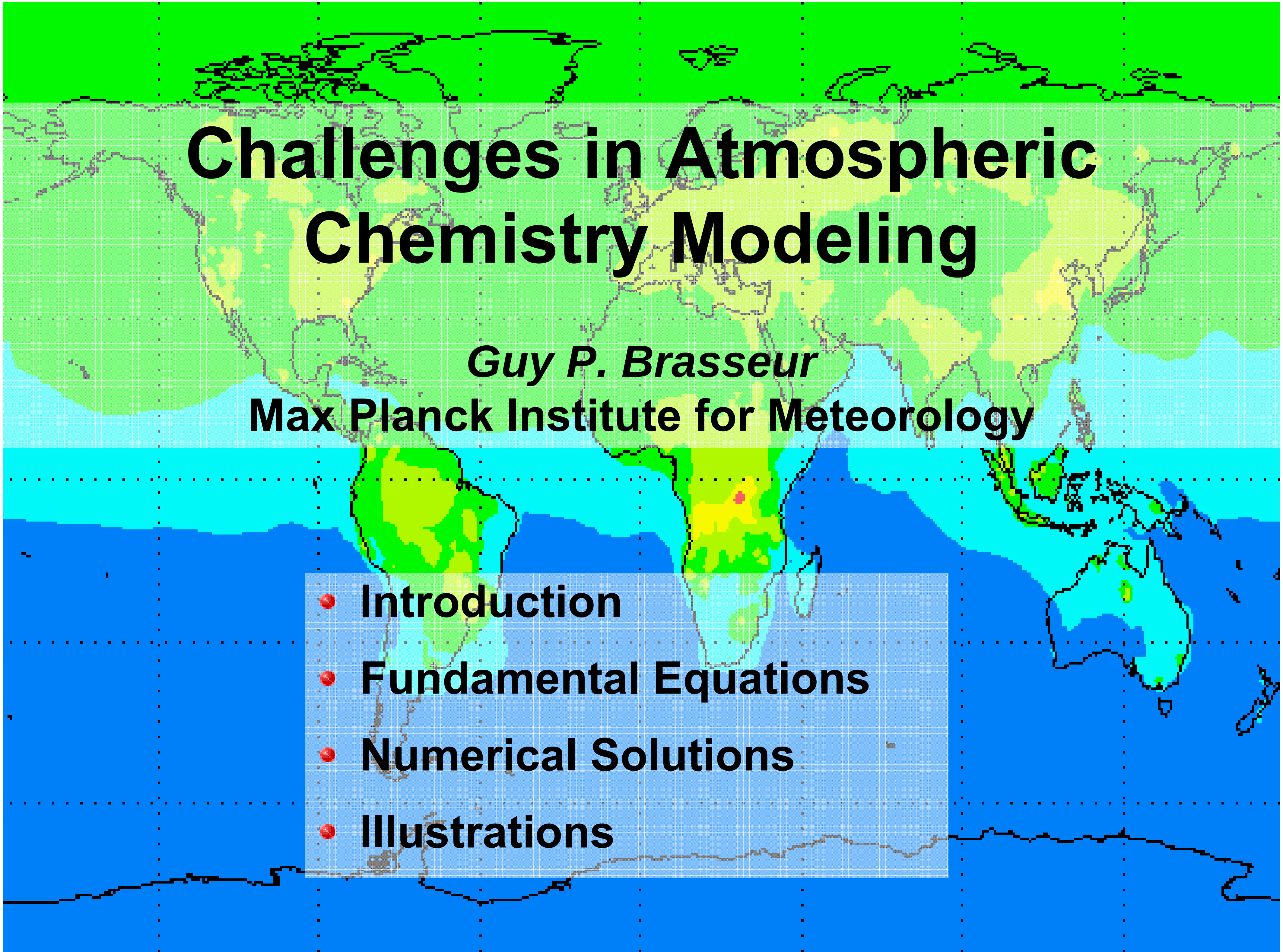

Challenges in Atmospheric Chemistry Modeling

Guy P. Brasseur
Max Planck Institute for Meteorology

- **Introduction**
- **Fundamental Equations**
- **Numerical Solutions**
- **Illustrations**

Acknowledgements

- Claire Granier, CNRS and CIRES.
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Part 1. Introduction

Chemical Transport Models

- The goal of CTMs is to calculate the spatial distribution and temporal evolution of chemically interactive species.
- Models are often used to diagnose observations, test hypotheses, calculate global and regional chemical budgets, and simulate the past and future evolution of the chemical composition for prescribed conditions (evolving boundary conditions).
- The calculation of atmospheric transport requires that dynamical parameters be specified.
- Chemical transport models are often coupled ‘on-line’ to general circulation models.

Part 2. Fundamental Equations

Fundamental Equations Governing the Atmosphere Evolution

$$\frac{\partial \vec{v}}{\partial t} = -\vec{v} \cdot \nabla \vec{v} - \frac{1}{\rho_a} \nabla p - g\vec{k} - 2\vec{\Omega} \times \vec{v} + \vec{F}_{visc}$$

(1), equation of motion (3 components)

$$\frac{\partial \rho_a}{\partial t} = -\nabla \cdot \rho_a \vec{v}$$

(2), air mass conservation

$$\frac{\partial \theta}{\partial t} = -\vec{v} \cdot \nabla \theta + Q_\theta$$

(3), first law of thermodynamics

$$\frac{\partial r_n}{\partial t} = -\vec{v} \cdot \nabla r_n + Q_{r_n}$$

(4), water mass mixing ratio conservation

$$\frac{\partial s_{[\eta]}}{\partial t} = -\vec{v} \cdot \nabla s_{[\eta]} + Q_{s_{[\eta]}}$$

(5), gases/aerosols mass mixing ratio conservation

Q represents the loss/production rate

Continuity Equation for Chemical Species

Mathematically describes the dynamical and chemical processes that determine the distribution of chemical species

flux form :

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v}) = S_i$$

Transport

Chemical forcing

advective form :

$$\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla f_i = \frac{S_i}{\rho_a}$$

or $df_i/dt = S_i/\rho_a$ (f_i is a conserved quantity along the motion)

where,

ρ_i is the mass (or number) density of species i

ρ_a is the air mass (or number) density

$f_i = \frac{\rho_i}{\rho_a}$ is the mass (or volume) mixing ratio

S_i is the production and loss rate of species i

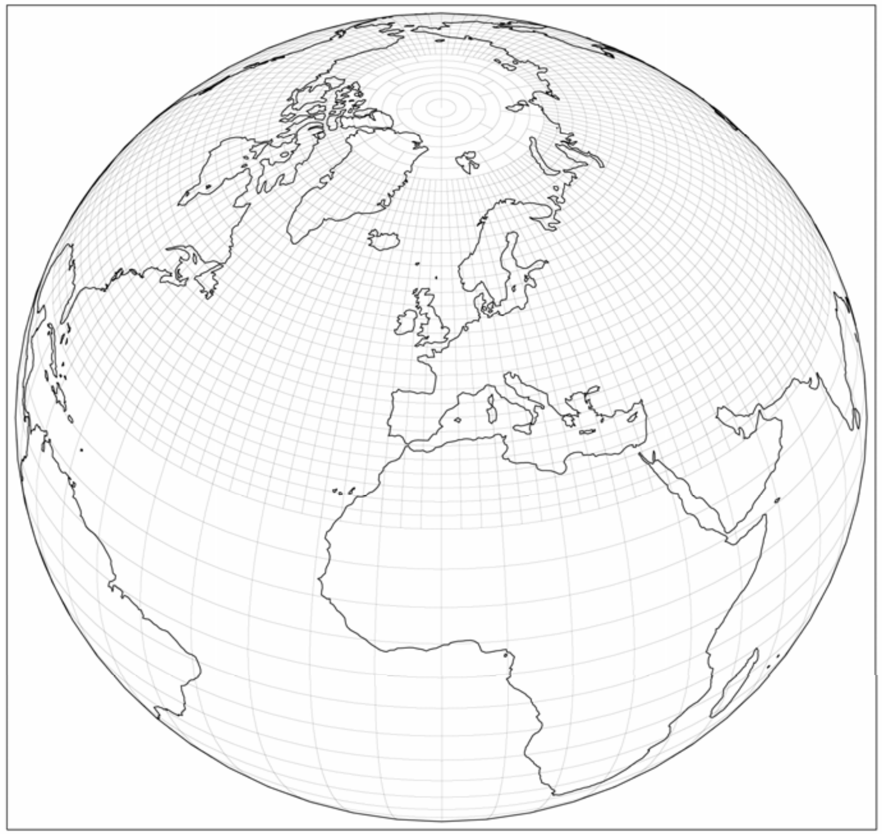
$\mathbf{v}$ is the wind velocity vector

Chemical Composition of the Atmosphere

Concentration ρ_i of atmospheric trace gas i: ($i=1,N$)

Change in concentration is determined by

- Emissions
- Deposition
- Transport at various scales [resolved by the spatial resolution of the model and subscale (parameterisation)]
- Chemical and photochemical reactions



$$\frac{d\rho_i}{dt} = \left(\frac{\partial \rho_i}{\partial t}\right)_{emission} + \left(\frac{\partial \rho_i}{\partial t}\right)_{deposition} + \left(\frac{\partial \rho_i}{\partial t}\right)_{transport} + \left(\frac{\partial \rho_i}{\partial t}\right)_{chemistry}$$

On-line (coupled) versus off-line models

- In ***"o***ff-line" models, transport is driven using outputs provided at regular intervals (e.g., 3 hours) by an atmospheric general circulation model or by atmospheric analyses (data assimilation).

- In "on-line" models, the solution for chemical species is obtained simultaneously with the solutions of the dynamic equations. This has some considerable benefits:

a) Uses the same spatial and temporal resolution (e.g., 20 min)

b) Uses exactly the same coordinate system

c) Accounts for feedbacks between dynamics and chemistry.

d) More easy treatment of the model output (real time weather and air quality forecasts).

e) But… can be computationally expensive.

Part 3. Numerical Solutions

Solving the Continuity Equations for N Chemical Species

- *N* species leads to *N* coupled non-linear equations which rarely have an analytic solution.
- System is solved with numerical methods at discrete locations (“grid-points”).
- Differentials replaced by finite differences.
- Finite resolution (time or space) implies that some transport processes are unresolved (e.g. diffusion).
- Chemistry and transport handled as separate operations.

Part 3. Numerical Solutions

- 1. Transport
- 2. Chemistry
- 3. Surface Processes

Advection

- Desired properties of an advection scheme:
  - Accuracy
  - Stability
  - Mass conservation
  - Monotonicity (shape preservation)
  - Positive definite fields
  - Local
  - Efficient

Three groups of algorithms:

- Eulerian
- Lagrangian
- Semi-Lagrangian

Advection

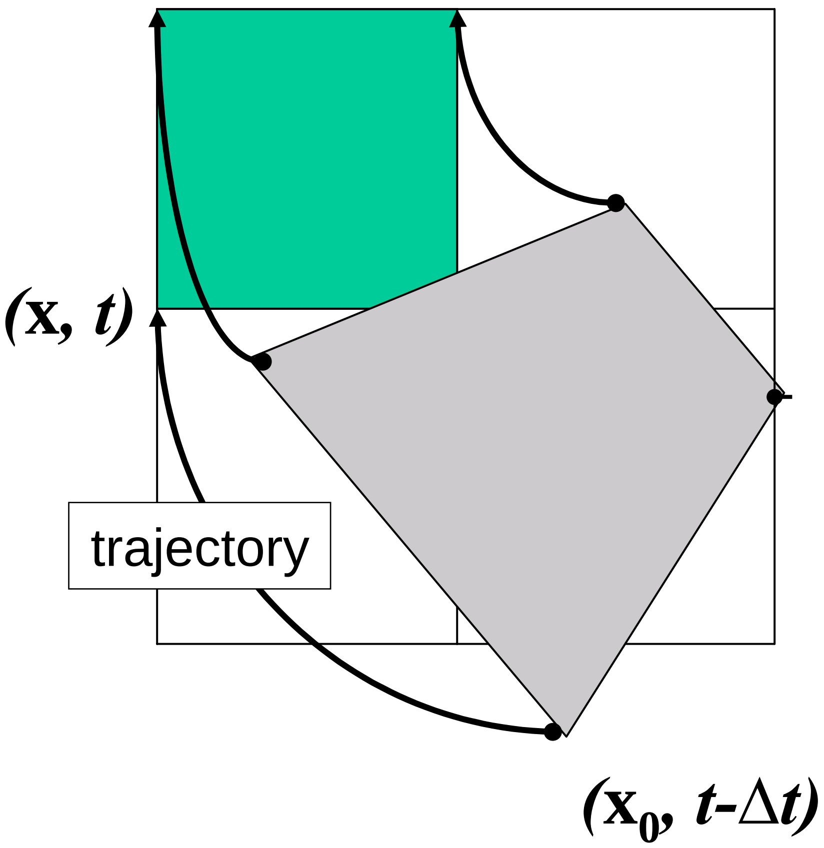
- **Eulerian Methods**:
  - The Euler forward (explicit) scheme is unconditionally unstable
  - The Upwind method is diffusive
  - The Leapfrog method is not monotonic
  - Improved methods: Smolarkiewicz, Bott, Prather (transport of moments).
  - The CFL condition must be verified to ensure stability.

$$\frac{|c|\Delta t}{\Delta x} \leq Const, \ with \ Const \approx 1$$

- **Lagrangian methods**: Simple concept, but air parcels can ‘bunch up’ in certain areas during the integration. (no mixing)

- **Semi-Lagrangian methods**: Not limited by timestep, but not mass conserving, unless adapted (e.g., Lin and Rood)

Semi-Lagrangian Transport



$$\mathbf{x}_0 = \mathbf{x} + \int_t^{t-\Delta t} \mathbf{v}(\mathbf{x}, t)\,dt$$

Calculation of back trajectory requires iterations (since wind speed v is not known everywhere along the trajectory)

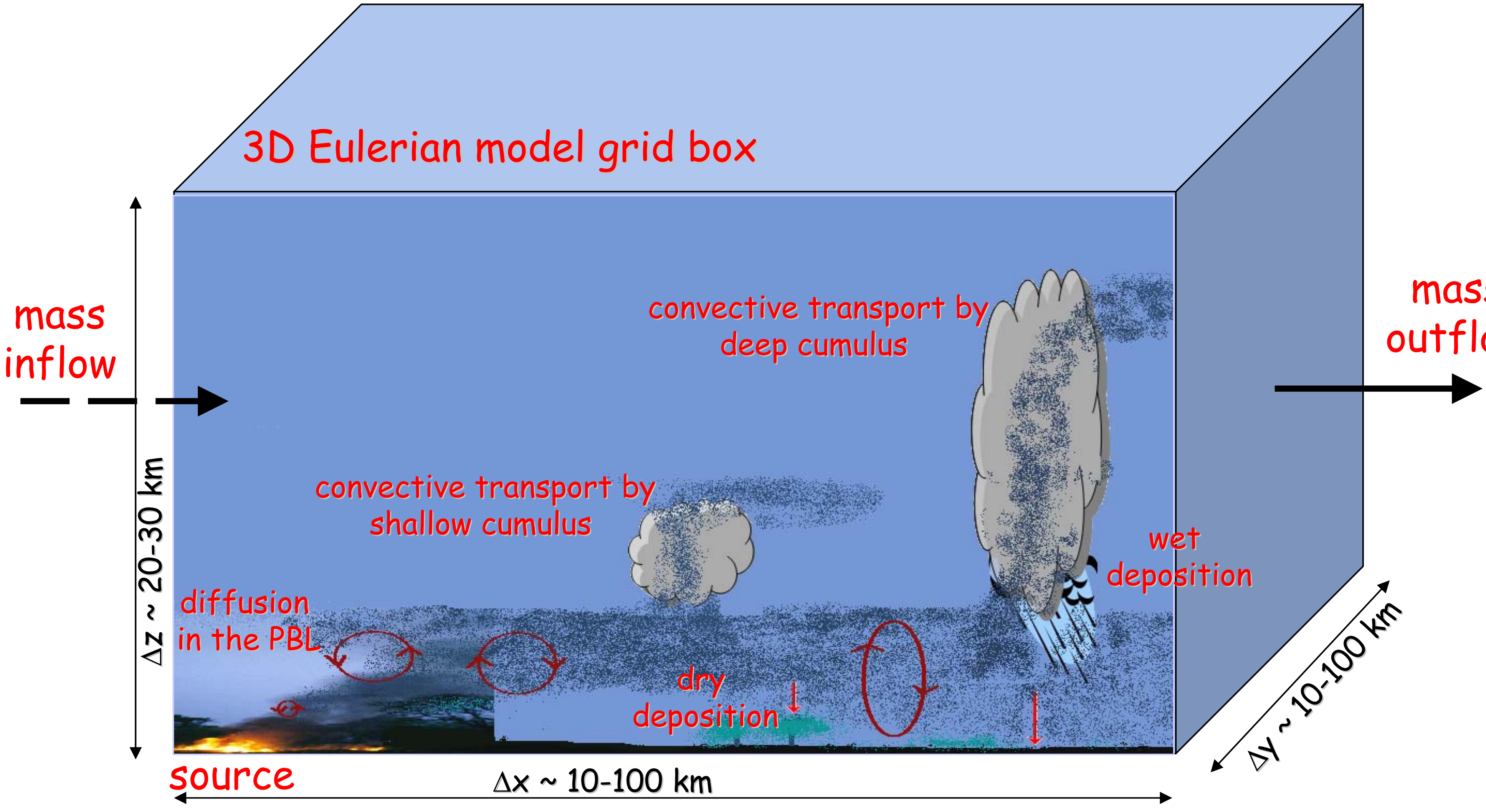
Accuracy depends greatly on Interpolation scheme used to determine the mixing ratio at departure point.

Common in modern GCMs, but not mass conservative…..

Conservative Semi-Lagrangian Methods

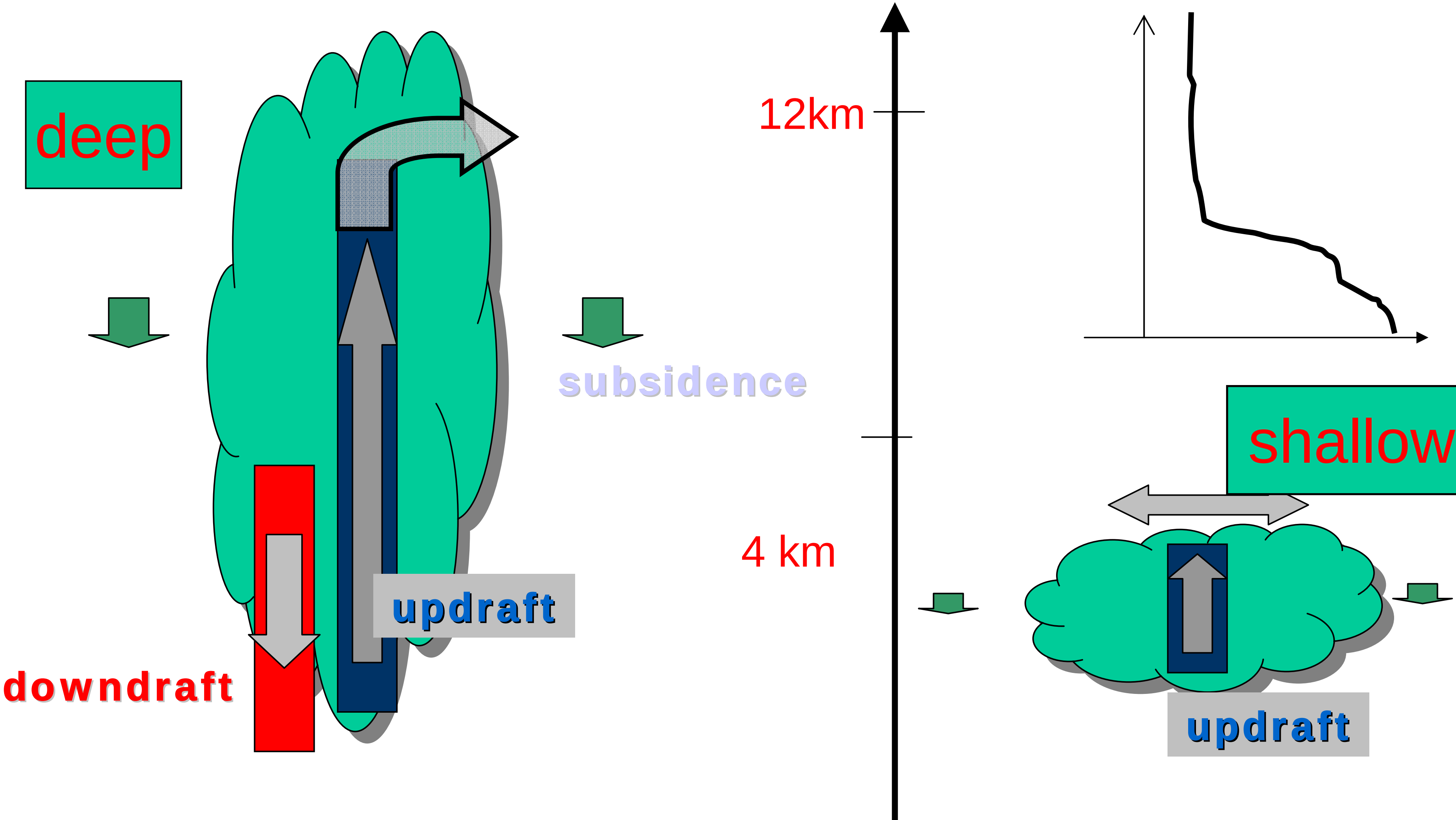
- Rather than considering variables at specific grid points, one can transport *integral* quantities or ***average*** values over finite cell volumes.
- In finite-volume-based Semi-Lagrangian methods, the value of the advected field at a new time level is just the average value of the departure cell defined by its upstream position at the previous timestep.
- Lin and Rood (1996) have developed a mass conservative **finite volume semi-Lagrangian method**, in which the boundaries (“ departure walls” rather than “departure points”) of the grid volumes are transported to the next step (“arrival walls”). Mass is conserved in the box during a timestep. The CFL restriction does not apply.

Some sub-grid Process involved in Gases/Aerosols Transport



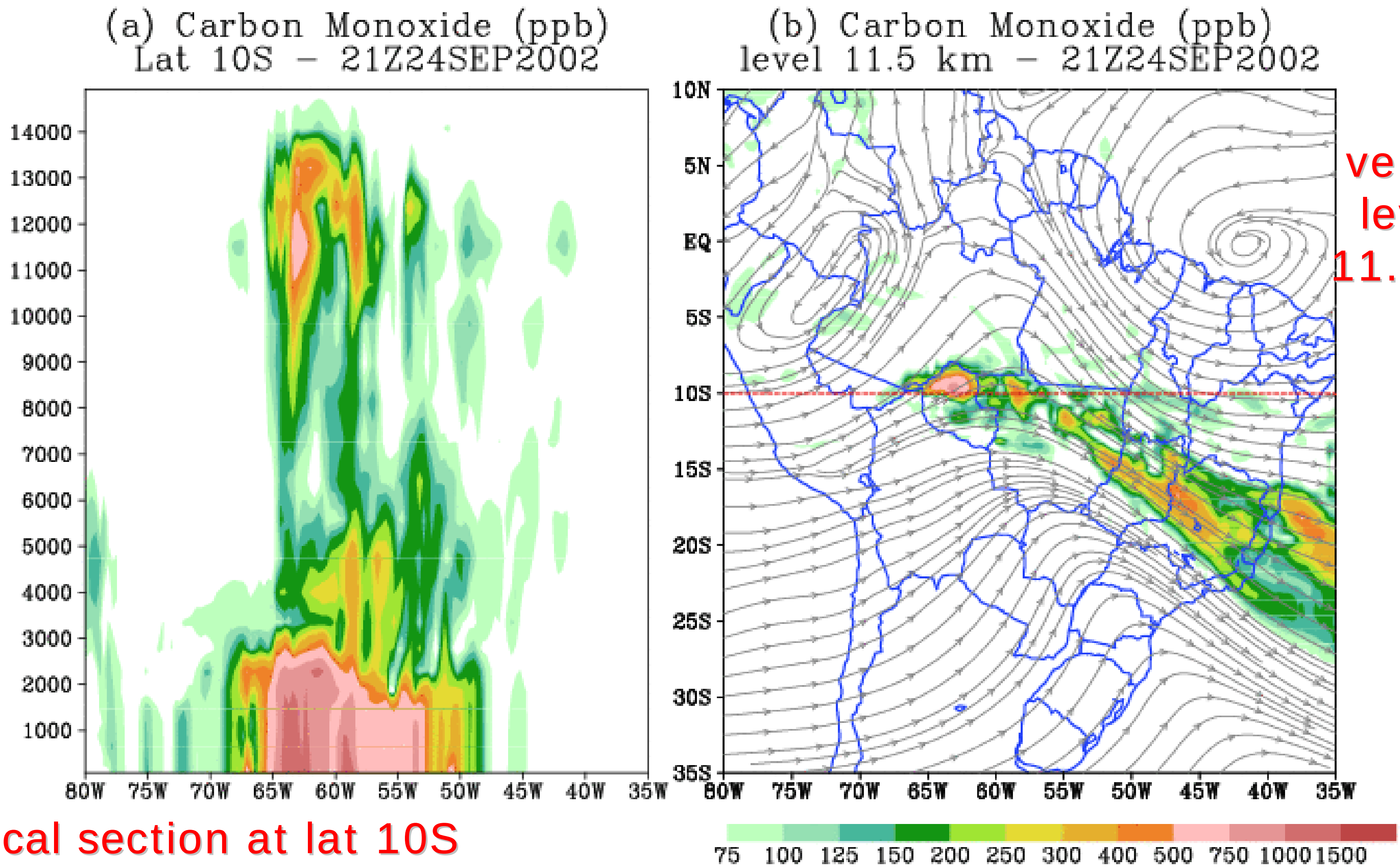
Sub-grid Convective Transport

Cloud venting is a very important mechanism transporting pollutants from the PBL to the upper levels, affecting the chemistry of troposphere and the biogeochemical cycles.



Deep Convective Transport of CO

21Z 24 Sep 2002



vertical level 11.5 km

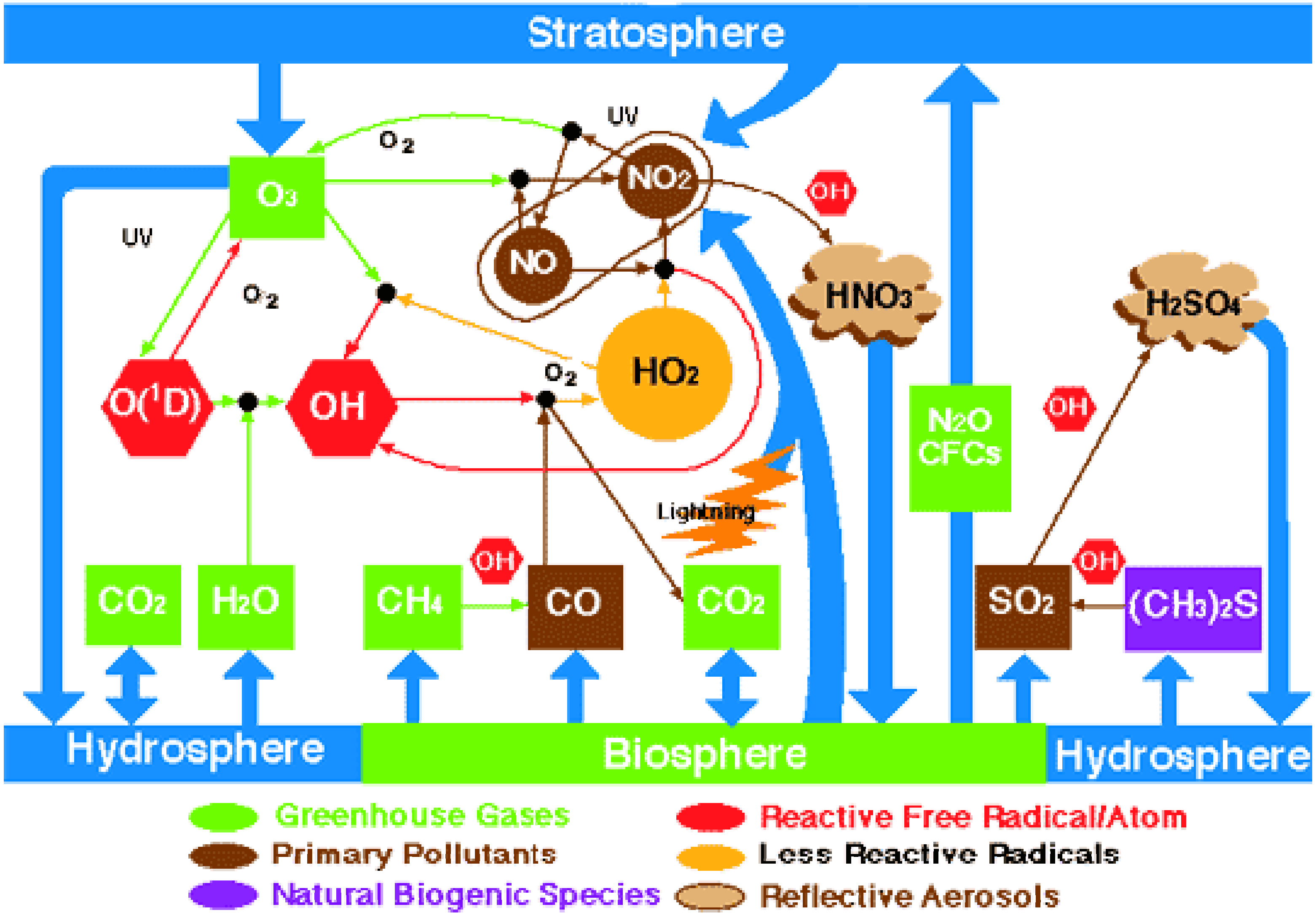
Vertical section at lat 10S

CO (ppb)

Part 3. Numerical Solutions

- 1. Transport
- 2. Chemistry
- 3. Surface Processes

Tropospheric Chemistry



Chemistry: Solving df/dt = S/ρ

- This is a system of N equations (N being the number of chemical species in the model – typically 50 to 150).
- The system is non-linear and 'stiff' (time constants of species varying from microseconds to centuries).
- The numerical method must be stable and accurate for a timestep that is sufficiently large for the system to be efficiently integrated.

Chemical forcing (S)
(i.e. production and loss)

First-order forcing
Photolysis, airglow, …

$$\frac{\mathbf{S}(\mathbf{f},\mathbf{x},t)}{\rho_a} = \mathbf{e}(\mathbf{x},t) - \mathbf{A}(\mathbf{x},t)\cdot\mathbf{f} + \mathbf{B}(\mathbf{f},\mathbf{x},t)\cdot\mathbf{f}$$

External forcing
Independent of **f**

Non-linear forcing
Bi-molecular and
tri-molecular reactions

For N species, A and B are NxN matrices

Chemistry: Solving df/dt = S/ρ

Simplest method is fully explicit:

$$\mathbf{f}^{n+1} = \mathbf{f}^{n} + \Delta t \cdot \mathbf{S}(t_n, \mathbf{f}^{n}) / \rho_a$$

Euler Forward

$\mathbf{f}^{n+1}$ expressed in terms of known quanities

Requires very small time-steps.

Fully implicit is stable for any Δt:

$$\mathbf{f}^{n+1} = \mathbf{f}^{n} + \Delta t \cdot \mathbf{S}(t_{n+1}, \mathbf{f}^{n+1}) / \rho_a$$

Euler backward

However, **S** contains non-linear terms, and

accuracy is comprimised for large Δt.

Iterative techniques are often used to

improve the accuracy of implicit methods.

Prominent is the Newton-Raphson iteration which requires that the Jacobian matrix of the chemical system be calculated.
The convergence is achieved for sufficently small timesteps

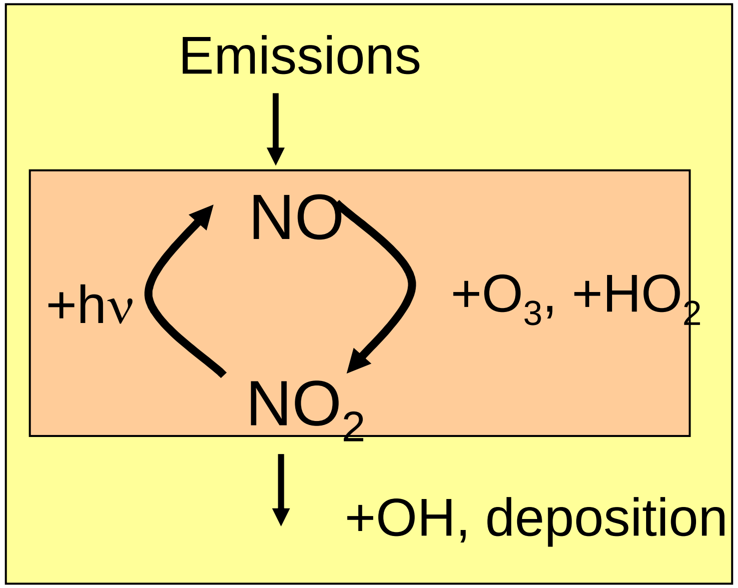
Chemistry: Solving df/dt = S/ρ

- A multi-step method very appropriate for “stiff” systems has been developed by **Gear** (1971).
- This algorithm is composed of the so-called backward difference formulas up to order six.
- The method is extremely robust and stable but does require solving nonlinear algebraic systems (like Euler backward algorithm).
- Time step and order of the method are continuously adapted to meet user-specified solution error tolerances.
- Codes require much computer memory and tine; not practical for multi-dimensional models.

Chemistry: Solving df/dt = S/ρ: Chemical Families

Species are grouped together within specified chemical familes Because of the longer lifetime associated with the families, relatively large timestep can be use to integrtate the equations

Partitioning between members of the family are made by assuming equilibrium conditions for fast reactive species within the family.



Example: **$NO_x = NO + NO_2$**

$$\frac{d\mathrm{NO}}{dt} = \mathrm{Emissions} + j_{NO_2} \cdot \mathrm{NO_2} - \mathrm{NO}\left(k_1 \cdot \mathrm{O_3} + k_2 \cdot \mathrm{HO_3}\right)$$

$$\frac{d\mathrm{NO_2}}{dt} = \mathrm{NO} \cdot \left(k_1 \cdot \mathrm{O_3} + k_2 \cdot \mathrm{HO_3}\right) - j_{NO_2} \cdot \mathrm{NO_2} - k_3 \cdot \mathrm{NO_2} \cdot \mathrm{OH} - \mathrm{deposition}$$

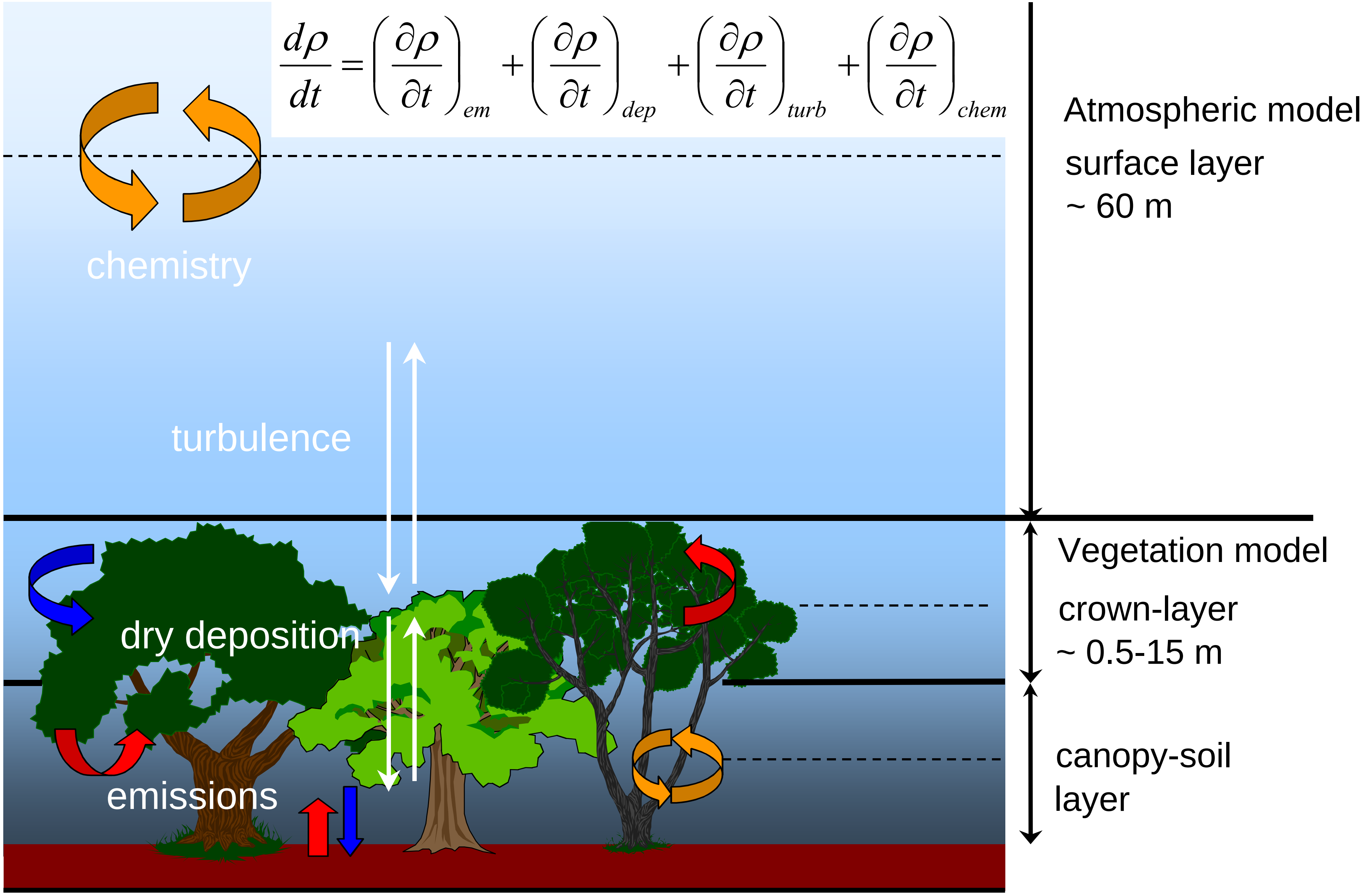
$$\frac{d\mathrm{NO_x}}{dt} = \frac{d\mathrm{NO}}{dt} + \frac{d\mathrm{NO_2}}{dt} = \mathrm{Emissions} - k_3 \cdot \mathrm{NO_2} \cdot \mathrm{OH} - \mathrm{deposition}$$

Part 3. Numerical Solutions

- 1. Transport
- 2. Chemistry
- 3. Surface Processes

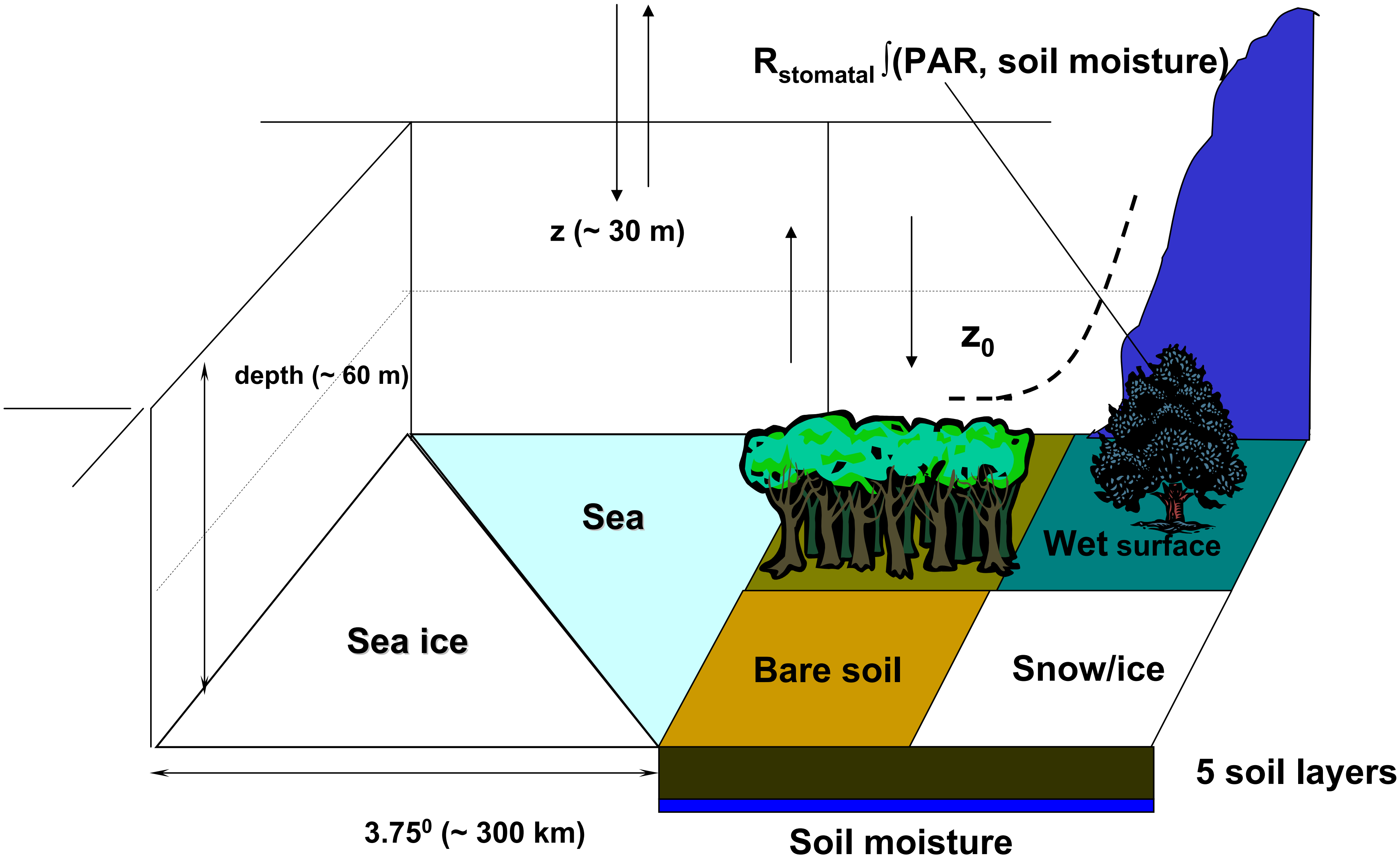
Surface exchanges: emission-deposition

$$\frac{d\rho}{dt} = \left(\frac{\partial\rho}{\partial t}\right)_{em} + \left(\frac{\partial\rho}{\partial t}\right)_{dep} + \left(\frac{\partial\rho}{\partial t}\right)_{turb} + \left(\frac{\partial\rho}{\partial t}\right)_{chem}$$



Vegetation and wet skin fraction

Model surface description



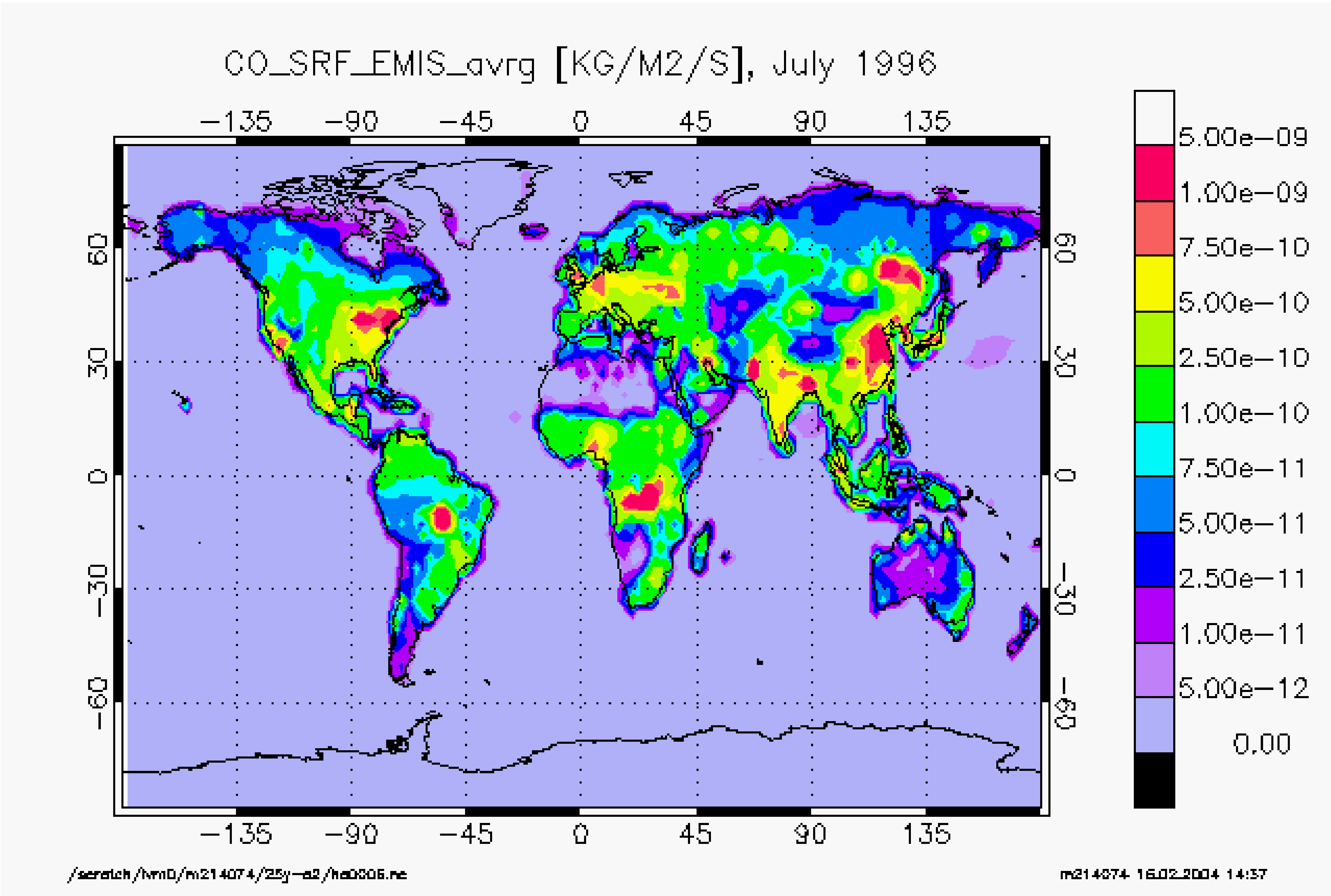
Emissions

Typical categories of „bottom-up“ emissions inventories include:

- fossil fuel combustion
- biofuel combustion
- vegetation fires
- biogenic emissions (plants and soils)
- volcanic emissions
- oceanic emissions
- agricultural emissions (incl. fertilisation)

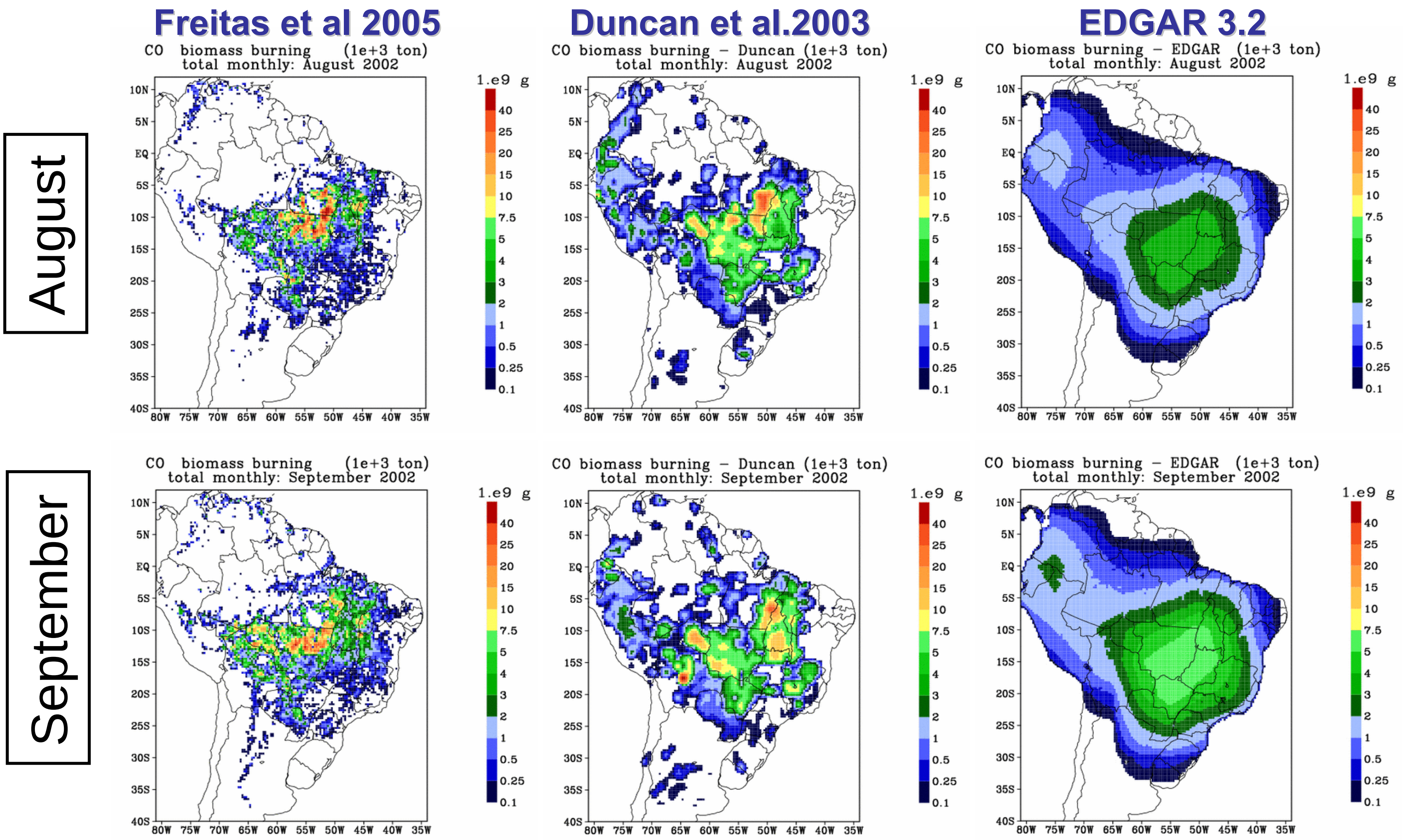
etc.

Emissions of Carbon Monoxide



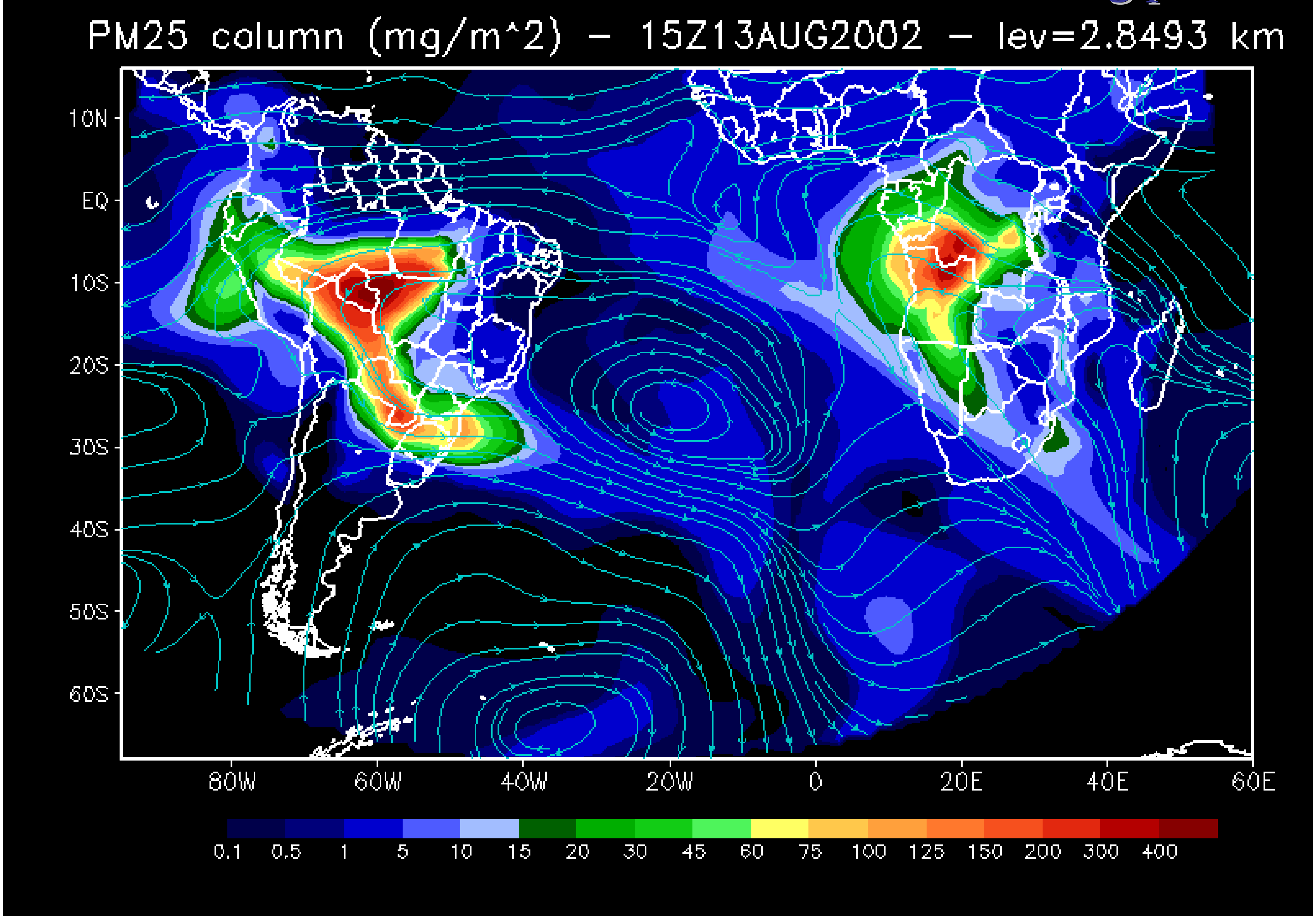
Monthly Carbon Monoxide Emission Estimation for 2002

Hybrid remote sensing fire products: GOES WF_ABBA AVHRR and GOES (INPE) MODIS (NASA) From INPE/CPTEC, Brazil



Model output for PM2.5 column – Aug 2002 (INPE, Brazil)

South American and African biomass burning plumes



Dry Deposition

Transport of gaseous and particulate species from the atmosphere onto surfaces in the absence of precipitation

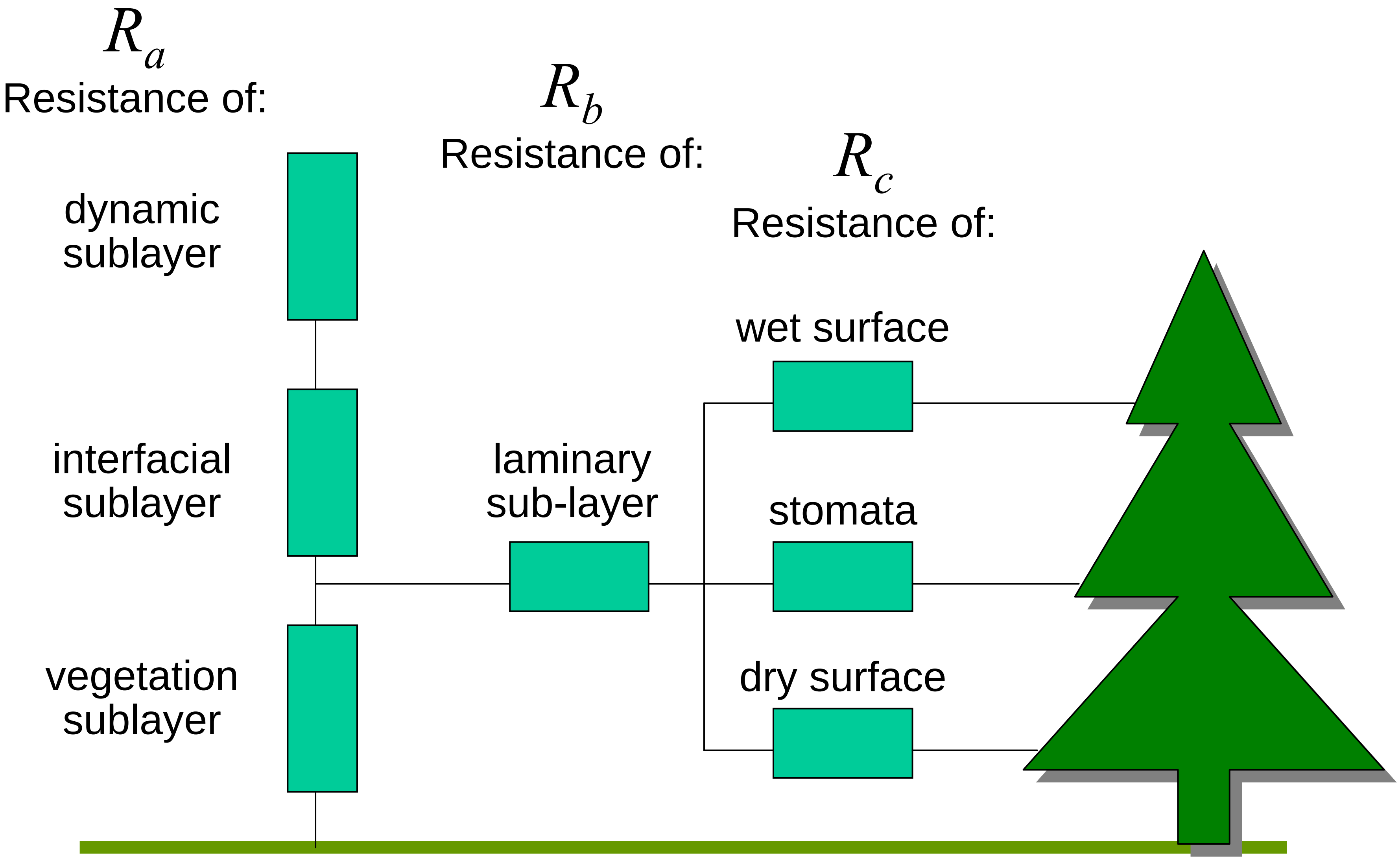
Controlling factors: atmospheric turbulence, chemical properties of species, and nature of the surface

Deposition flux: $$F = -v_d C$$

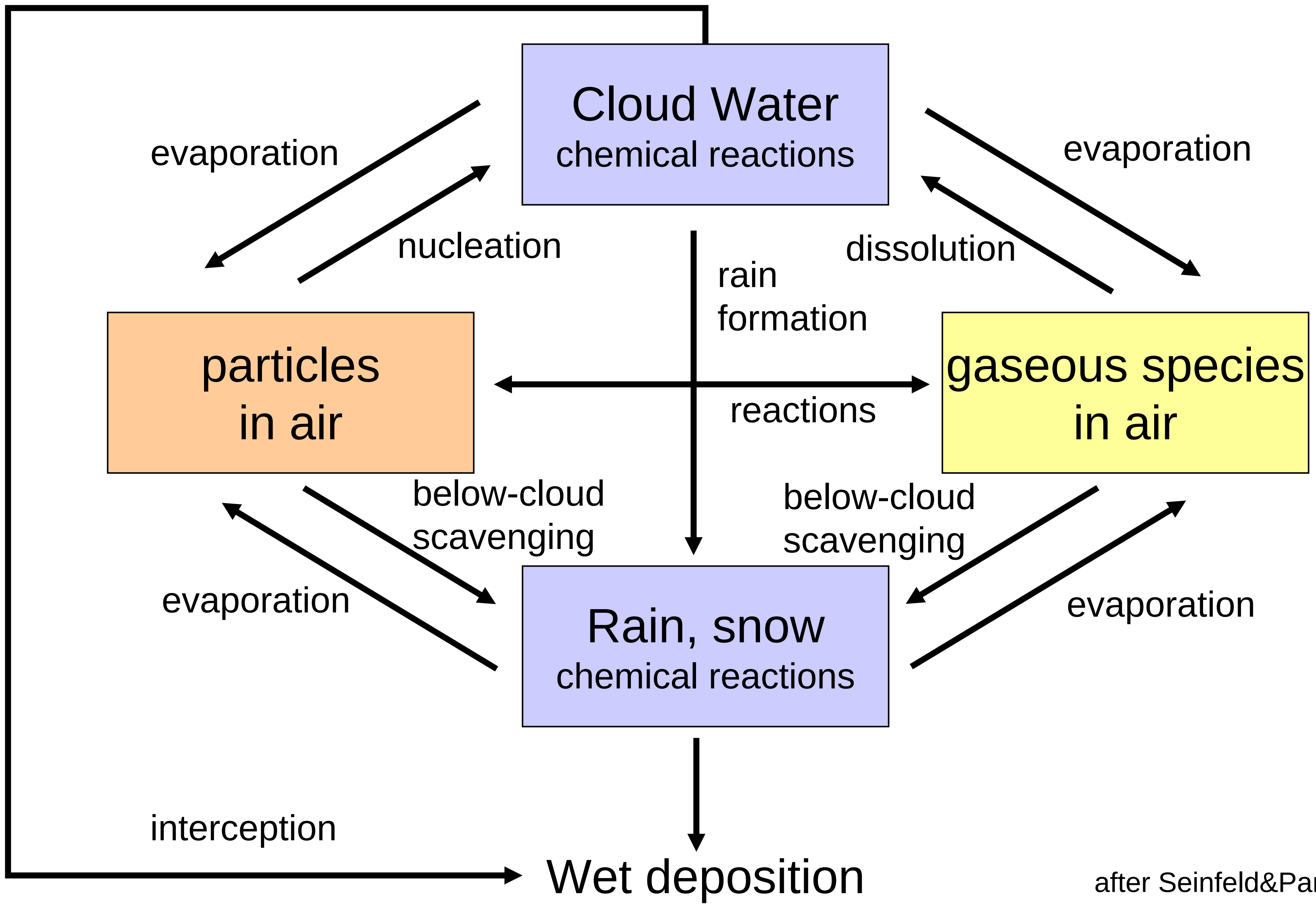
v_d: deposition velocity
C: concentration of species at reference height (~10 m)

Dry deposition velocity

$$V_d = \frac{1}{R_a + R_b + R_c}$$



Wet deposition



after Seinfeld&Pandis, 1998

Part 4: Illustrations

- Global Tropospheric Chemistry

  (MOZART-2 and –4)

- Stratospheric Chemistry

  (MOZART-3)

-2 and

-4

Surface to 30 km

MOZART-2: Model set-up

- Uses analysed winds (e.g. ECMWF, NCEP) or GCM output (T, q, u, v, p_s, ...)
- Standard chemistry scheme comprises of 65 species and 170 reactions. Chemistry is easily adaptable by means of a preprocessor code
- Runs efficiently on almost any computer platform (parallel and vectorized)
- Flexible output specification; postprocessing tools available

Brasseur *et al*., JGR, 1998; Horowitz *et al*., JGR, 2004.

Parameterisations

- Model physics and hydrological cycle based on CCM model (Rasch et al., 1997)
- Boundary layer: Holtslag and Boville, 1993
- Advection: Lin and Rood, 1996
- Convection: Zhang and McFarlane, 1995; Hack, 1994
- Dry deposition: Wesely, 1989, Hess et al., 2000
- Scavenging: Giorgi ad Chameides, 1985; Brasseur et al., 1998
- Lightning NOx production: Price, Penner, and Prather, 1997

MOZART-4: New Features

- Extended chemical mechanism (hydrocarbons)
- Interactive biogenic emissions and updated anthropogenic and fire emissions.
- New upper boundary conditions in the stratosphere
- SYNOZ (tracer with a specified source region (30S-30N, 10-70 hPa) and rate (400-500 Tg/yr); relaxed to 25 ppbv below 500 hPa)
- Improved radiative parameterisation for photolysis
- Aerosols coupled with gas phase chemistry
- Dry deposition interactive
- Improved albedo

Chemical Mechanism (MZ-4)

- 97 compounds (with aerosols and no OX group)
- New hydrocarbons (instead of C4H10)
- Terpene oxidation mechanism updated with new lab data
- Minor corrections and rates updated to JPL 2002
- Photolysis rates updated to TUV
- OX - as group, or O_3, $O(^1D)$, O each transported
- Aerosols: as in *Tie et al*. [2005], with updates
- Heterogeneous rxns: HO2, NO2 [NO3, N2O5 in MZ2]
- Dust: offline monthly means [from N. Mahowald]
- SYNOZ available (constrains the cross tropopause flux)

Emissions

MOZART-2

Based on EDGAR-2, Hao and Liu biomass burning climatology

MOZART-4

POET (EDGAR-3), biomass burning based on satellite fire counts

Ocean Emissions

MZ-2: CO, C2H6, C3H8, C2H4, C3H6, C4H10, CH3OH, Acetone

MZ-4: CO

Species	MOZART-2	MOZART-4
NO (TgN/yr)	40.8	45.3
CO (Tg/yr)	1194.7	1357.0
C2H6 (Tg C/yr)	9.6	9.3
C3H8 (Tg C/yr)	8.3	8.5
C2H4 (Tg C/yr)	19.2	14.3
C3H6 (Tg C/yr)	8.5	4.6
C4H10 (Tg C/yr)	29.9	--
BIGALK (Tg C/yr)	--	67.8
BIGENE (Tg C/yr)	--	7.0
TOLUENE (Tg C/yr)	--	30.7
ISOP (Tg C/yr)	410.5	452.1
C10H16 (Tg C/yr)	129.1	65.7
CH2O (Tg C/yr)	2.8	1.7
CH3COCH3 (Tg C/yr)	23.0	17.9
CH3OH (Tg C/yr)	116.9	89.9
C2H5OH (Tg C/yr)	--	5.3
CH3CHO (Tg C/yr)	--	5.4
MEK (Tg C/yr)	--	3.1

On line Emissions –
Isoprene and Terpenes

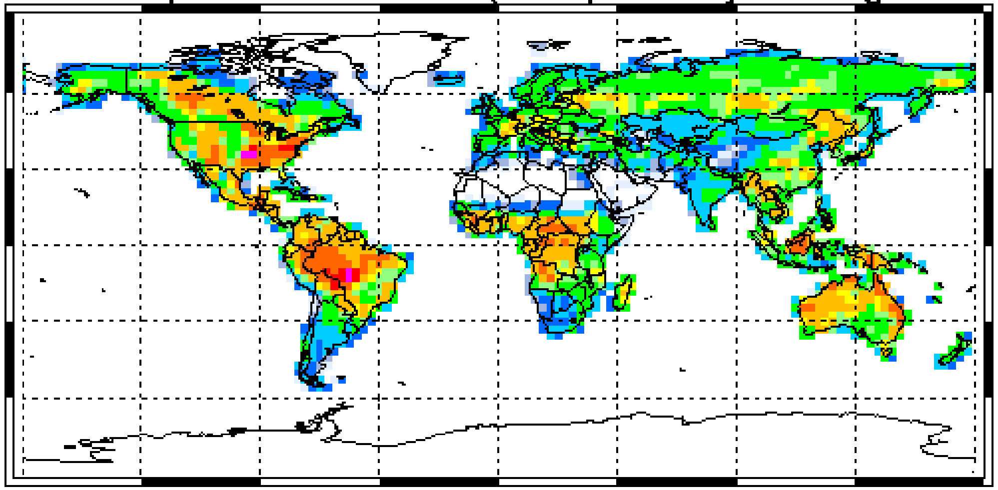
- **Online Calculation of isoprene *(and monoterpene)* emissions based on MEGAN (Alex Guenther and others)**

- **Input**
  - Temperature, Radiation, ...
  - Global distribution of emission factors
  - Global maps of Leaf Area Index (LAI)
  - Global maps of Plant Functional Type (PFT)

- **LAI and PFT from CLM (Community Land Model) - AVHRR**
- **LAI and PFT from Yuhong Tian (2004) - MODIS**
- **LAI and PFT from Peter Lawrence (CU) - MODIS**

Effect of Vegetation Maps

Isoprene Emissions (CLM) for July: 30 Tg



Global annual emissions

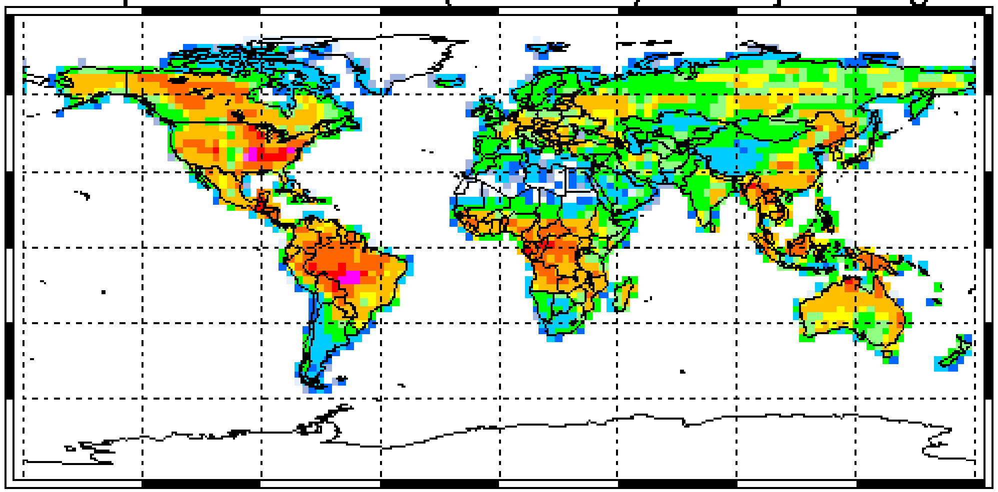
CLM: 304 Tg C/yr

Lawrence: 466

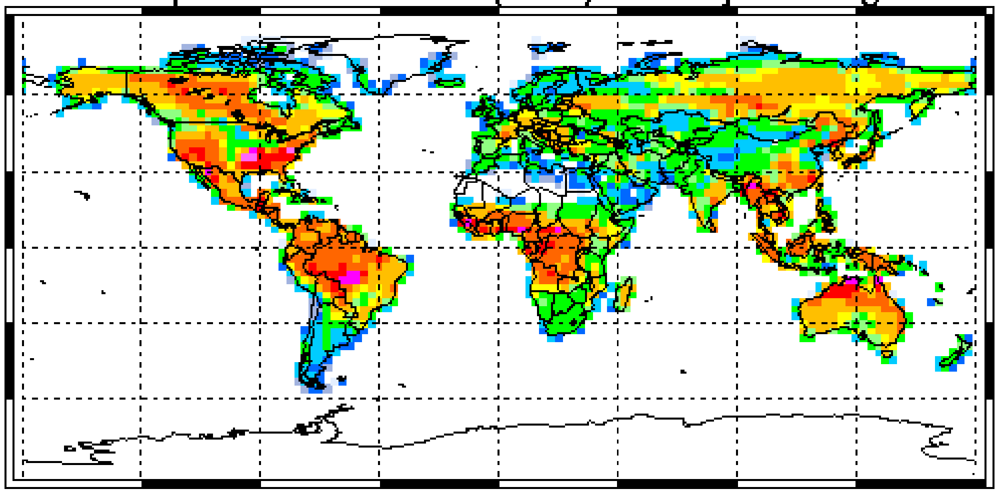
Tian: 599

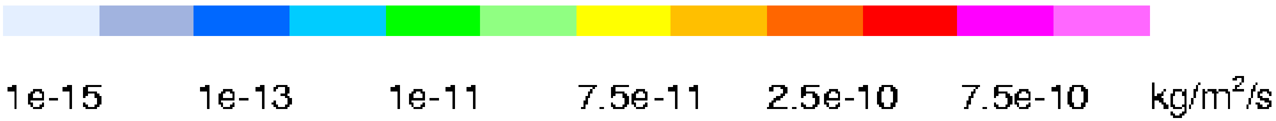
- Using Lawrence's maps in MZ4

Isoprene Emissions (Lawrence) for July: 46 Tg



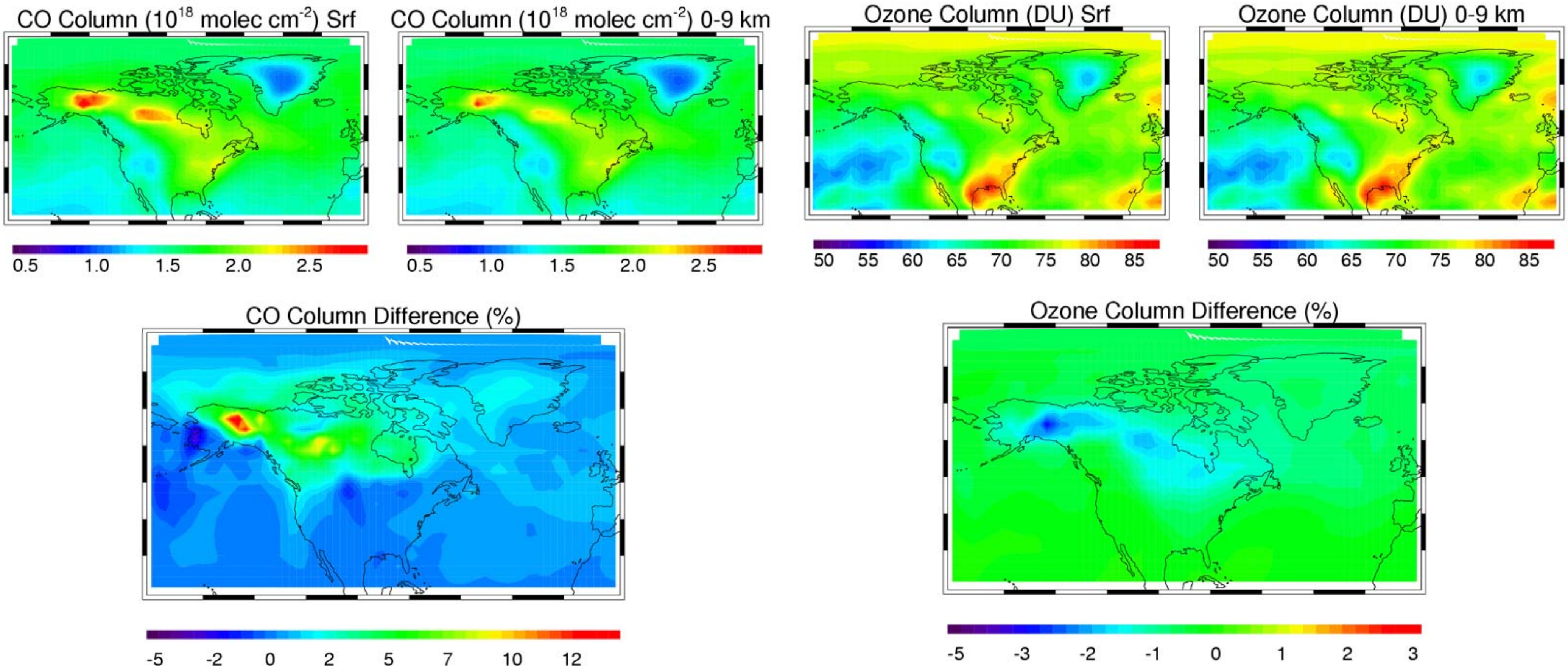
Isoprene Emissions (Tian) for July: 60 Tg



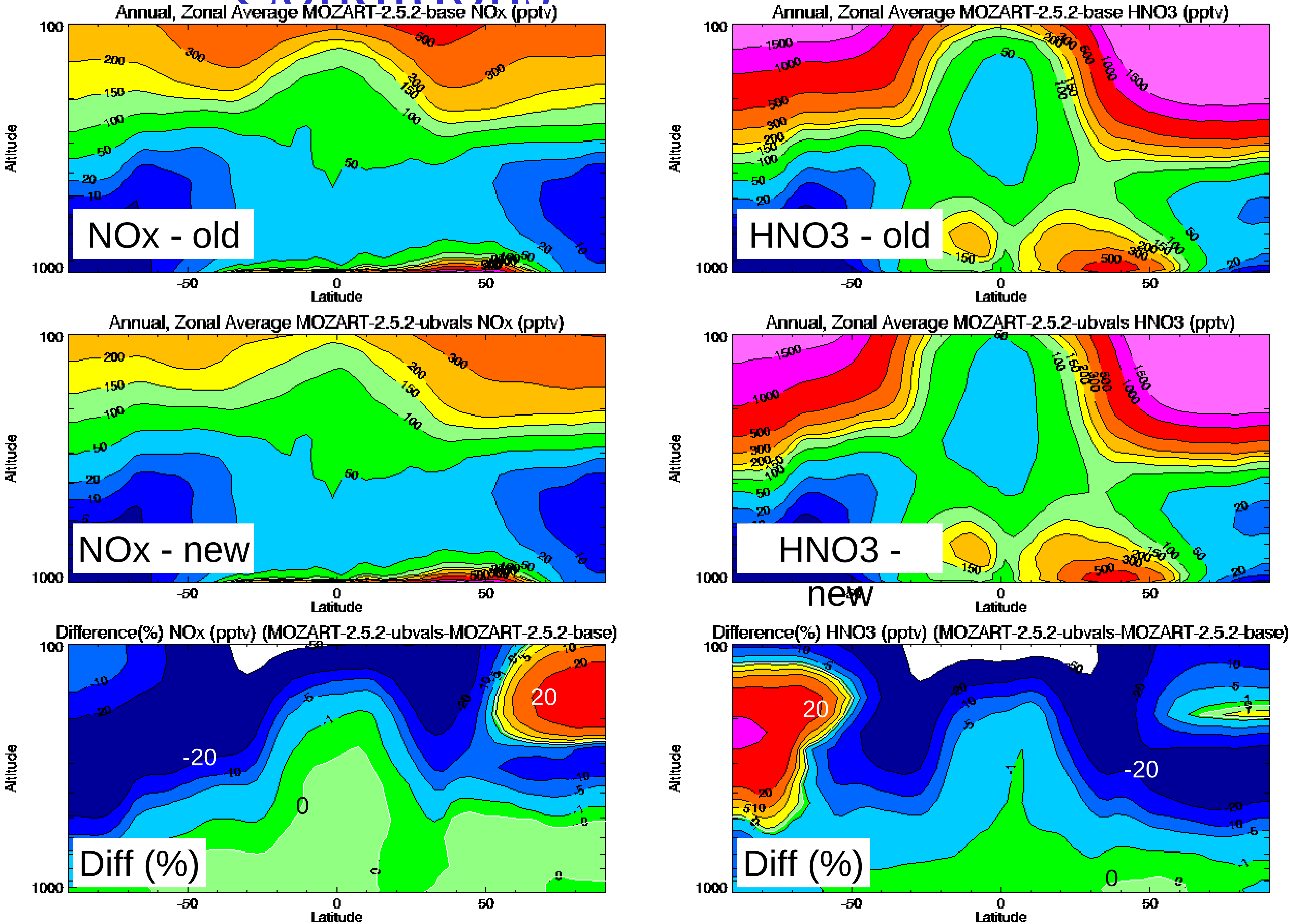


Vertically distributed emissions

Averages of July and August, 2004 - emissions only at surface vs. distributed over 0-9 km



Impact of Upper Boundary Conditions



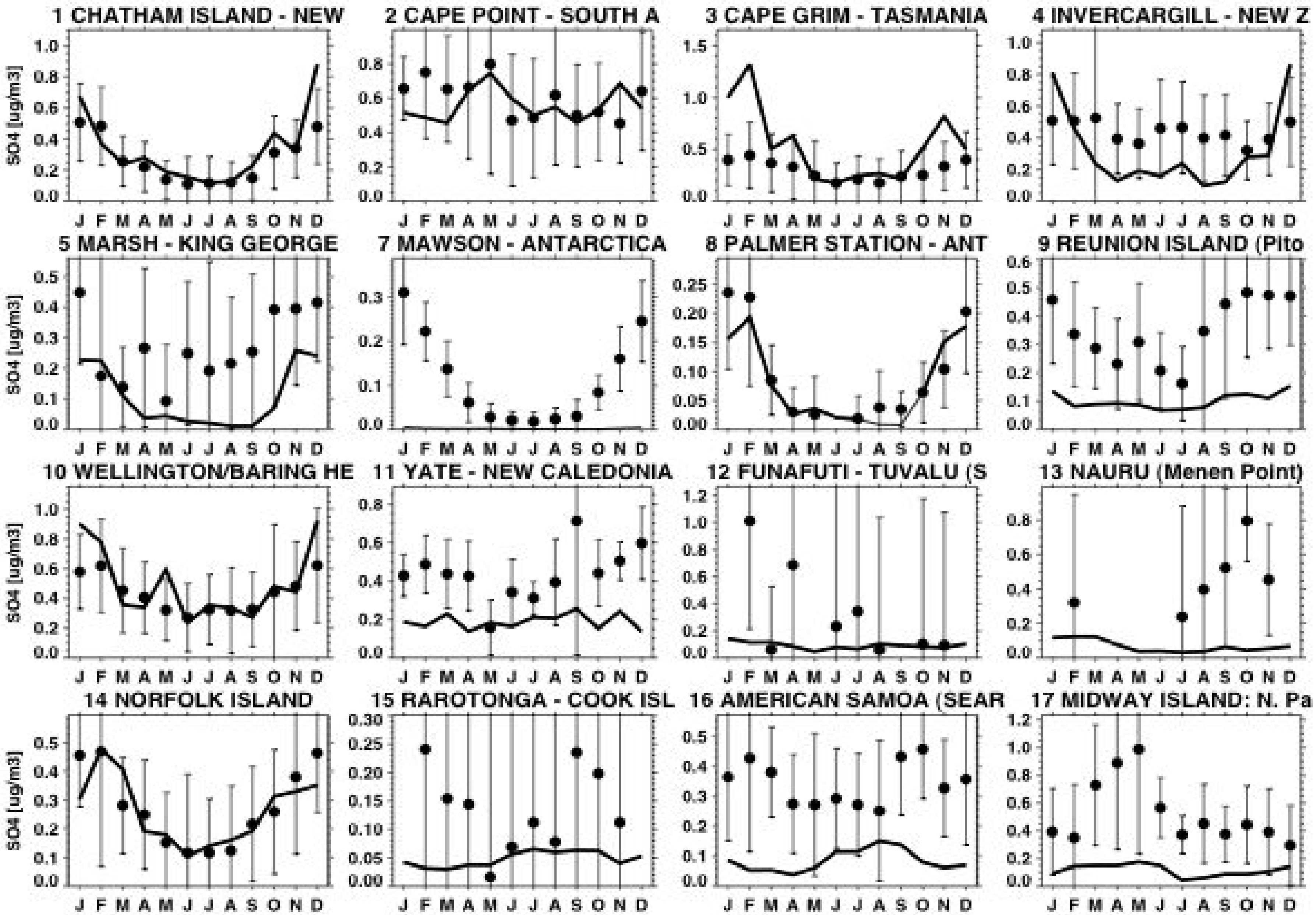
SYNOZ

- Since the use of analyzed winds (e.g., NCEP) in MOZART usually results in too large stratospheric flux of ozone, SYNOZ is used
- SYNOZ is a tracer with a specified source region (30S-30N, 10-70 hPa) and rate (400-500 Tg/yr); relaxed to 25 ppbv below 500 hPa
- Ozone is set to SYNOZ above the tropopause, if SYNOZ > 100 ppbv
- O3RAD is set to the stratospheric ozone climatology and used for photolysis
- Requires 3-5 years spin-up for IC (provided)

Simulated Aerosol Species

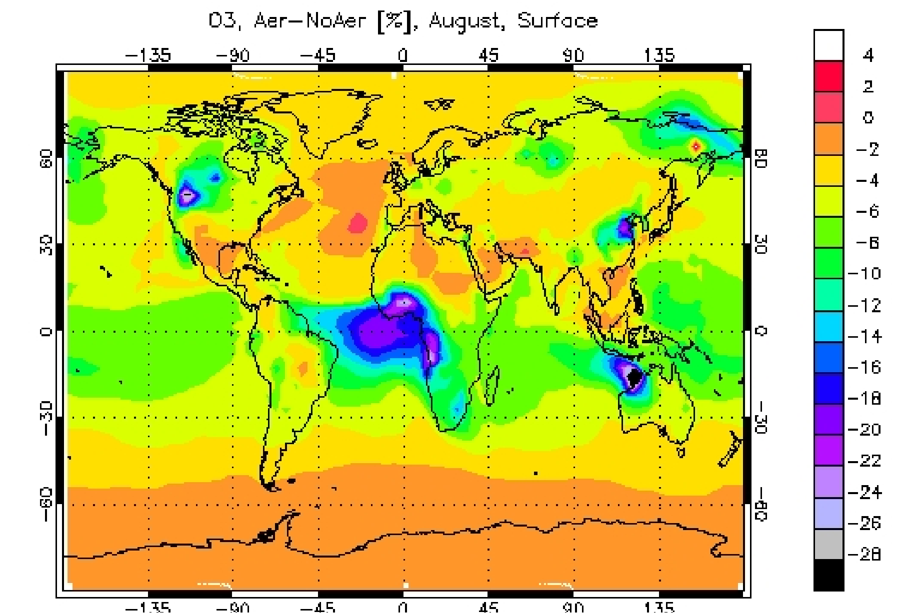
- SO_2, SO_4, DMS
- NH_3, NH_4, NH_4NO_3
- OC (hydrophobic, hydrophilic)
- BC (hydrophobic, hydrophilic)
- Sea-salt (4 bins)
- SOA

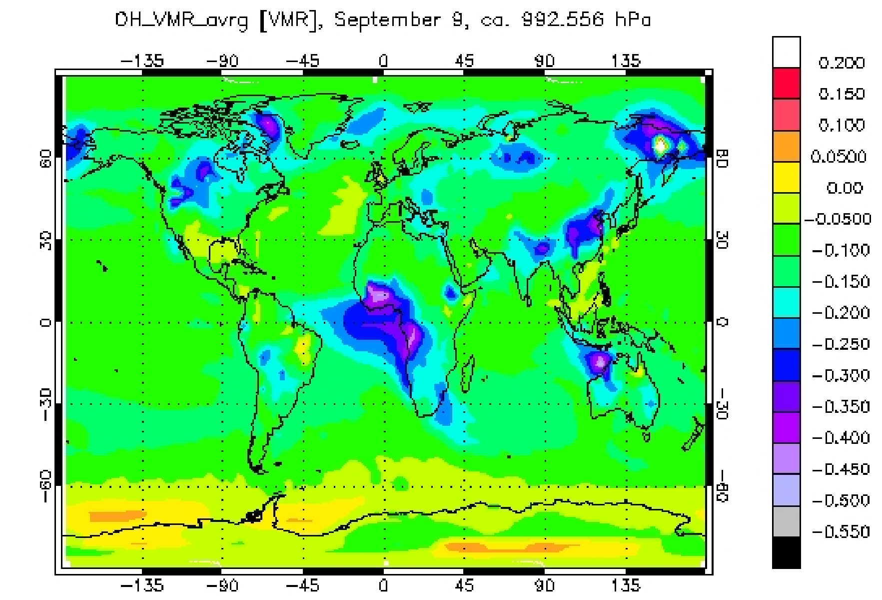
SO_4 at RSMAS sites

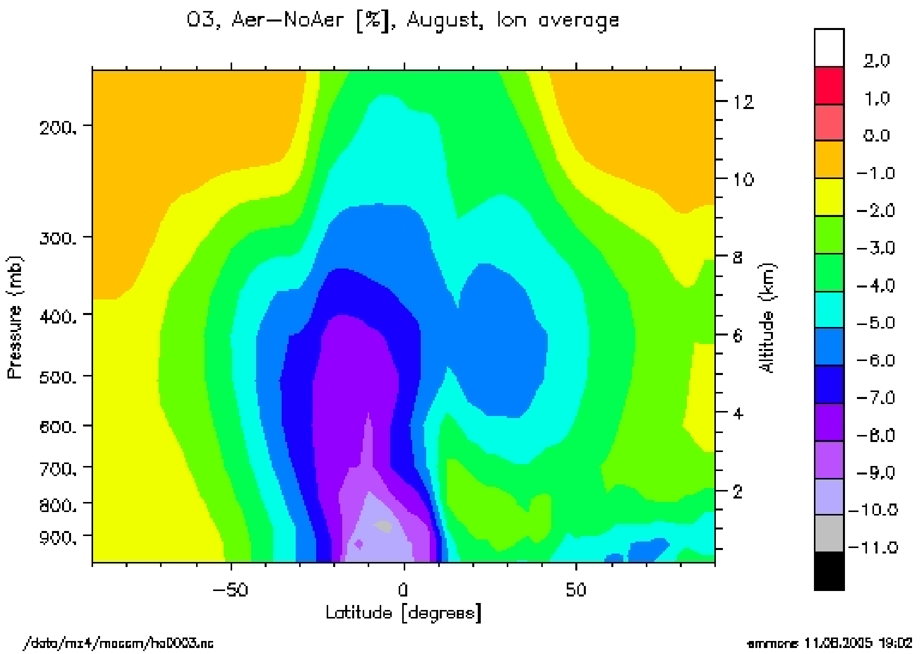


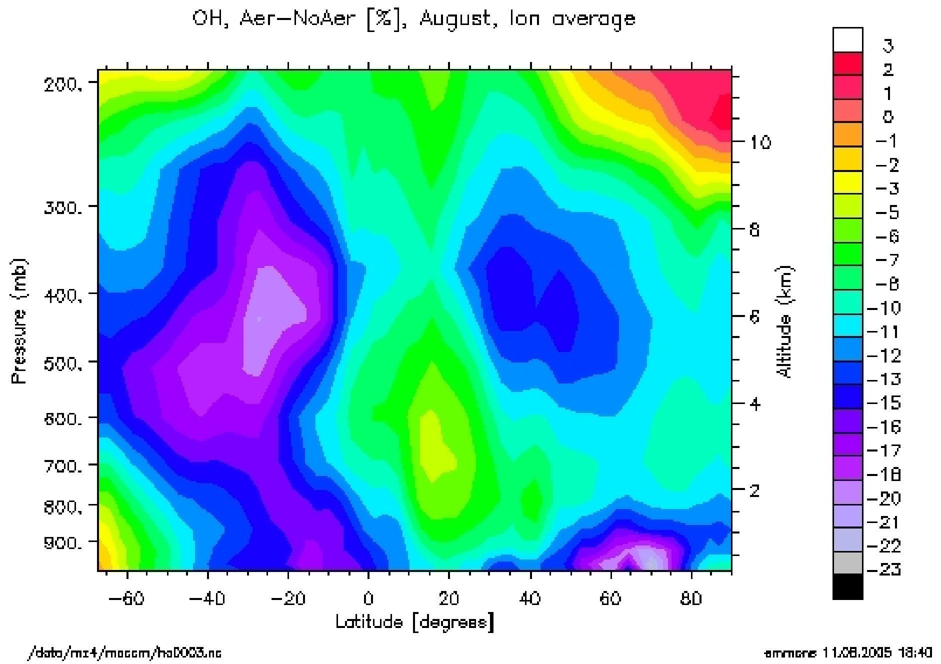
Overall Effect of Aerosols

[FTUV: Aerosols vs no aerosols]



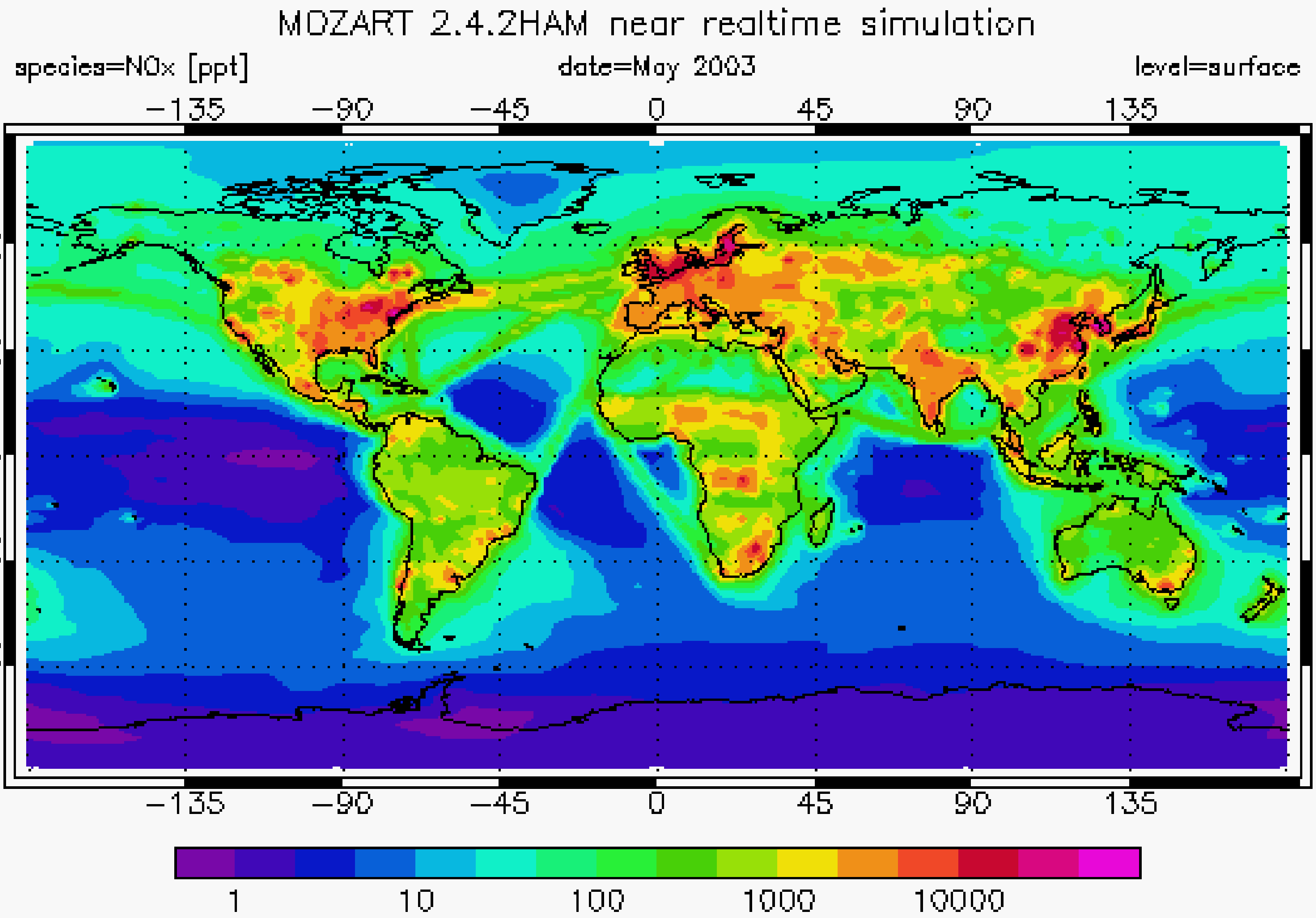




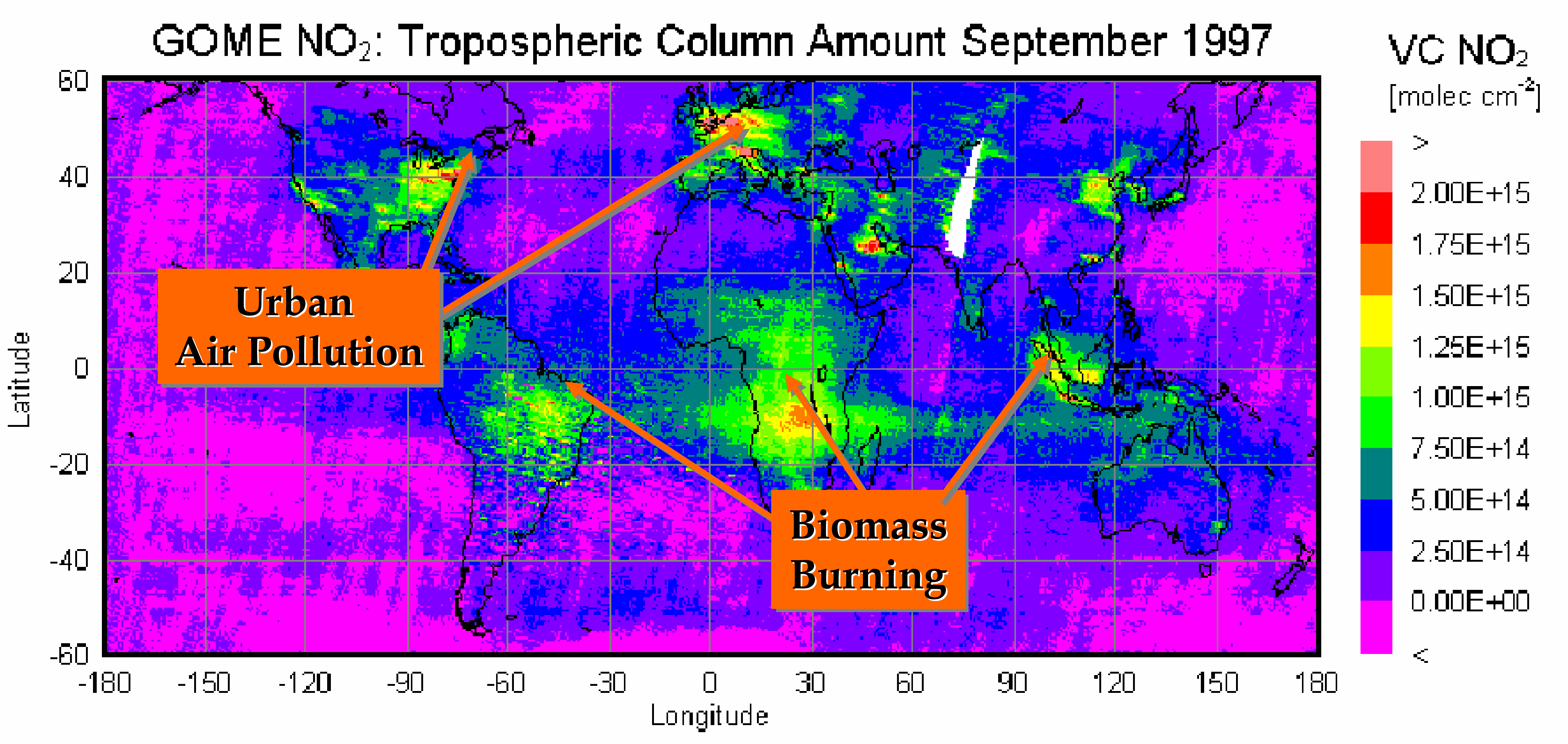


Results from MOZART-2

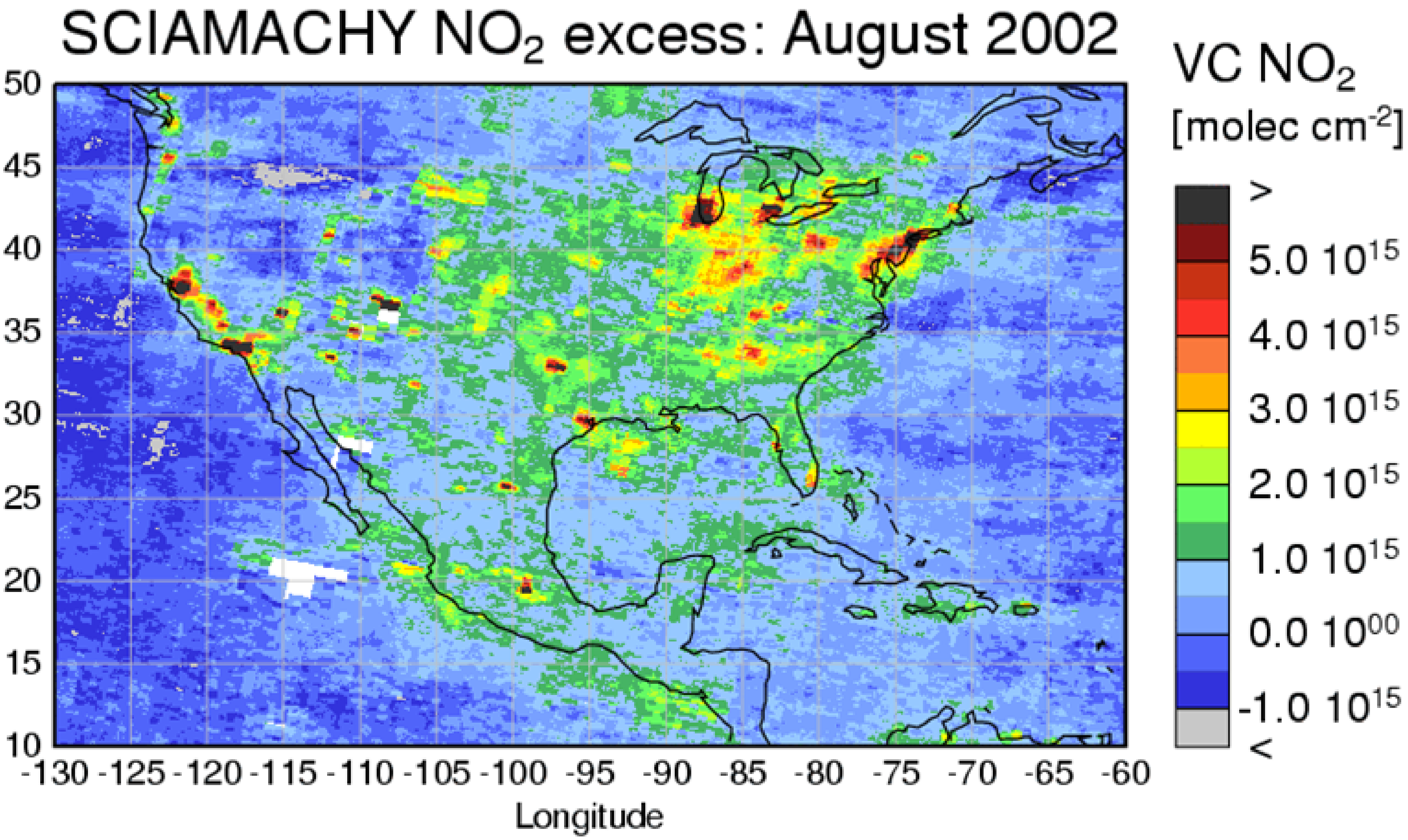
Nitrogen Oxides (pptv) May



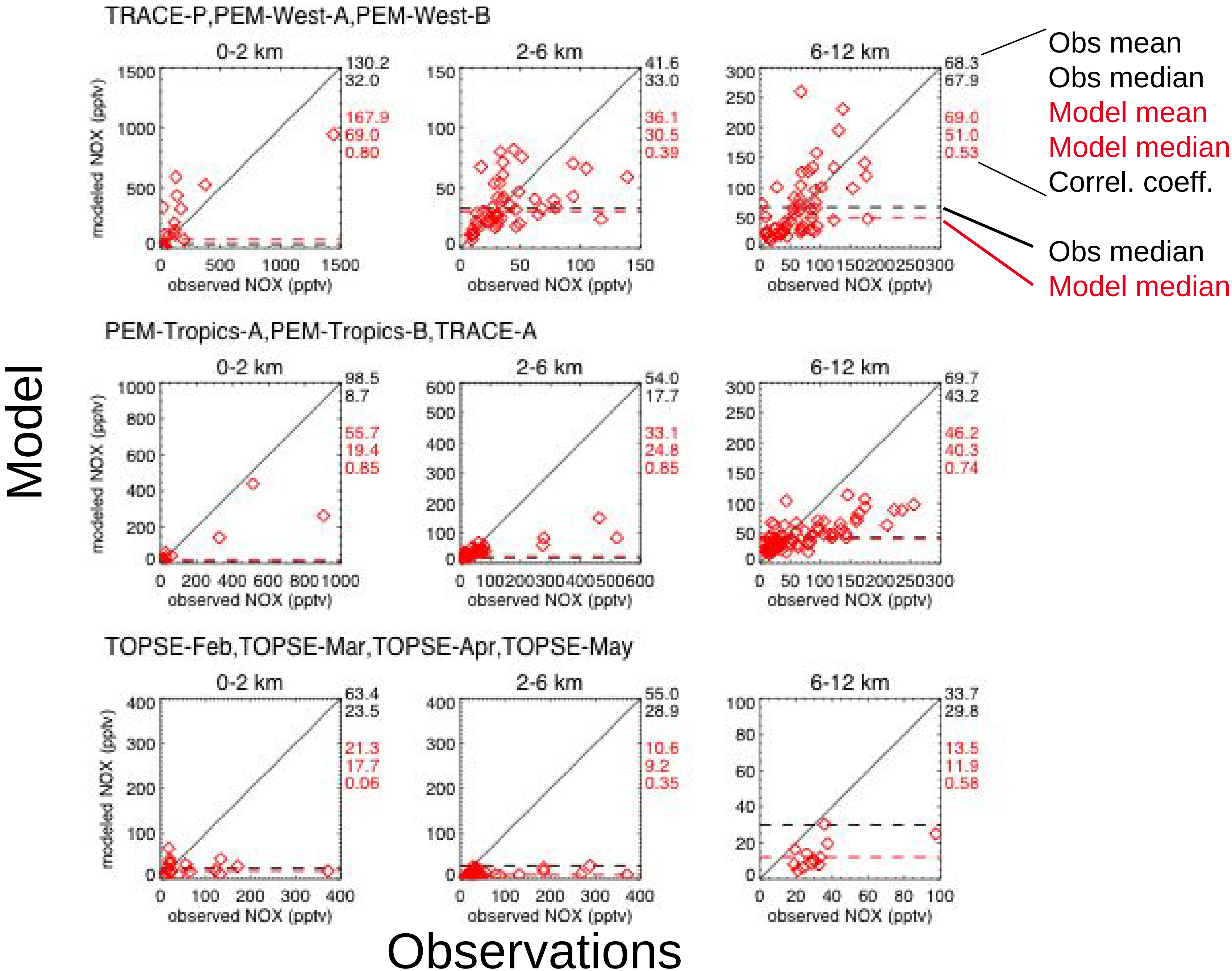
Example: Air Pollution and Biomass Burning



Chemical Weather seen from Space

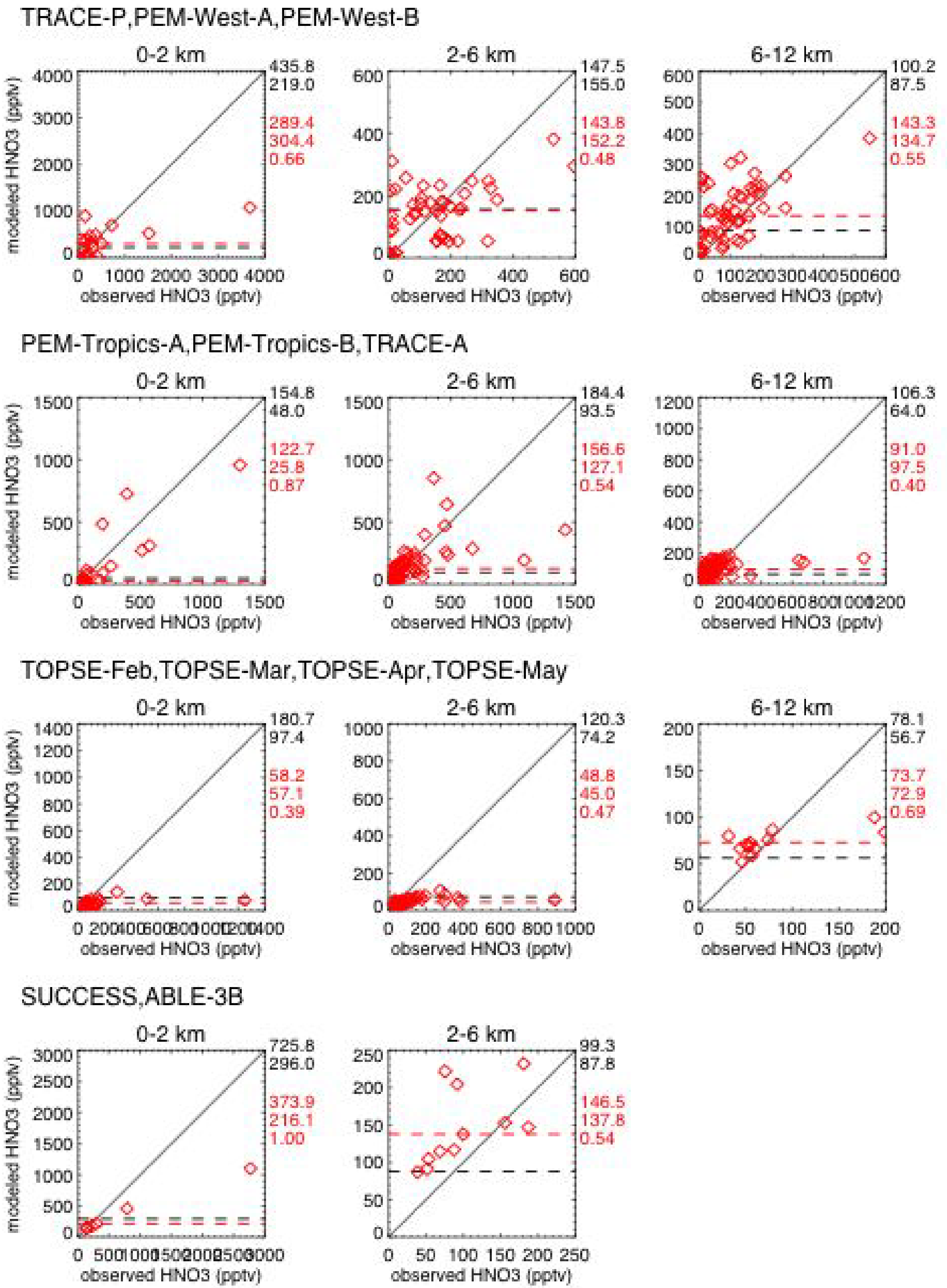


NOx



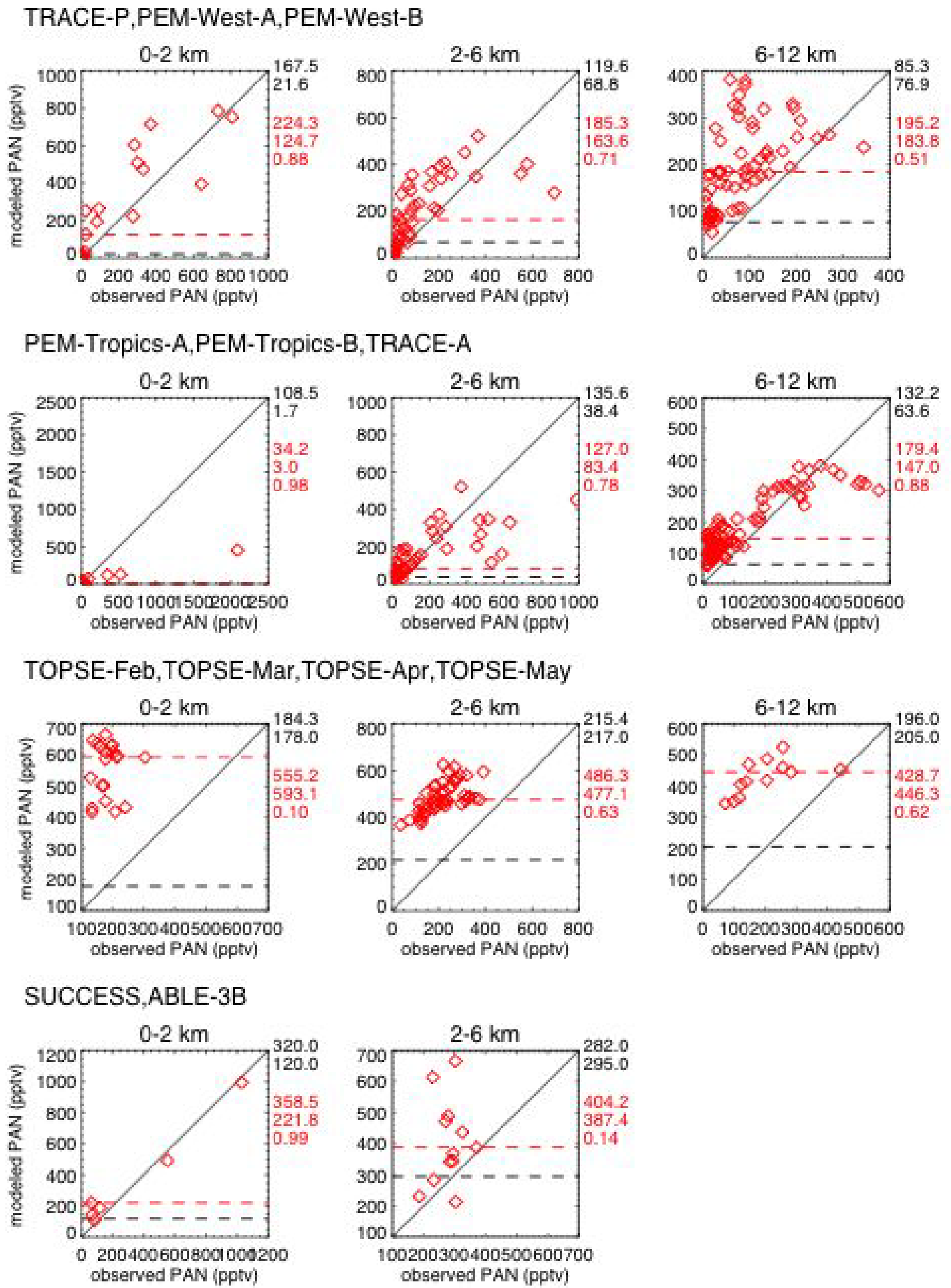
TRACE-P,PEM-West-A,PEM-West-B
0-2 km
130.2
32.0
167.9
69.0
0.80
2-6 km
41.6
33.0
36.1
30.5
0.39
6-12 km
68.3
67.9
69.0
51.0
0.53
Obs mean
Obs median
Model mean
Model median
Correl. coeff.
Obs median
Model median
PEM-Tropics-A,PEM-Tropics-B,TRACE-A
0-2 km
98.5
8.7
55.7
19.4
0.85
2-6 km
54.0
17.7
33.1
24.8
0.85
6-12 km
69.7
43.2
46.2
40.3
0.74
TOPSE-Feb,TOPSE-Mar,TOPSE-Apr,TOPSE-May
0-2 km
63.4
23.5
21.3
17.7
0.06
2-6 km
55.0
28.9
10.6
9.2
0.35
6-12 km
33.7
29.8
13.5
11.9
0.58
modeled NOX (pptv)
observed NOX (pptv)
Model
Observations

HNO_3

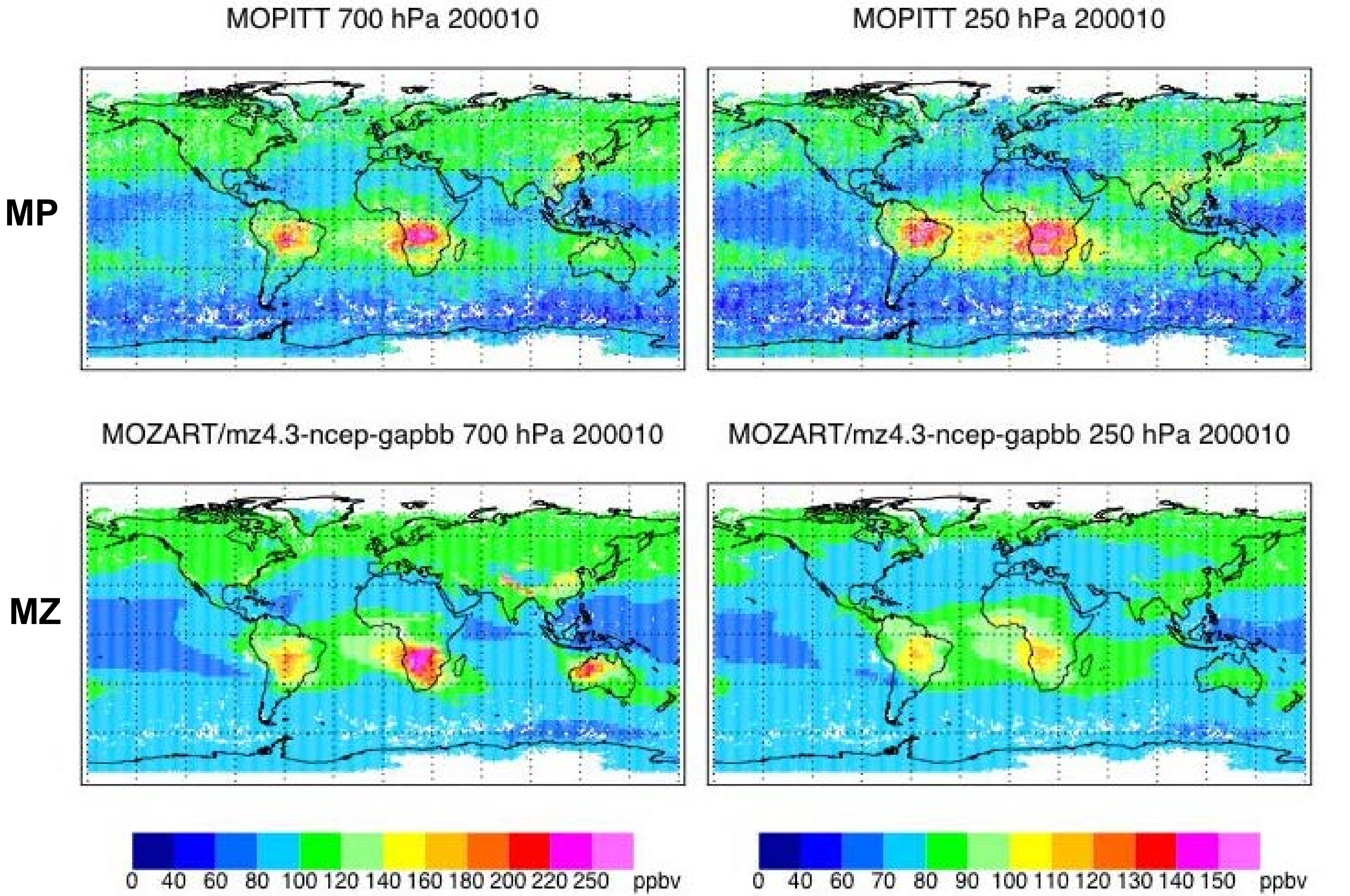


TRACE-P,PEM-West-A,PEM-West-B
0-2 km
2-6 km
6-12 km
435.8
219.0
289.4
304.4
0.66
147.5
155.0
143.8
152.2
0.48
100.2
87.5
143.3
134.7
0.55
PEM-Tropics-A,PEM-Tropics-B,TRACE-A
154.8
48.0
122.7
25.8
0.87
184.4
93.5
156.6
127.1
0.54
106.3
64.0
91.0
97.5
0.40
TOPSE-Feb,TOPSE-Mar,TOPSE-Apr,TOPSE-May
180.7
97.4
58.2
57.1
0.39
120.3
74.2
48.8
45.0
0.47
78.1
56.7
73.7
72.9
0.69
SUCCESS,ABLE-3B
725.8
296.0
373.9
216.1
1.00
99.3
87.8
146.5
137.8
0.54
modeled HNO3 (pptv)
observed HNO3 (pptv)

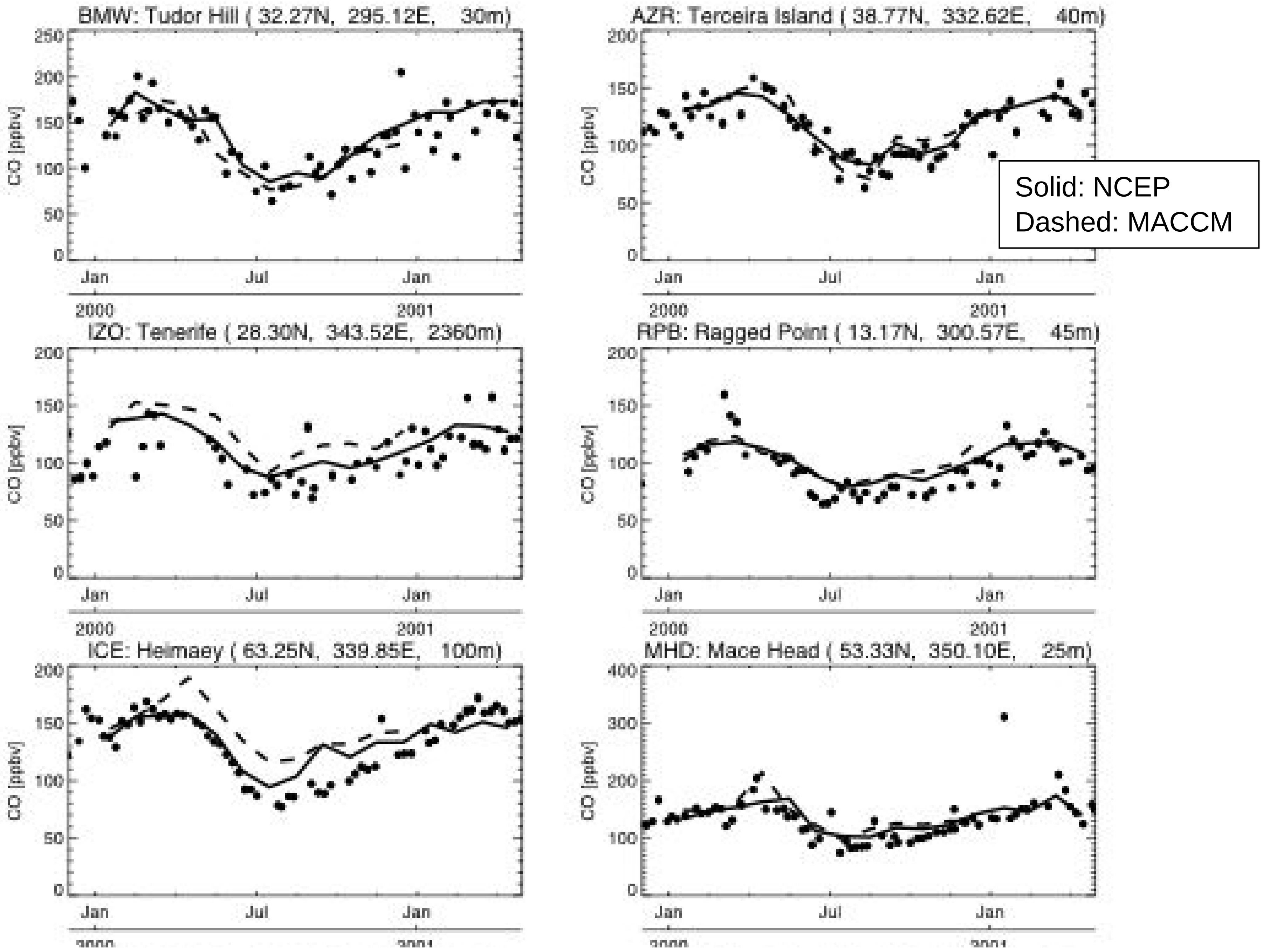
PAN


TRACE-P,PEM-West-A,PEM-West-B
0-2 km
167.5
21.6
224.3
124.7
0.88
2-6 km
119.6
68.8
185.3
163.6
0.71
6-12 km
85.3
76.9
195.2
183.8
0.51
PEM-Tropics-A,PEM-Tropics-B,TRACE-A
0-2 km
108.5
1.7
34.2
3.0
0.98
2-6 km
135.6
38.4
127.0
83.4
0.78
6-12 km
132.2
63.6
179.4
147.0
0.88
TOPSE-Feb,TOPSE-Mar,TOPSE-Apr,TOPSE-May
0-2 km
184.3
178.0
555.2
593.1
0.10
2-6 km
215.4
217.0
486.3
477.1
0.63
6-12 km
196.0
205.0
428.7
446.3
0.62
SUCCESS,ABLE-3B
0-2 km
320.0
120.0
358.5
221.8
0.99
2-6 km
282.0
295.0
404.2
387.4
0.14
modeled PAN (pptv)
observed PAN (pptv)

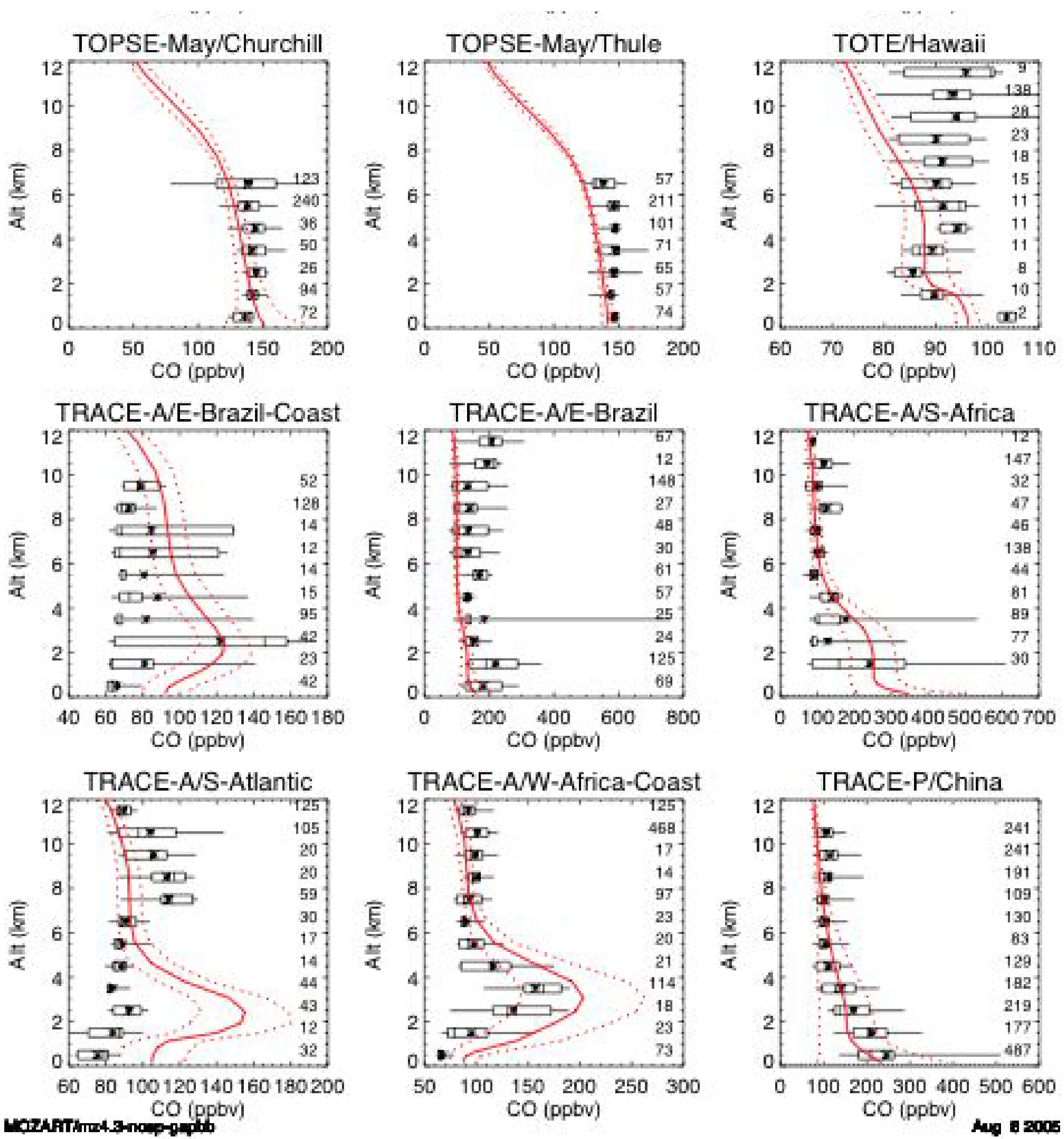
MOPITT - October 2000



CMDL CO - MZ4 - N.Atlantic

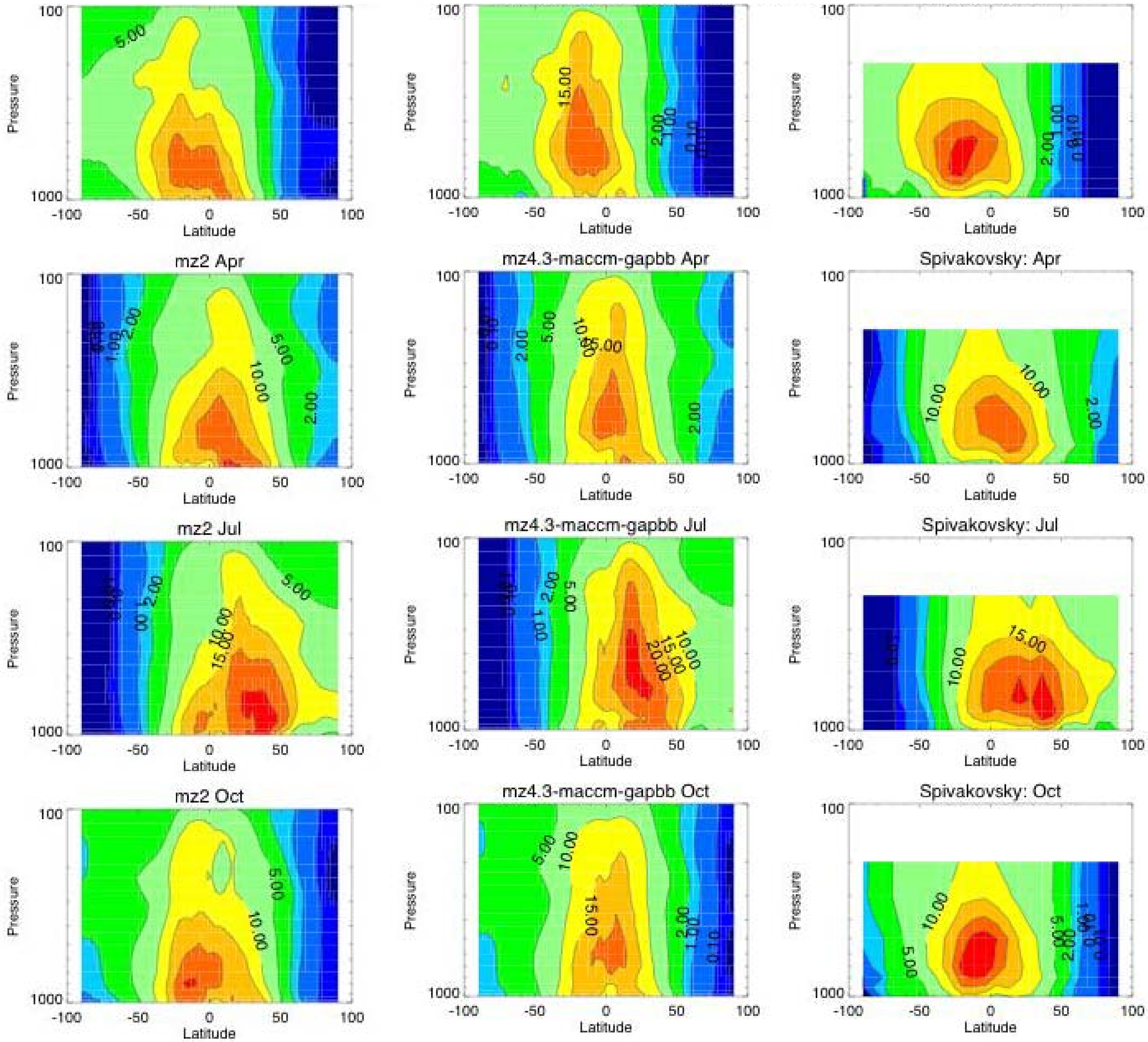


Comparison to aircraft data

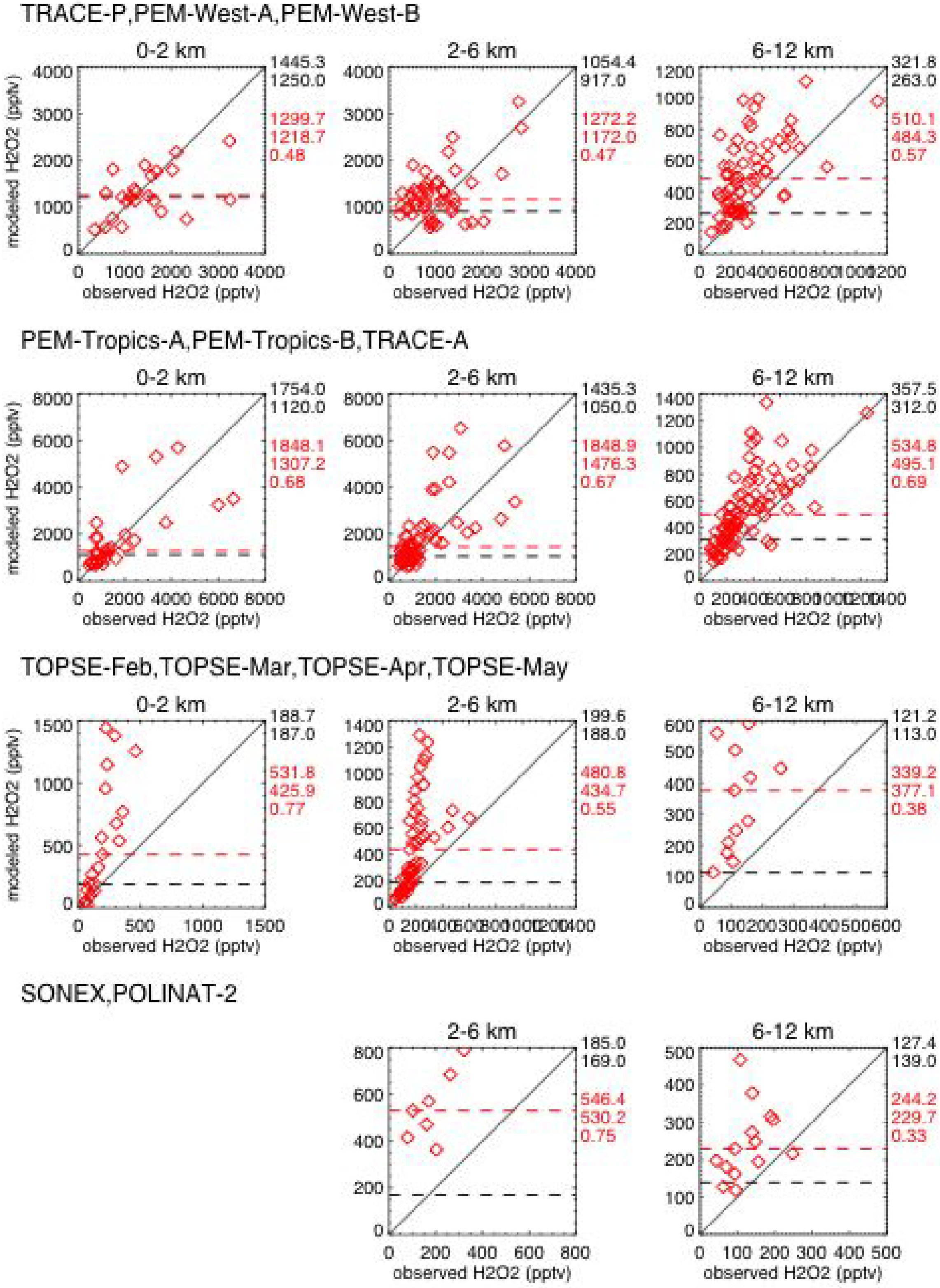


OH - Zonal Average (MACCM)

MOZART-2 MOZART-4 Spivakovsky

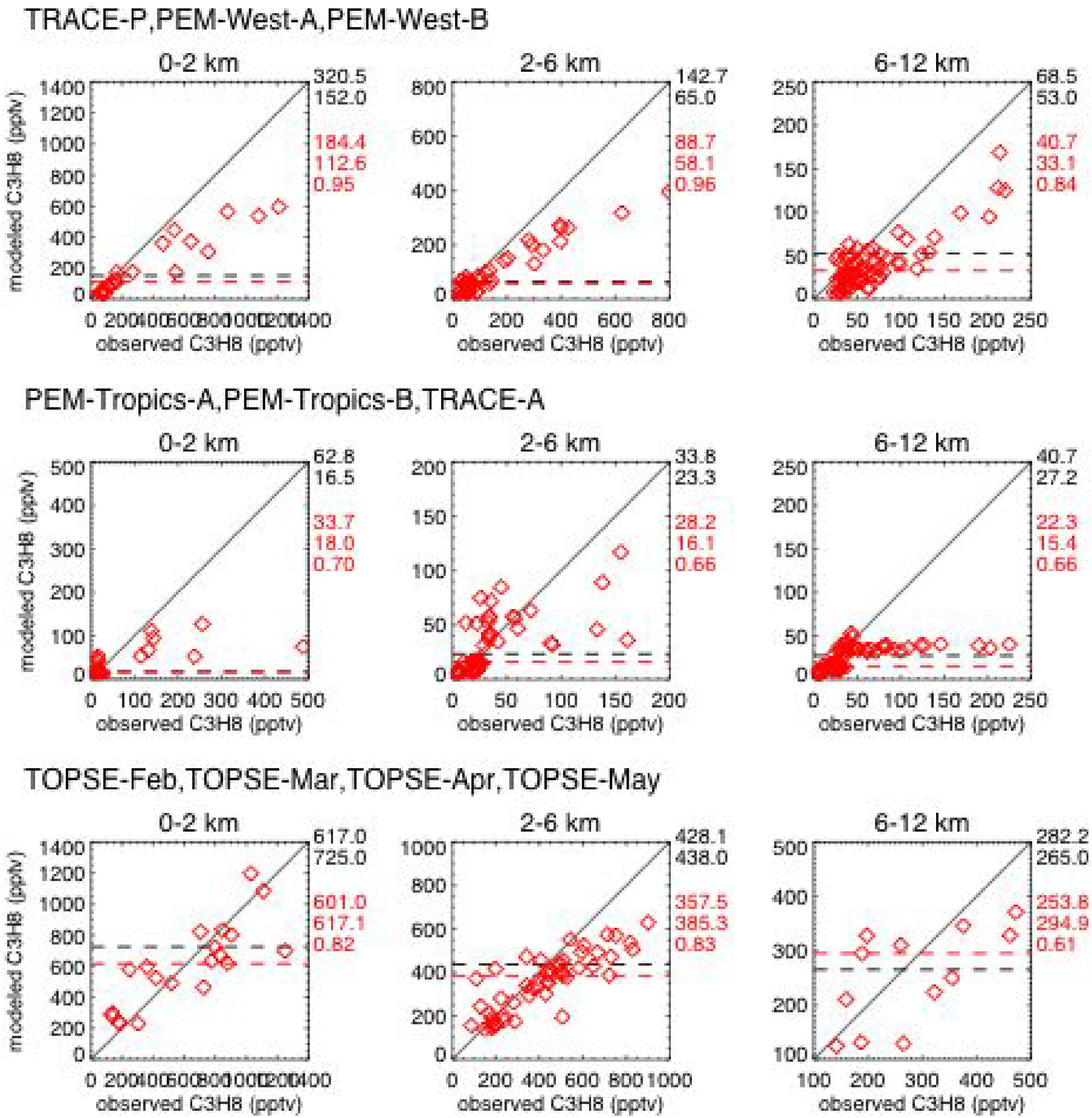


H2O2



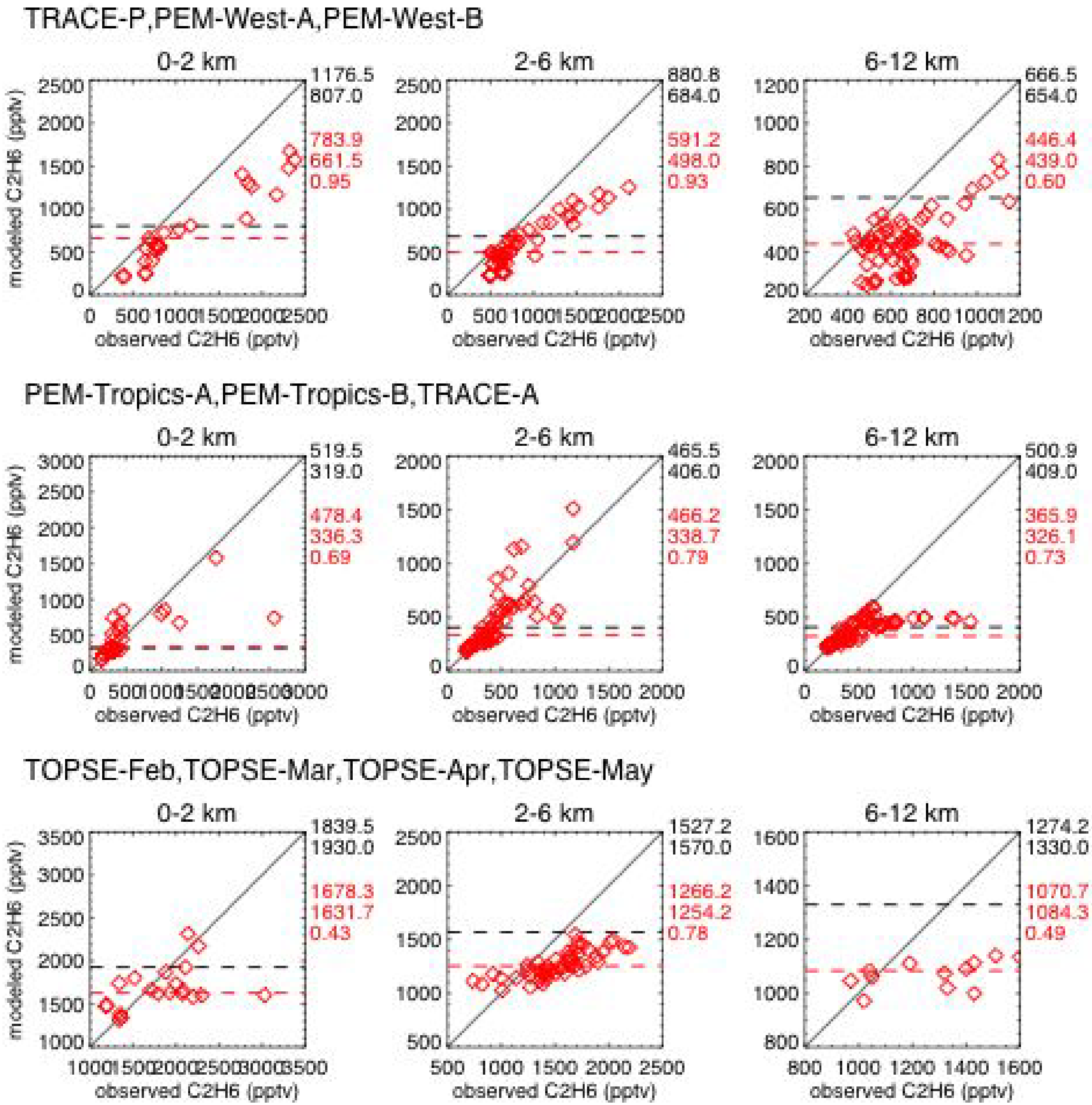
TRACE-P,PEM-West-A,PEM-West-B
0-2 km
2-6 km
6-12 km
1445.3
1250.0
1299.7
1218.7
0.48
1054.4
917.0
1272.2
1172.0
0.47
321.8
263.0
510.1
484.3
0.57
PEM-Tropics-A,PEM-Tropics-B,TRACE-A
0-2 km
2-6 km
6-12 km
1754.0
1120.0
1848.1
1307.2
0.68
1435.3
1050.0
1848.9
1476.3
0.67
357.5
312.0
534.8
495.1
0.69
TOPSE-Feb,TOPSE-Mar,TOPSE-Apr,TOPSE-May
0-2 km
2-6 km
6-12 km
188.7
187.0
531.8
425.9
0.77
199.6
188.0
480.8
434.7
0.55
121.2
113.0
339.2
377.1
0.38
SONEX,POLINAT-2
2-6 km
6-12 km
185.0
169.0
546.4
530.2
0.75
127.4
139.0
244.2
229.7
0.33
modeled H2O2 (pptv)
observed H2O2 (pptv)

C3H



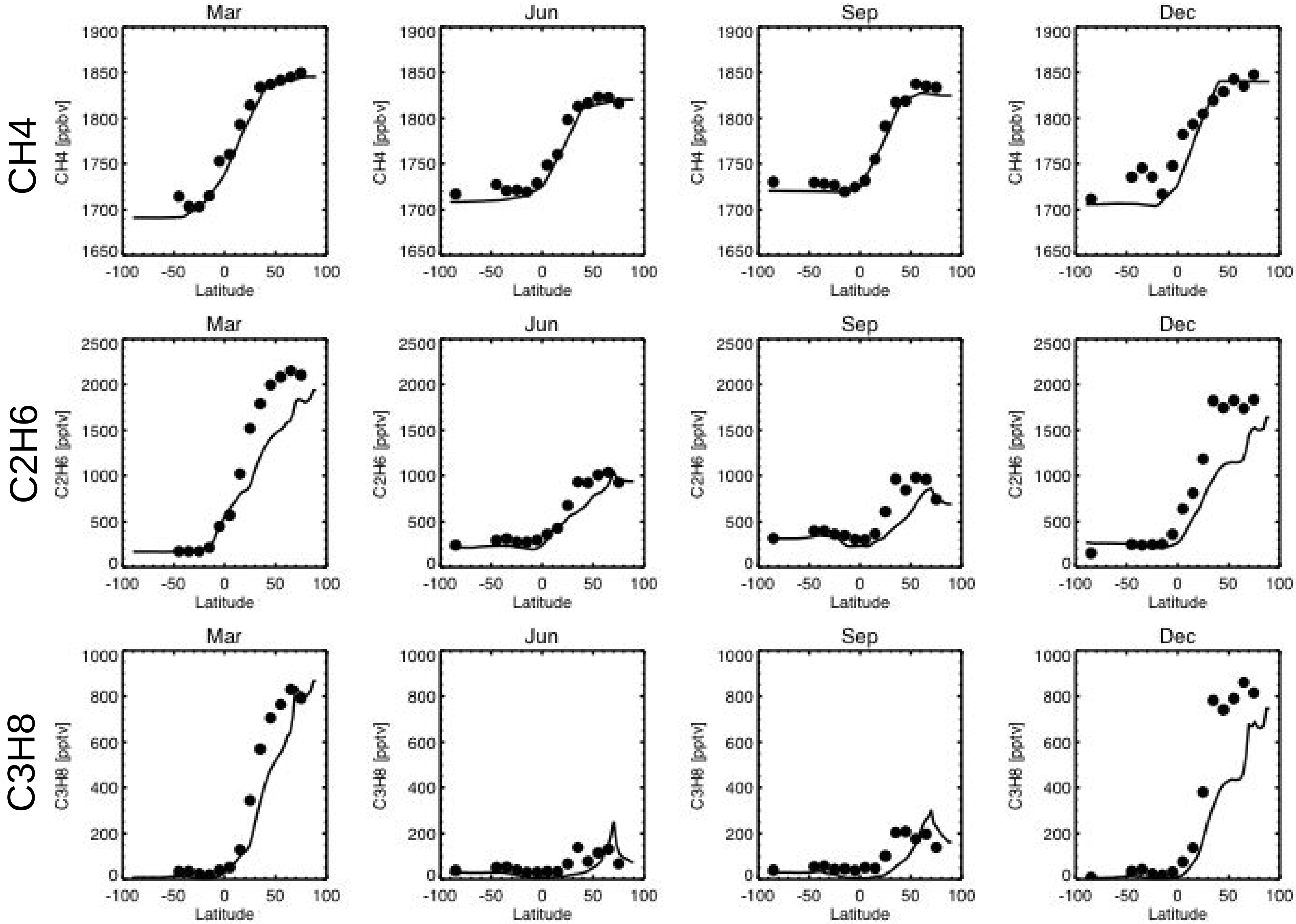
TRACE-P,PEM-West-A,PEM-West-B
0-2 km
2-6 km
6-12 km
320.5
152.0
184.4
112.6
0.95
142.7
65.0
88.7
58.1
0.96
68.5
53.0
40.7
33.1
0.84
PEM-Tropics-A,PEM-Tropics-B,TRACE-A
62.8
16.5
33.7
18.0
0.70
33.8
23.3
28.2
16.1
0.66
40.7
27.2
22.3
15.4
0.66
TOPSE-Feb,TOPSE-Mar,TOPSE-Apr,TOPSE-May
617.0
725.0
601.0
617.1
0.82
428.1
438.0
357.5
385.3
0.83
282.2
265.0
253.8
294.9
0.61
modeled C3H8 (pptv)
observed C3H8 (pptv)

C2H6

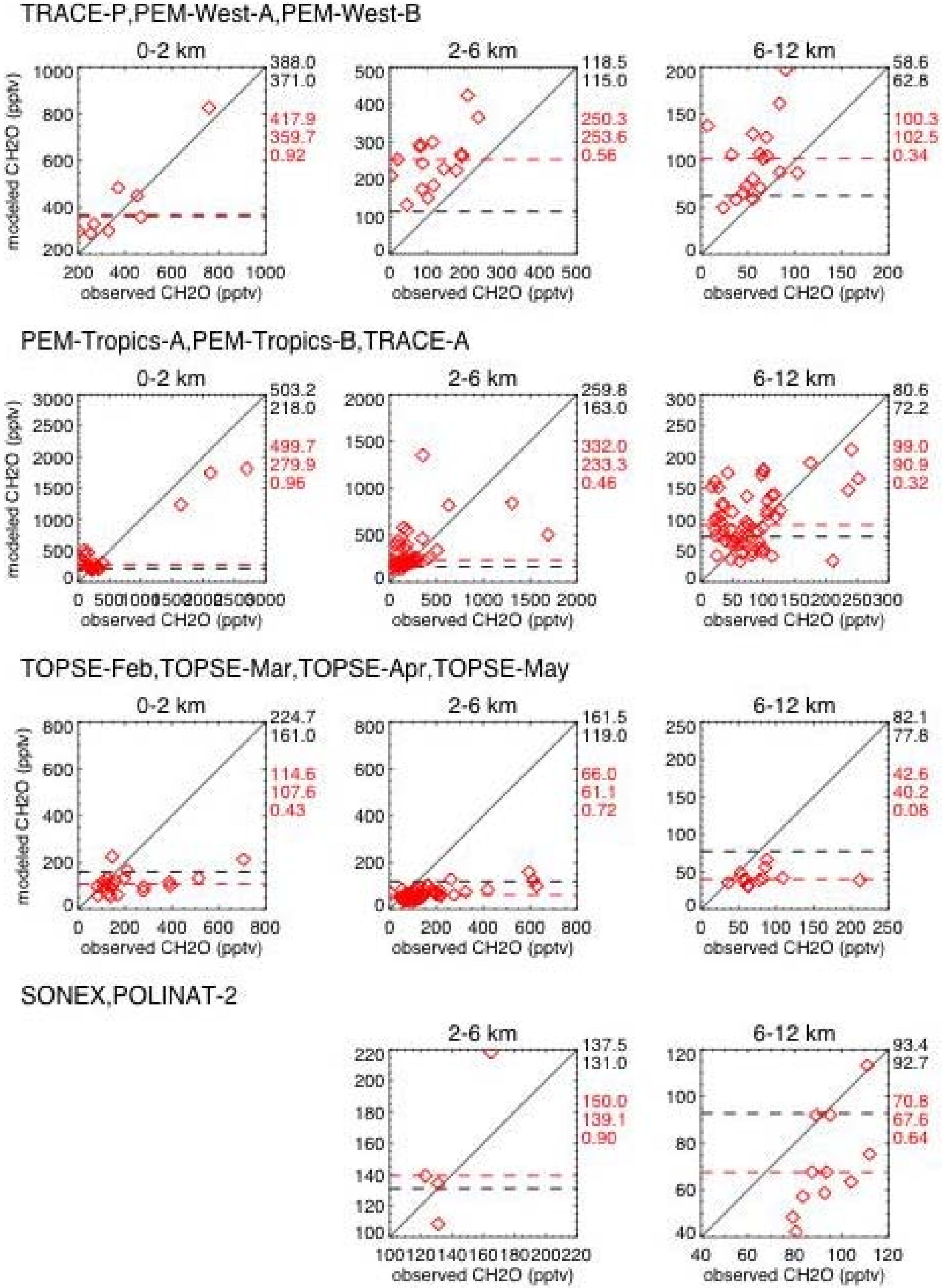


TRACE-P,PEM-West-A,PEM-West-B
0-2 km
2-6 km
6-12 km
1176.5
807.0
783.9
661.5
0.95
880.8
684.0
591.2
498.0
0.93
666.5
654.0
446.4
439.0
0.60
PEM-Tropics-A,PEM-Tropics-B,TRACE-A
519.5
319.0
478.4
336.3
0.69
465.5
406.0
466.2
338.7
0.79
500.9
409.0
365.9
326.1
0.73
TOPSE-Feb,TOPSE-Mar,TOPSE-Apr,TOPSE-May
1839.5
1930.0
1678.3
1631.7
0.43
1527.2
1570.0
1266.2
1254.2
0.78
1274.2
1330.0
1070.7
1084.3
0.49
modeled C2H6 (pptv)
observed C2H6 (pptv)

UC-Irvine HCs in remote Pacific

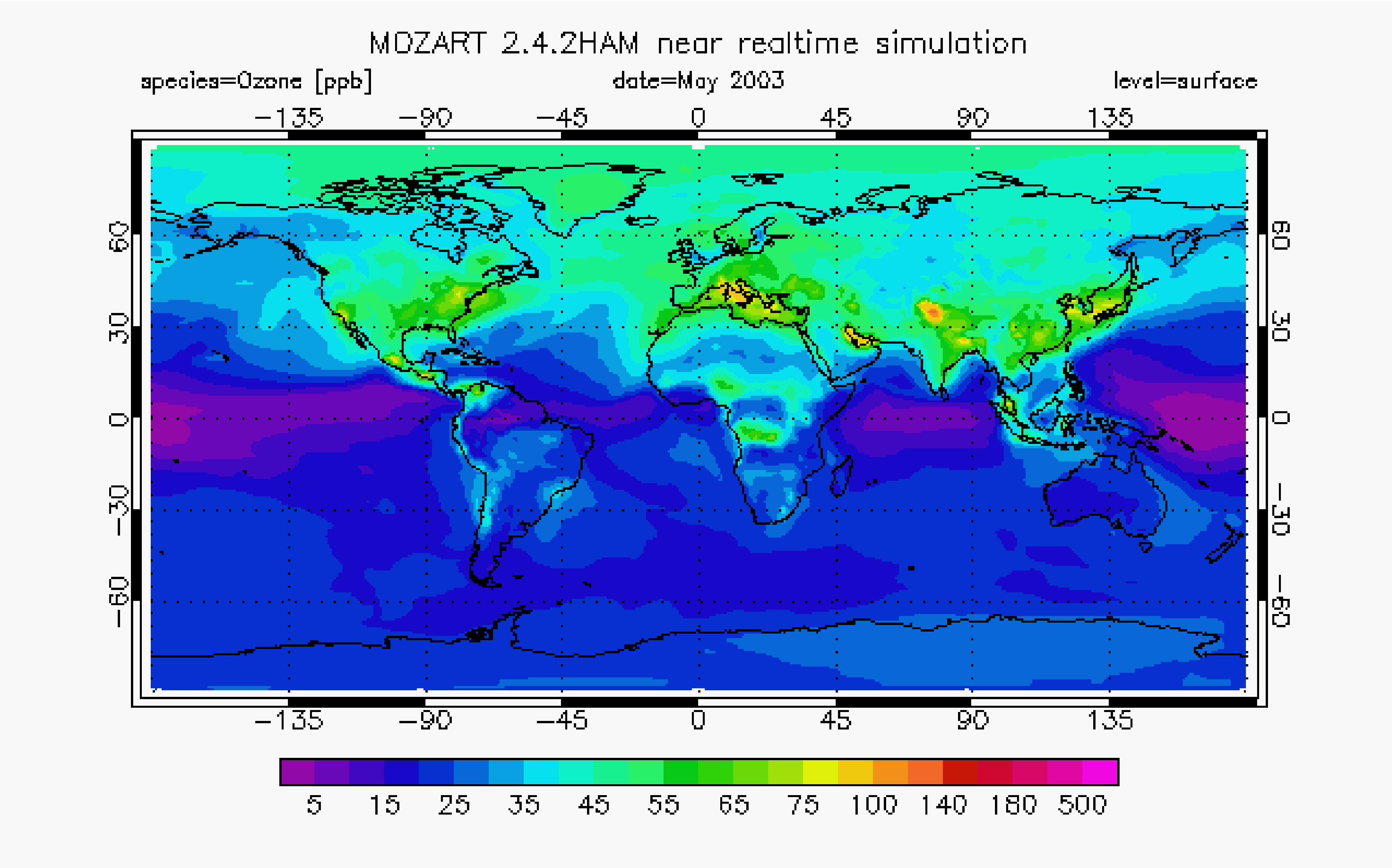


CH2O

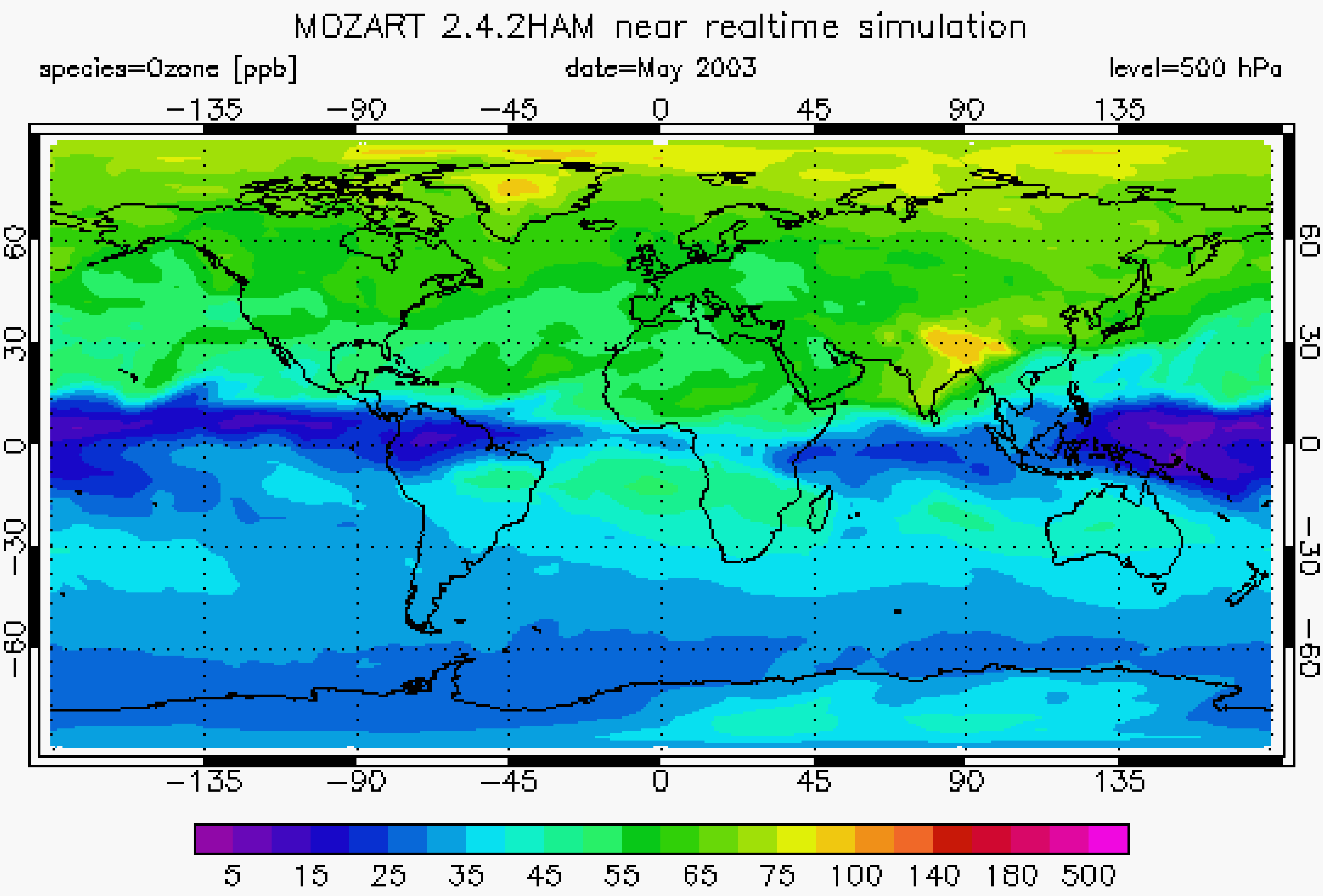


TRACE-P,PEM-West-A,PEM-West-B
0-2 km
2-6 km
6-12 km
388.0
371.0
417.9
359.7
0.92
118.5
115.0
250.3
253.6
0.56
58.6
62.8
100.3
102.5
0.34
PEM-Tropics-A,PEM-Tropics-B,TRACE-A
503.2
218.0
499.7
279.9
0.96
259.8
163.0
332.0
233.3
0.46
80.6
72.2
99.0
90.9
0.32
TOPSE-Feb,TOPSE-Mar,TOPSE-Apr,TOPSE-May
224.7
161.0
114.6
107.6
0.43
161.5
119.0
66.0
61.1
0.72
82.1
77.8
42.6
40.2
0.08
SONEX,POLINAT-2
137.5
131.0
150.0
139.1
0.90
93.4
92.7
70.8
67.6
0.64
modeled CH2O (pptv)
observed CH2O (pptv)

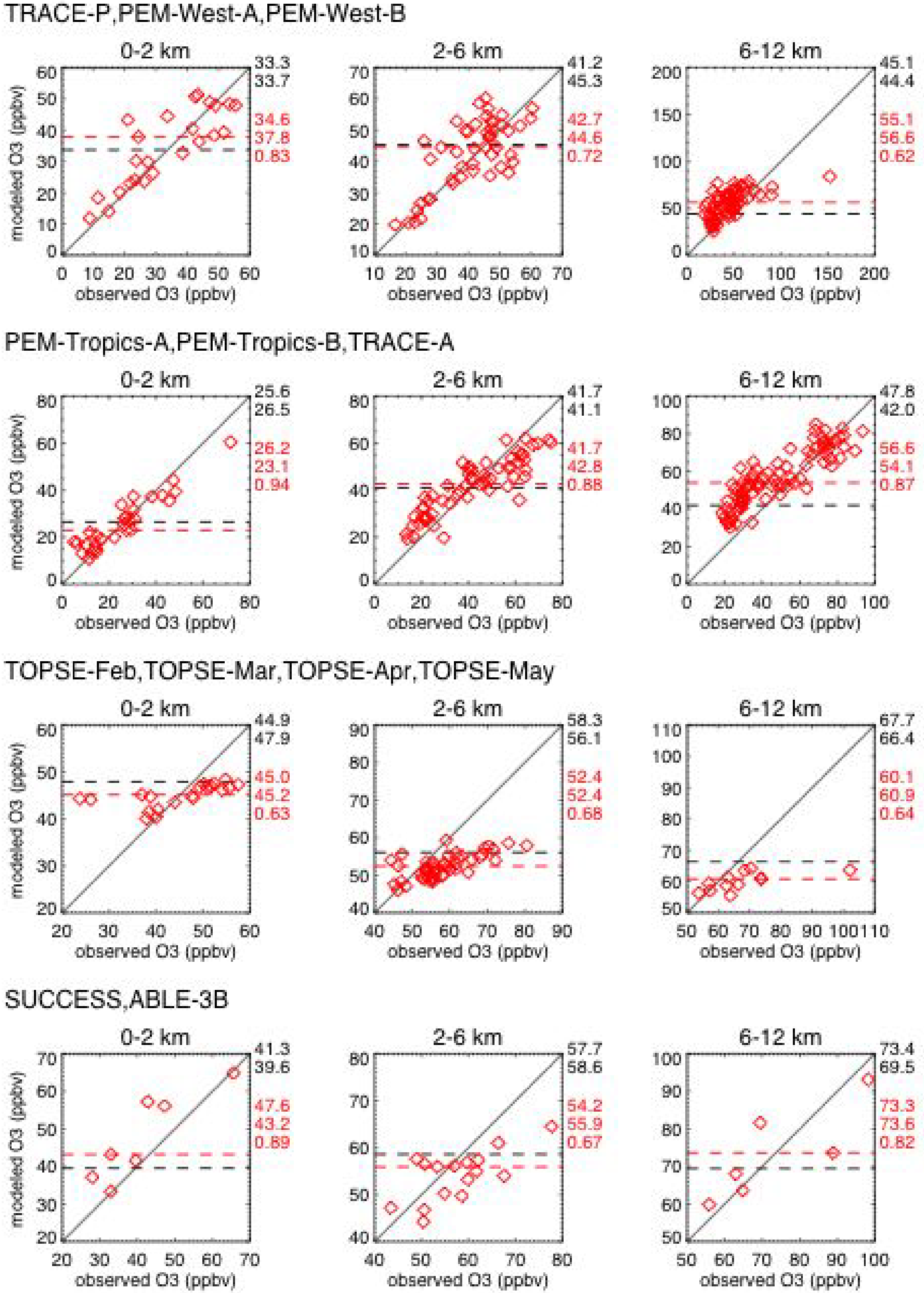
Ozone (ppbv) -- May Surface



Ozone (ppbv) -- May 500 hPa

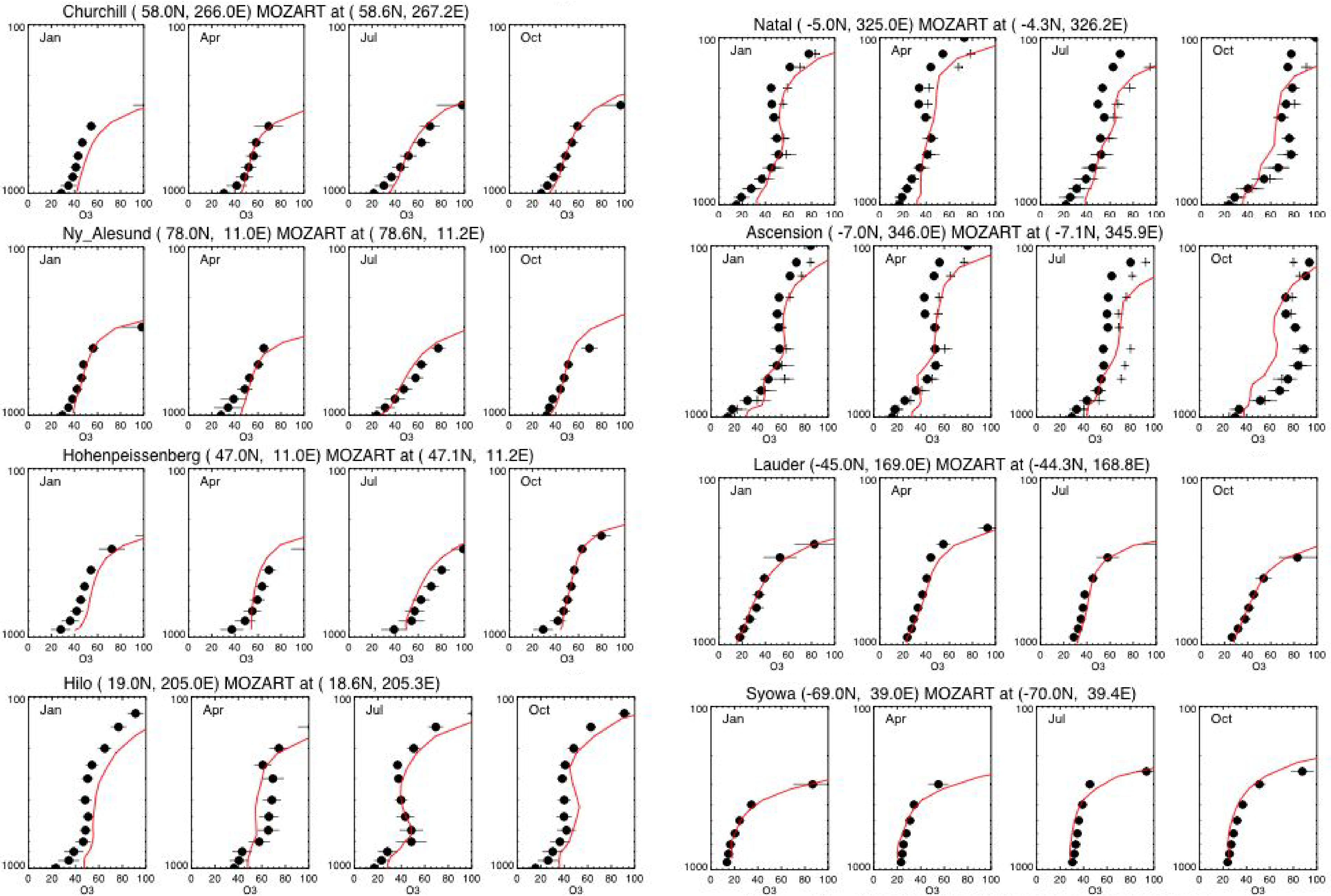


Ozone

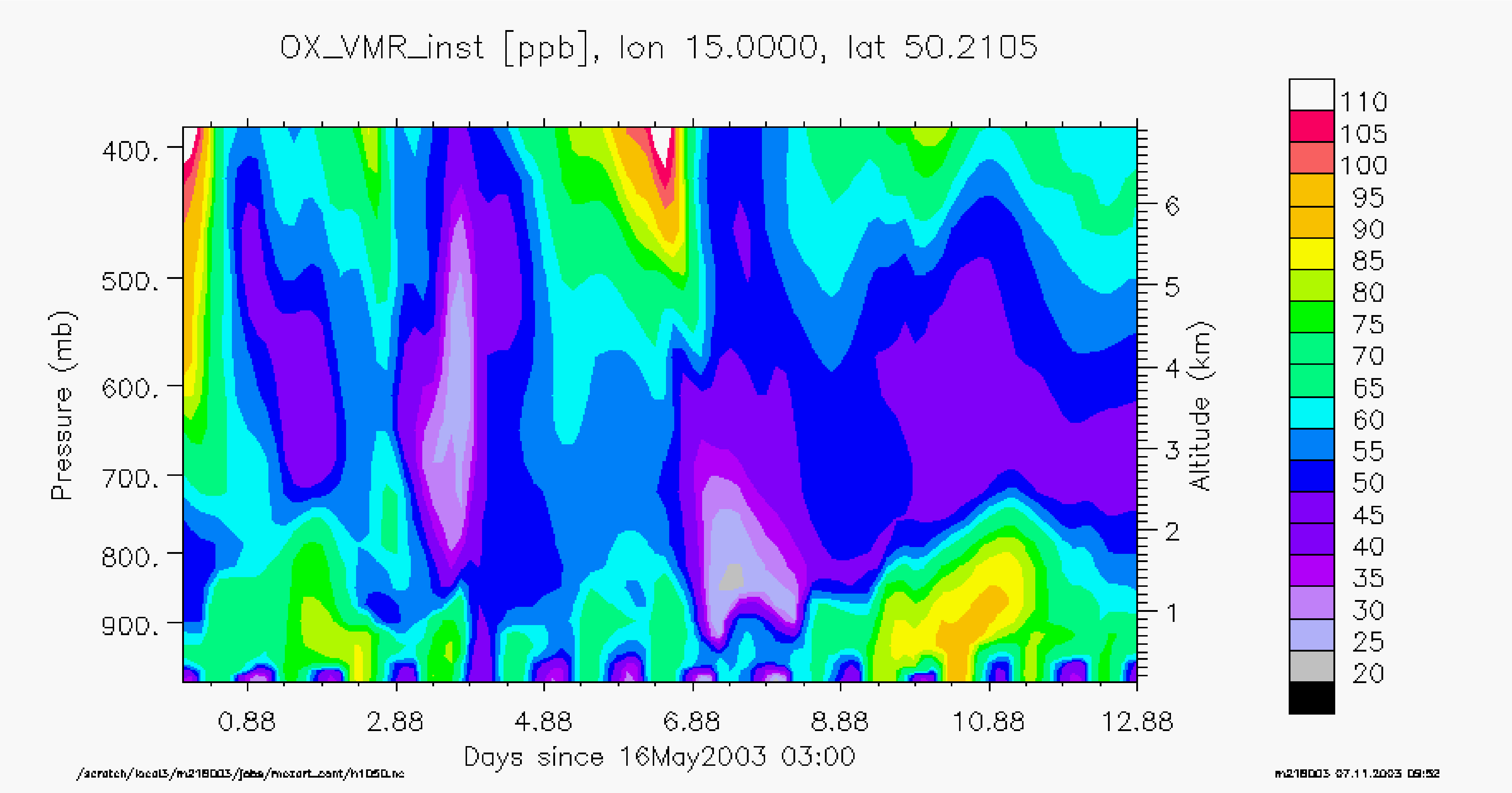


TRACE-P,PEM-West-A,PEM-West-B
0-2 km
33.3
33.7
34.6
37.8
0.83
2-6 km
41.2
45.3
42.7
44.6
0.72
6-12 km
45.1
44.4
55.1
56.6
0.62
PEM-Tropics-A,PEM-Tropics-B,TRACE-A
0-2 km
25.6
26.5
26.2
23.1
0.94
2-6 km
41.7
41.1
41.7
42.8
0.88
6-12 km
47.8
42.0
56.6
54.1
0.87
TOPSE-Feb,TOPSE-Mar,TOPSE-Apr,TOPSE-May
0-2 km
44.9
47.9
45.0
45.2
0.63
2-6 km
58.3
56.1
52.4
52.4
0.68
6-12 km
67.7
66.4
60.1
60.9
0.64
SUCCESS,ABLE-3B
0-2 km
41.3
39.6
47.6
43.2
0.89
2-6 km
57.7
58.6
54.2
55.9
0.67
6-12 km
73.4
69.5
73.3
73.6
0.82
modeled O3 (ppbv)
observed O3 (ppbv)

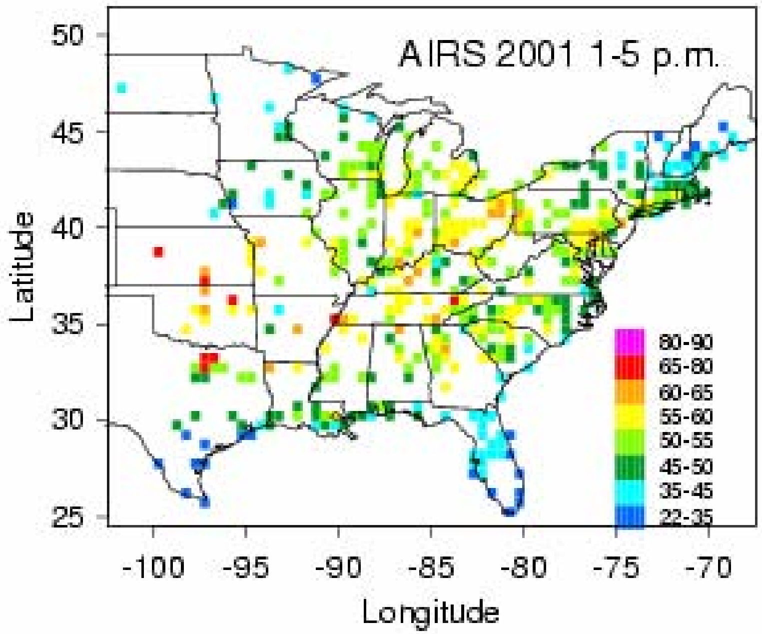
Ozone

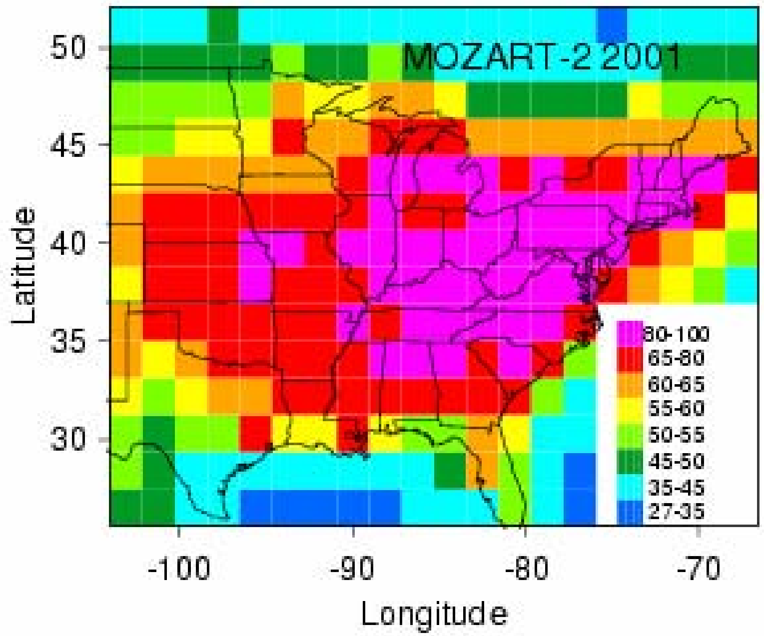

Churchill (58.0N, 266.0E) MOZART at (58.6N, 267.2E)
Ny_Alesund (78.0N, 11.0E) MOZART at (78.6N, 11.2E)
Hohenpeissenberg (47.0N, 11.0E) MOZART at (47.1N, 11.2E)
Hilo (19.0N, 205.0E) MOZART at (18.6N, 205.3E)
Natal (-5.0N, 325.0E) MOZART at (-4.3N, 326.2E)
Ascension (-7.0N, 346.0E) MOZART at (-7.1N, 345.9E)
Lauder (-45.0N, 169.0E) MOZART at (-44.3N, 168.8E)
Syowa (-69.0N, 39.0E) MOZART at (-70.0N, 39.4E)
Jan
Apr
Jul
Oct
100
1000
0 20 40 60 80 100
O3

Ozone Lindenberg, May 2003

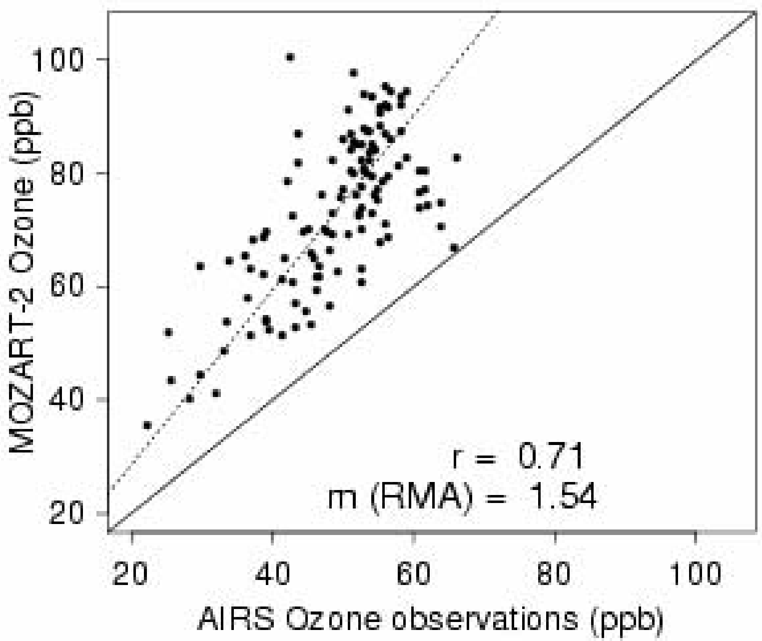


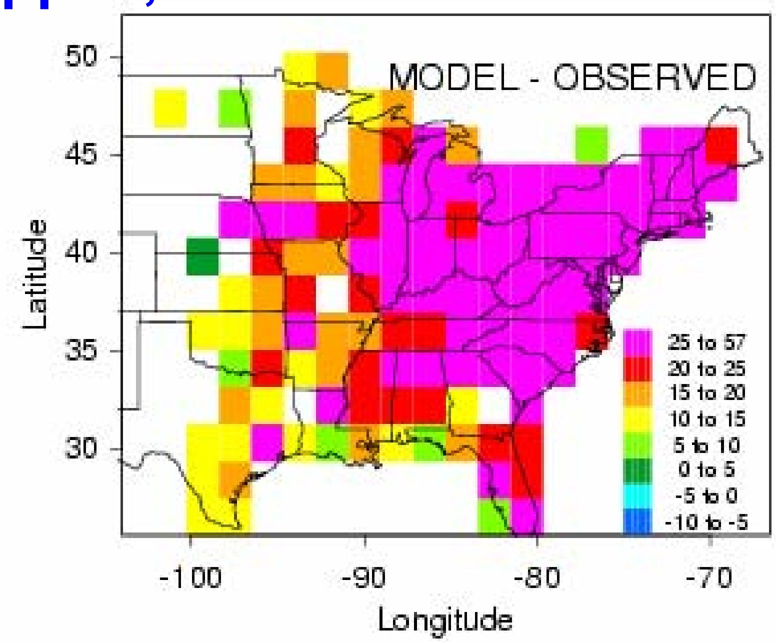
MOZART-2 Comparison with AIRS: July 2001 1-5 p.m. Surface O_3 (ppbv)



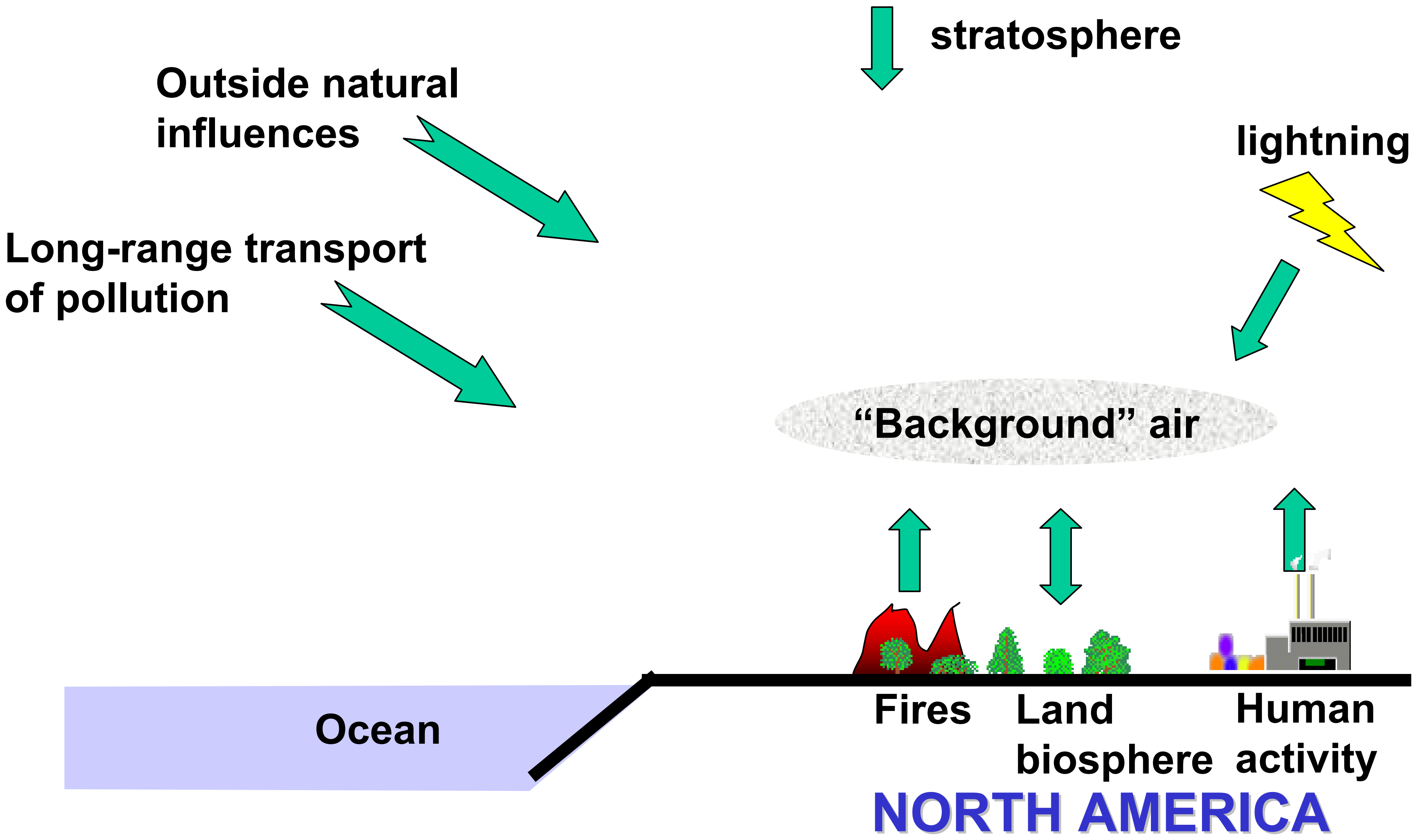


Mean Bias = 24±10 ppbv; r^2 = 0.50





Processes Contributing to Surface Ozone over North America



Isoprene Nitrates

ISOPO2 + NO $\rightarrow$ .08*ONITR + .92*NO2 + HO2 + .55*CH2O + .32*MVK + .37*HYDRALD

ONITR + OH $\rightarrow$ HYDRALD + .4*NO2 + HO2

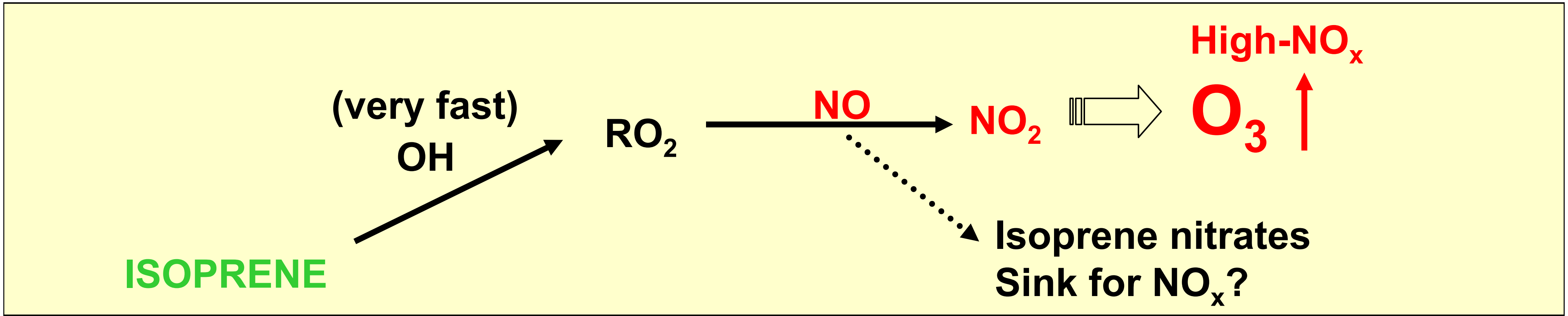
ONITR + NO3 $\rightarrow$ HYDRALD + NO2 + HO2

ISOPNO3 + NO $\rightarrow$ 1.206*NO2 + .794*ONITR + 0.794*HO2 + .072*CH2O + .039*MVK

ISOPNO3 + NO3 $\rightarrow$

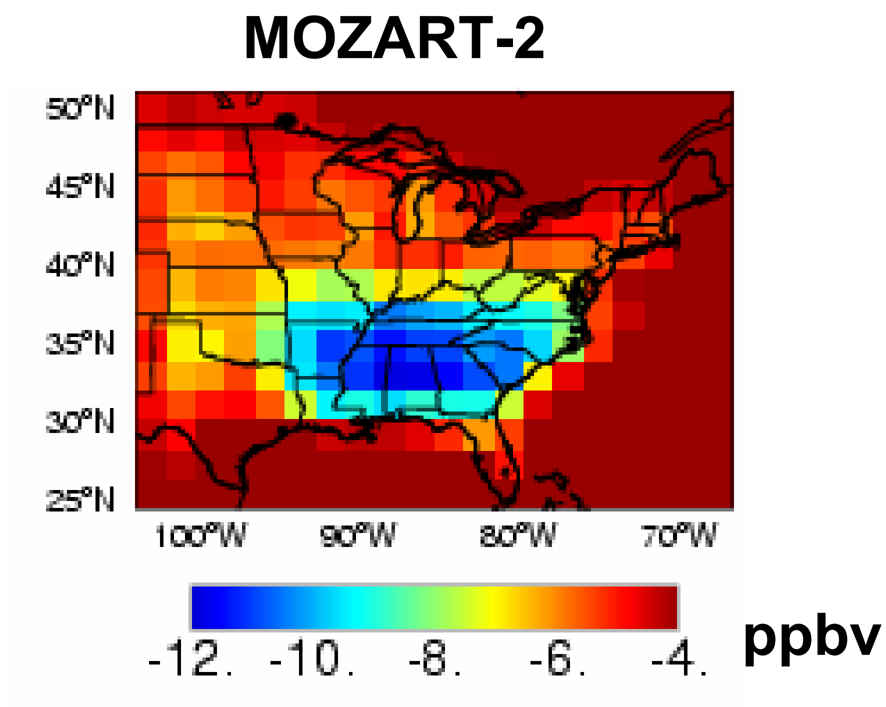
ISOPNO3 + HO2 $\rightarrow$ .206*NO2 + .794*ONITR +

Substantial O_3 sensitivity to the uncertain fate (and yield) of organic isoprene nitrates



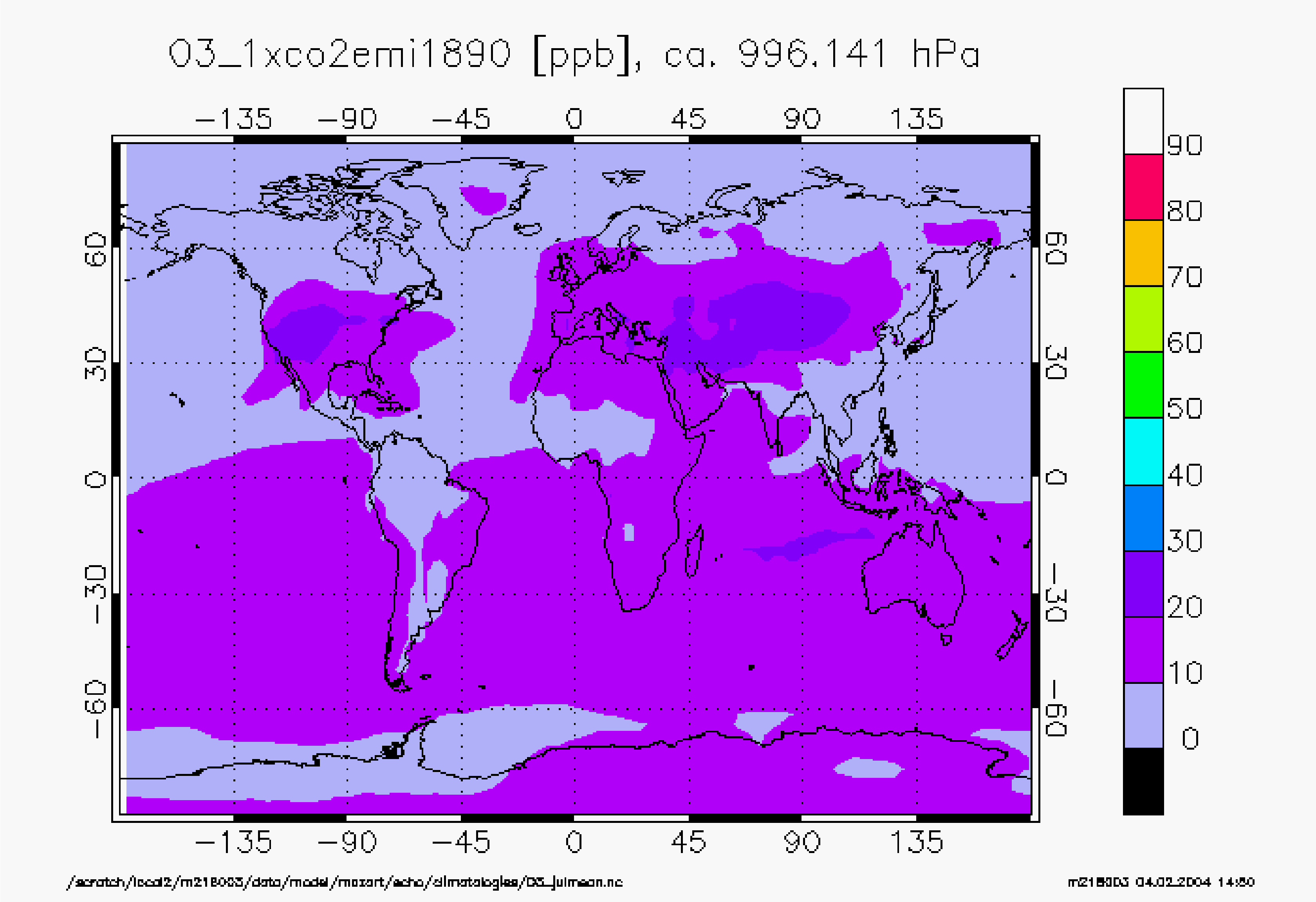
Change in July mean 1-5 p.m. surface O_3 when isoprene nitrates (at 12% yield) act as a NO_x sink

→ 4-12 ppbv impact!

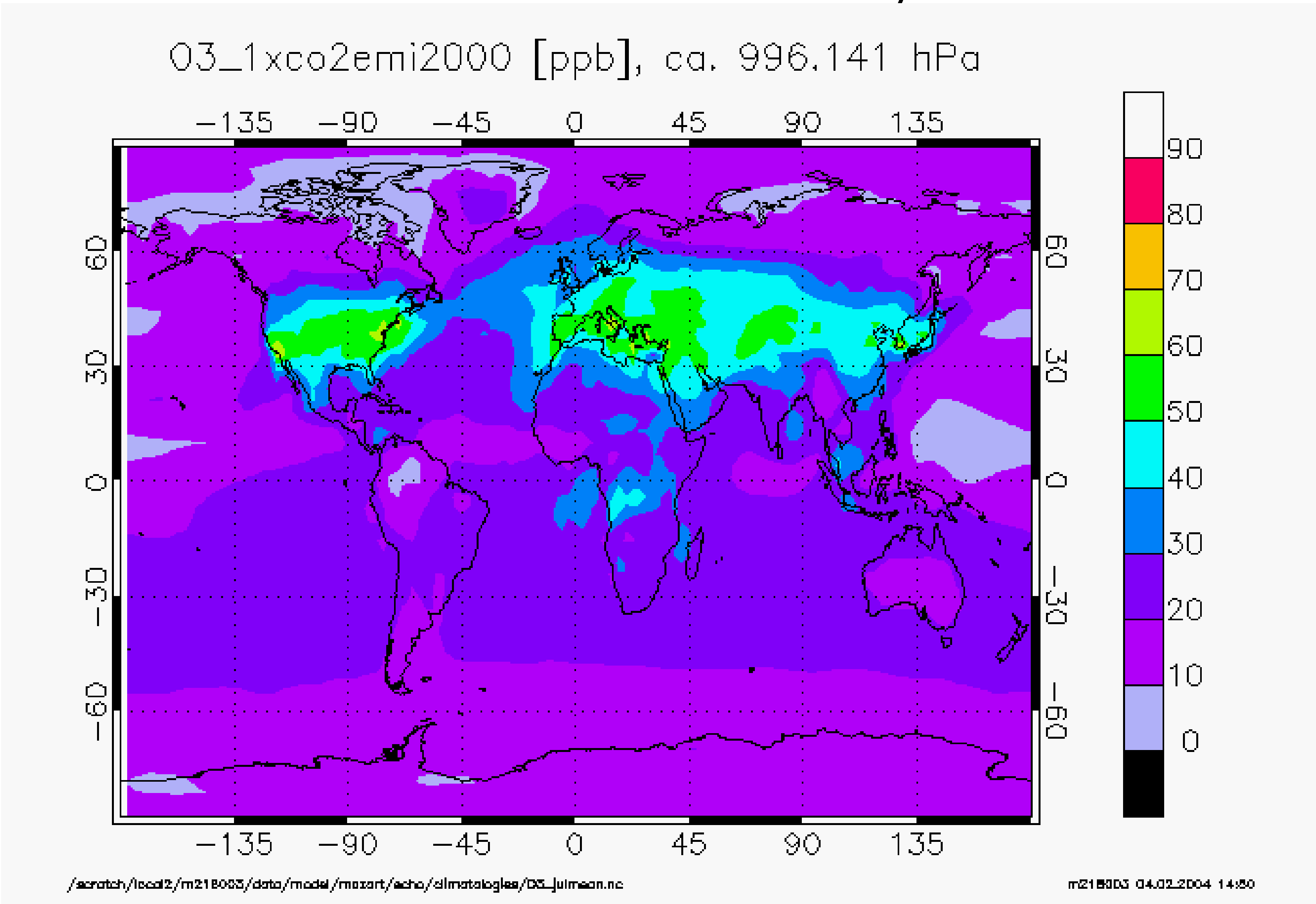


Fiore et al., *JGR*, 2005

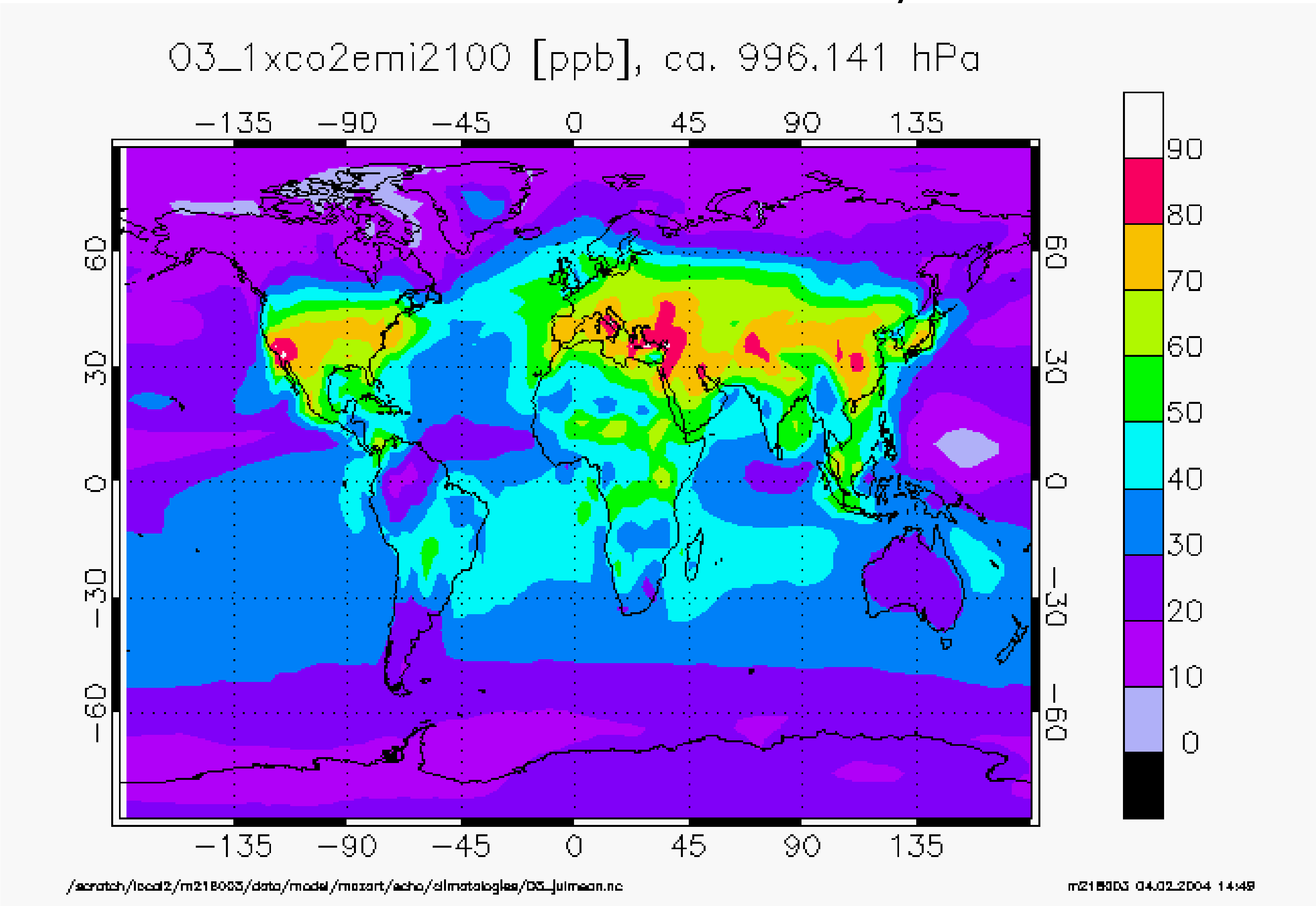
Surface Ozone July 1890



Surface Ozone July 2000



Surface Ozone July 2100



A2 Scenario SRES

-3

Surface to 80 km

MOZART-3 Set-up

- Extension of Tropospheric MOZART-2 and -4

  - 106 Species Mechanism (250 chemical and photochemical reactions- JPL-02).

    CO, CO_2, CH_4, H_2O, N_2O, CFC-11, CFC-12, CFC-113, HCFC-22, CH_3Cl, MCF, CCl_4, CH_3Br, H1211, H1301, organics

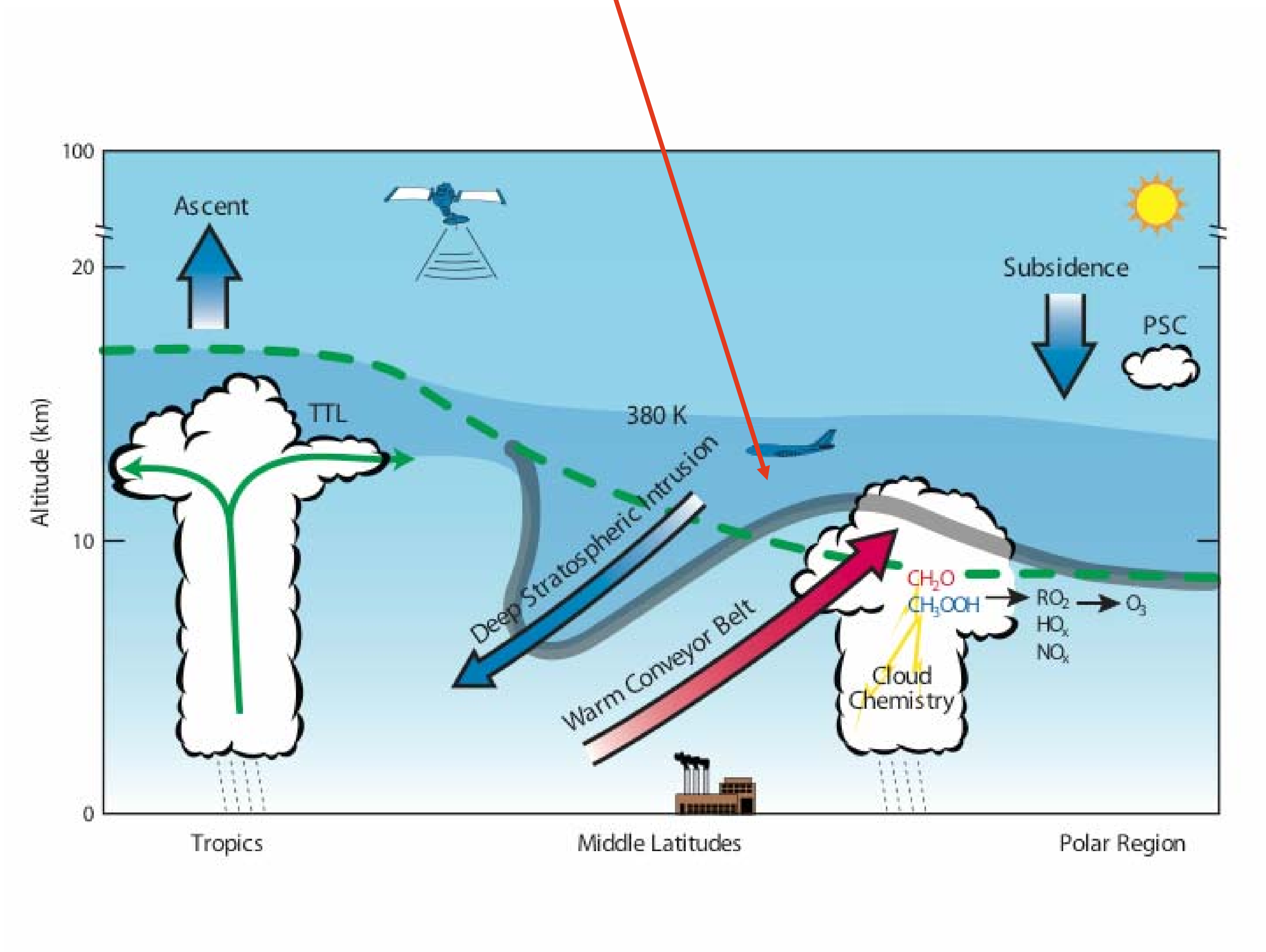
  - Radicals contained in: Ox, HOx, NOx, ClOx, and BrOx families

  - Heterogeneous Chemistry: Includes sulfate, nitric acid hydrate, and H_2O-ice aerosols

MOZART-3 Set-up

- Extension of Tropospheric MOZART-2 and -4
- Look-up table parameterization (STUV; 4-stream; 121-750nm)
- Surface Emissions (POET; C. Granier)
- Meteorological Fields
  - WACCM1b (2.8x2.8; 66 levels, 0-150 km)
  - ECMWF Operational (1.9 x 1.9; 60 levels, 0-65 km)
  - ECMWF ERA-1 (TBD)

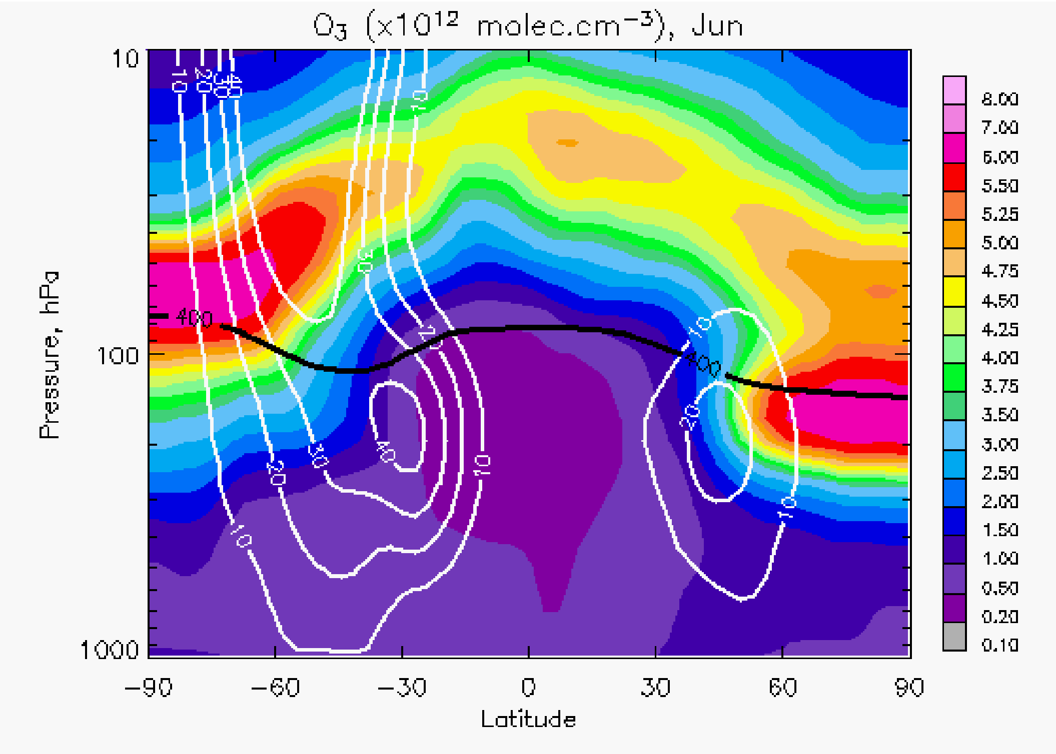
Middleworld



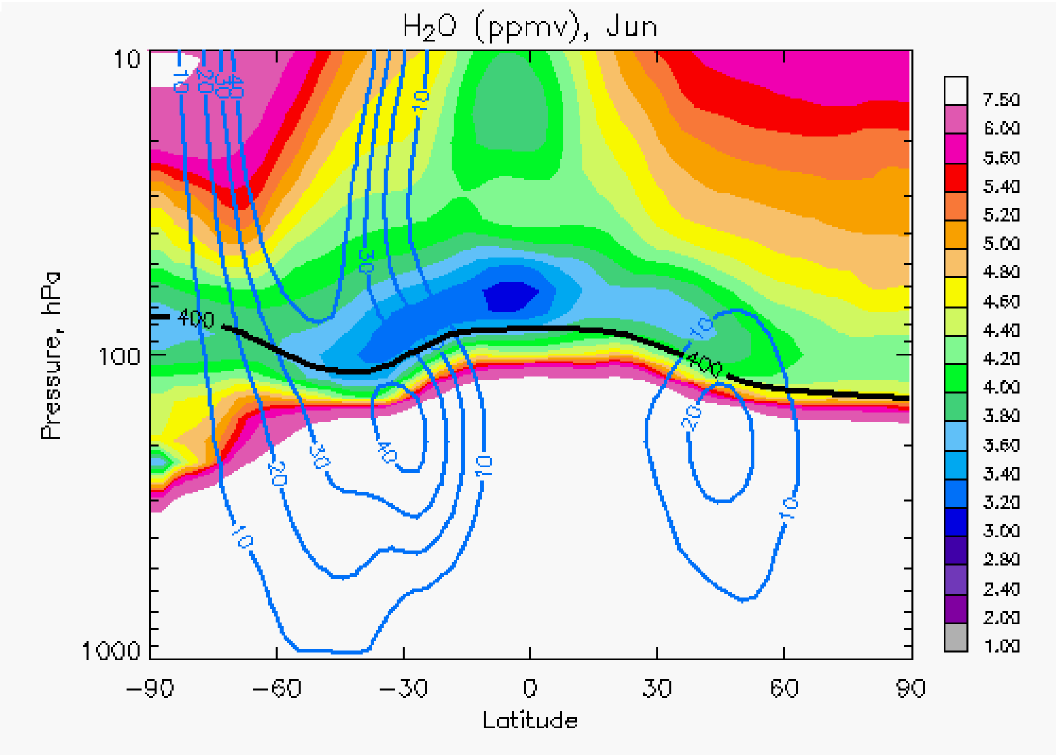
Courtesy of Laura Pan, NCAR

Mozart-3 / WACCM1b - June

Ozone, molecules cm^{-3}

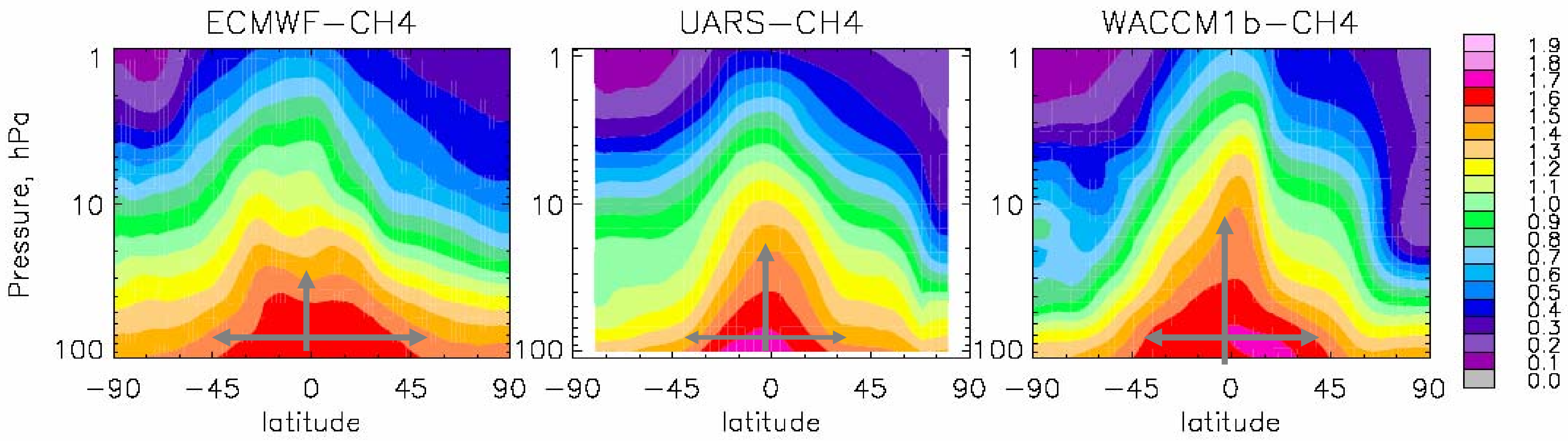


H_2O, ppmv

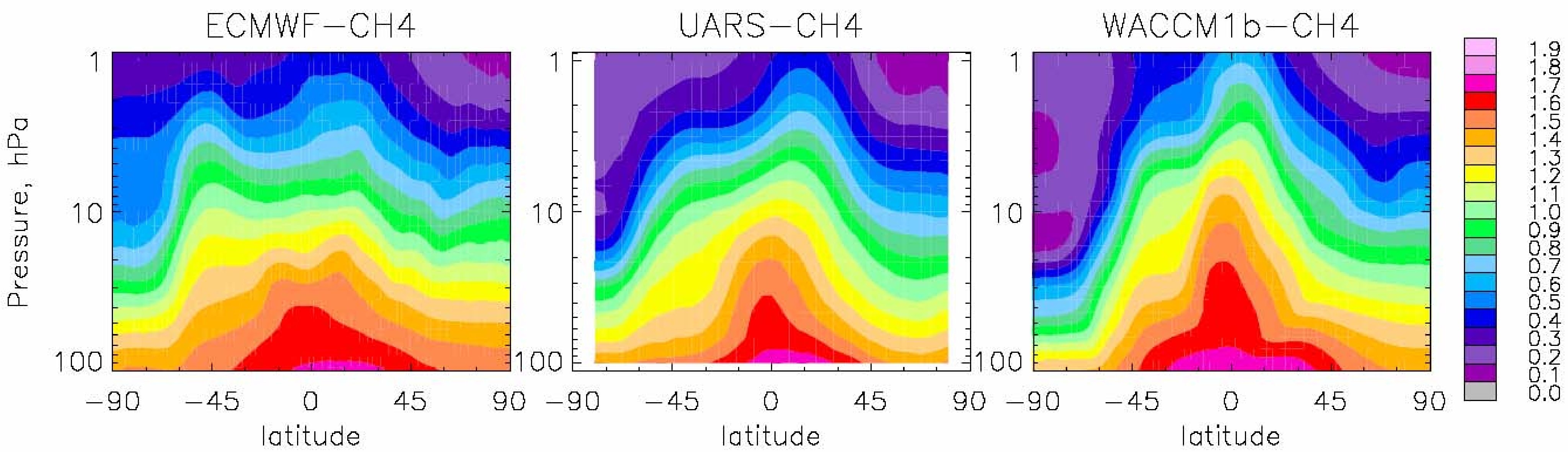


Comparison of Long-lived Tracers - CH_4 (ppmv)

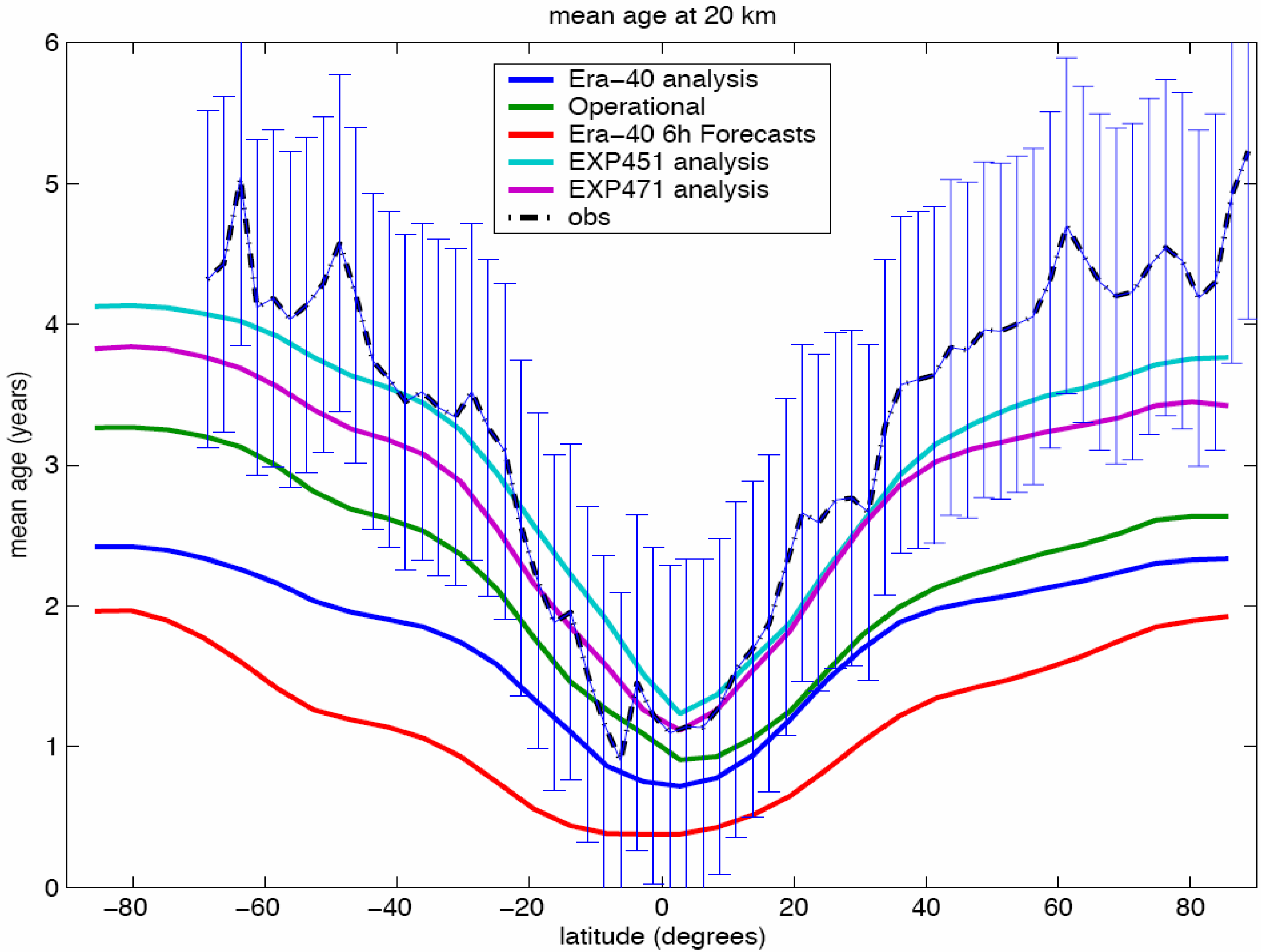
January



July



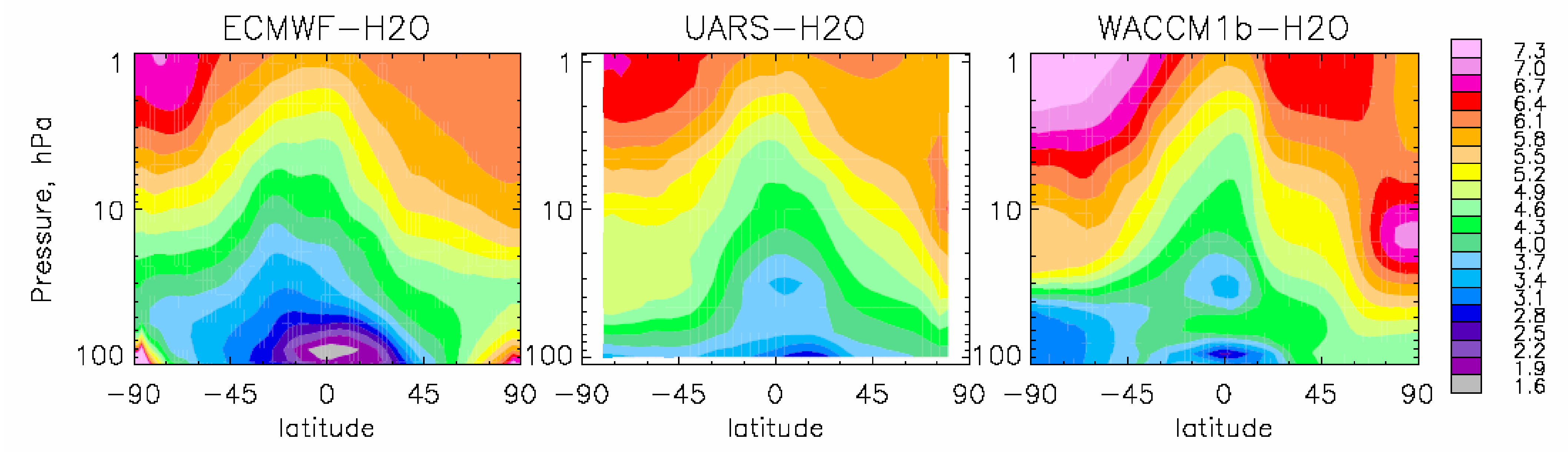
ECMWF Age-of-Air



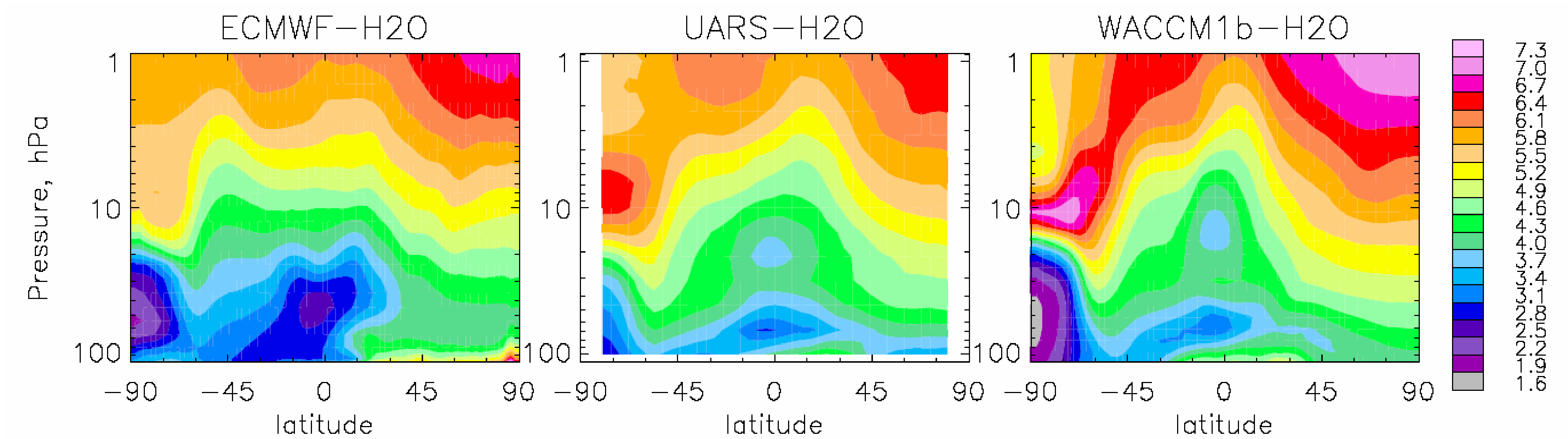
Courtesy of Simmons, ECMWF

Comparison of Long-lived Tracers - H_2O (ppmv)

January

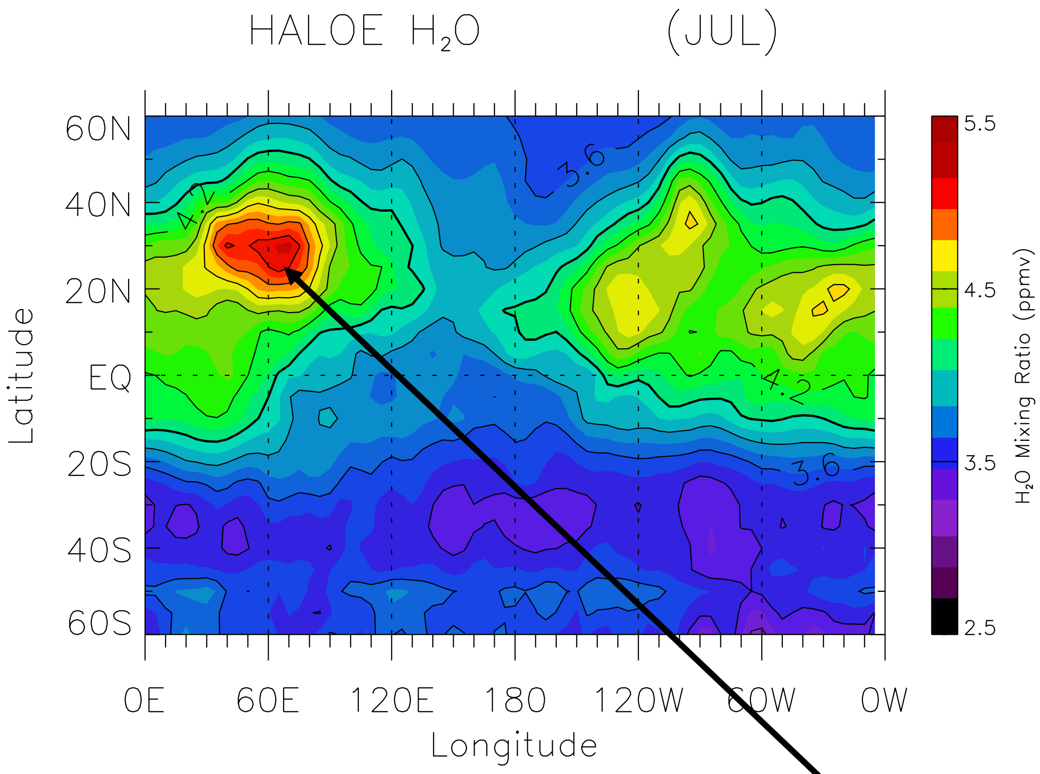


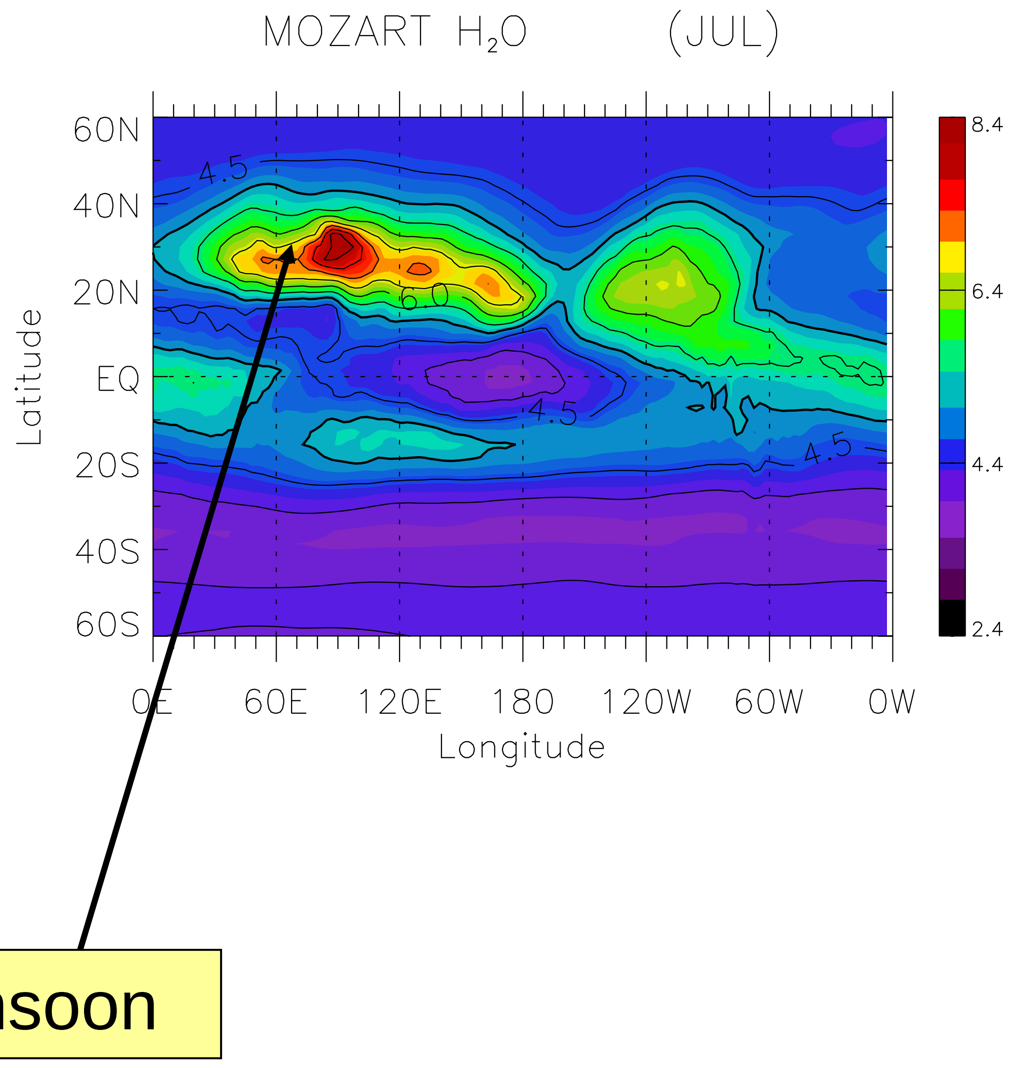
July



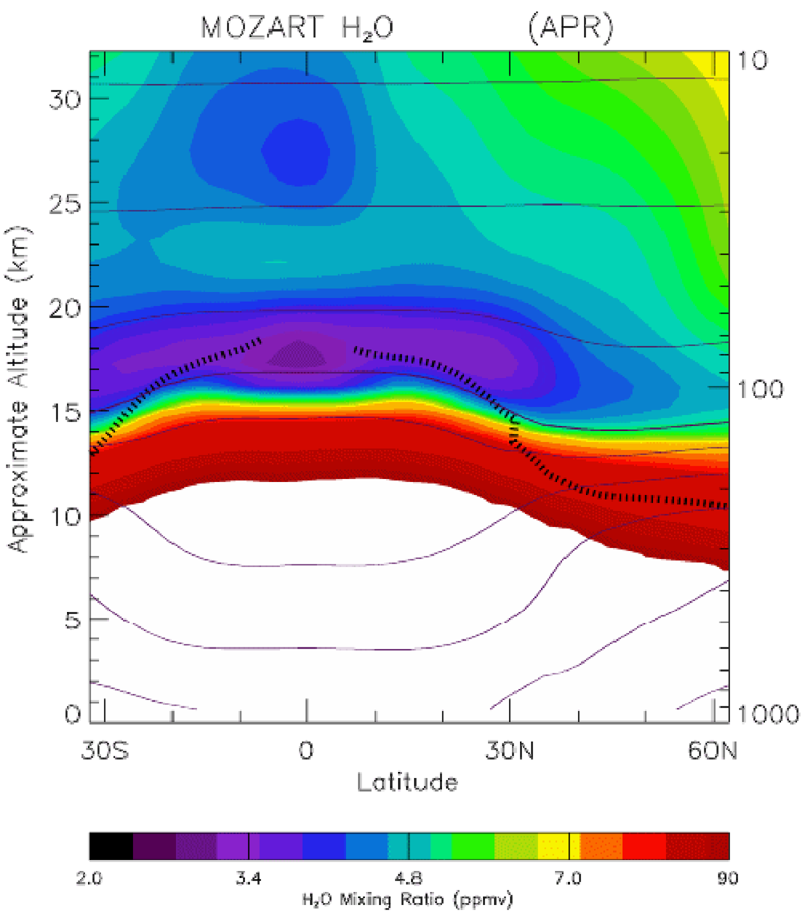
Comparison of HALOE and MZ3/WACCM H_2O (ppmv)

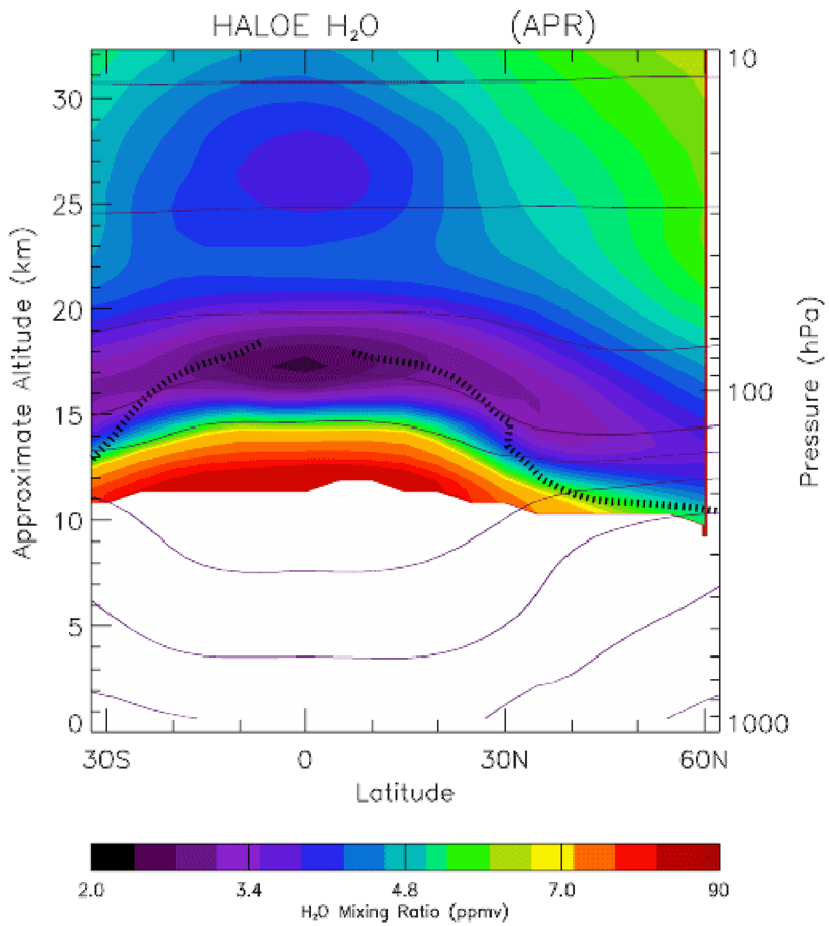
100 hPa





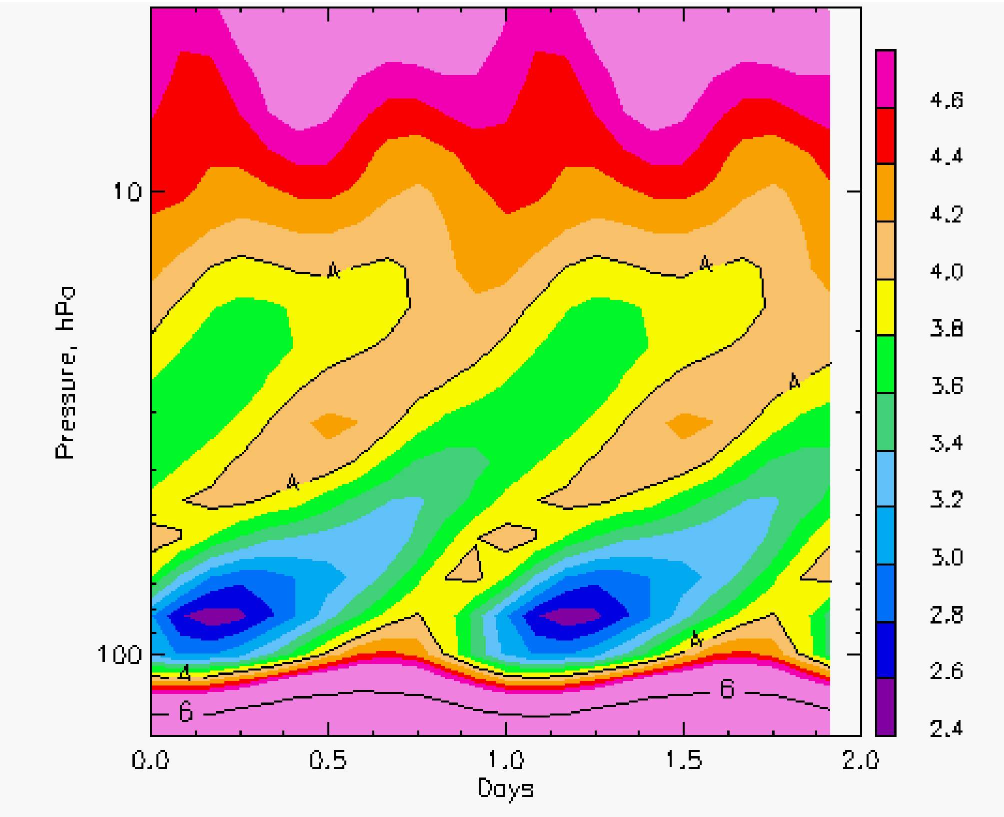
Comparison of HALOE and MOZART3/WACCM H_2O – Park et al. 2003

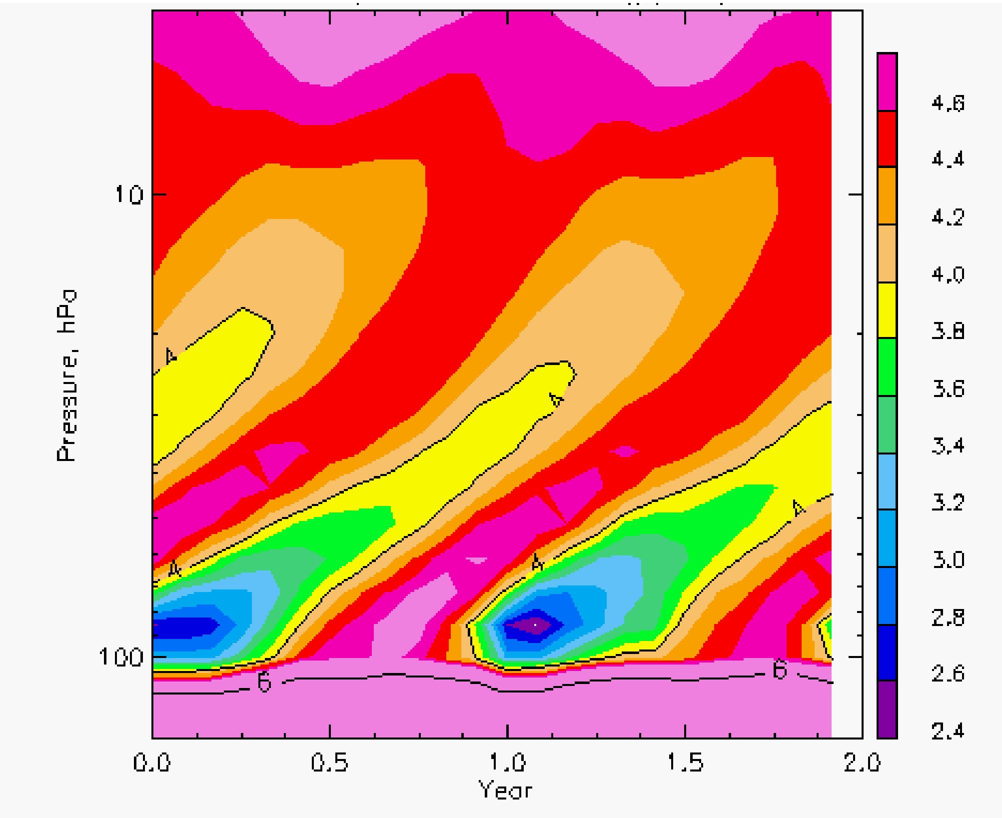




MOZART-3 / WACCM-01
EQ, Tape Recorder

UARS / HALOE **H_2O (ppmv); SST years 89-90**

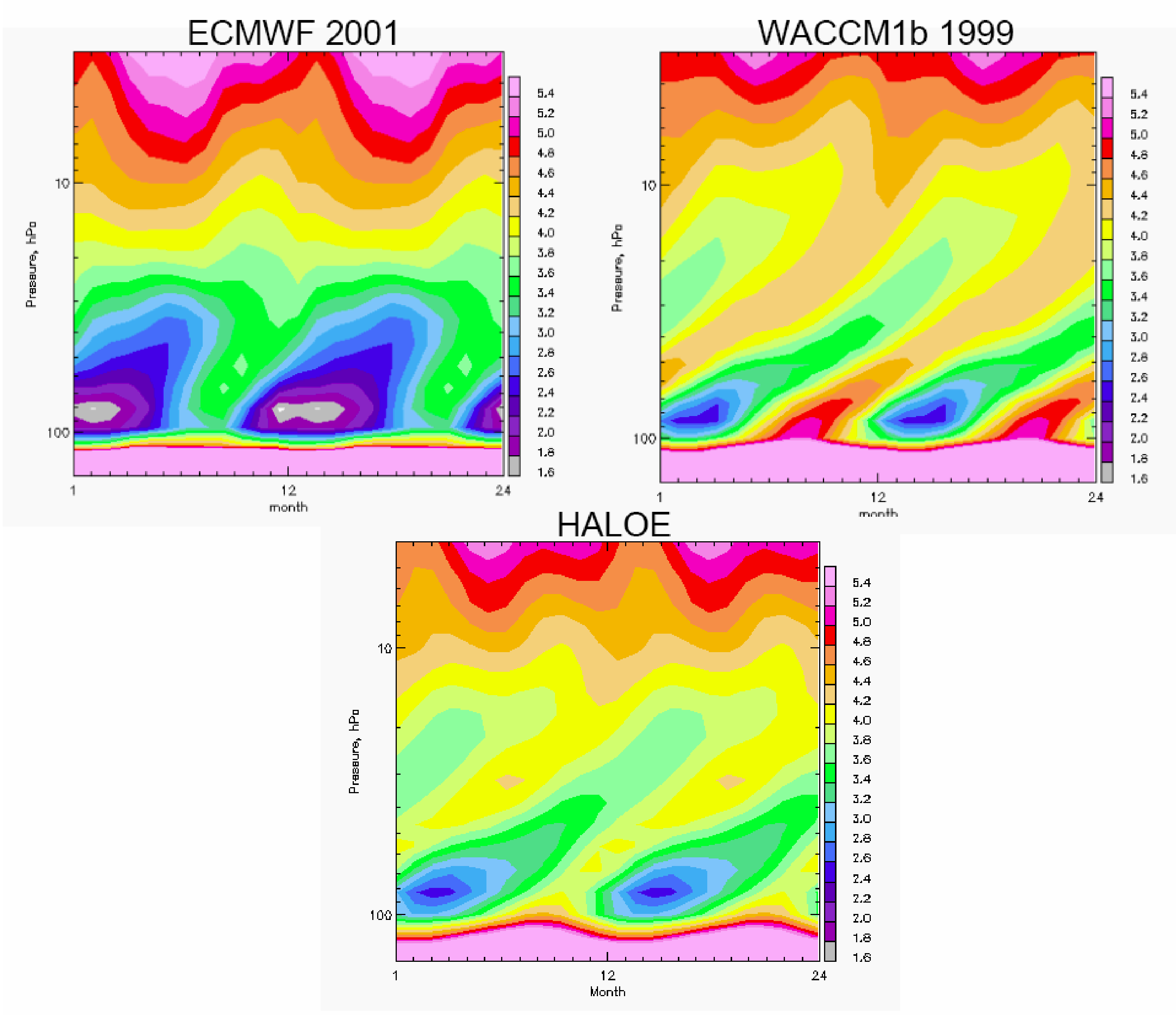




Randel, et al., JGR, 106, 14313, 2001

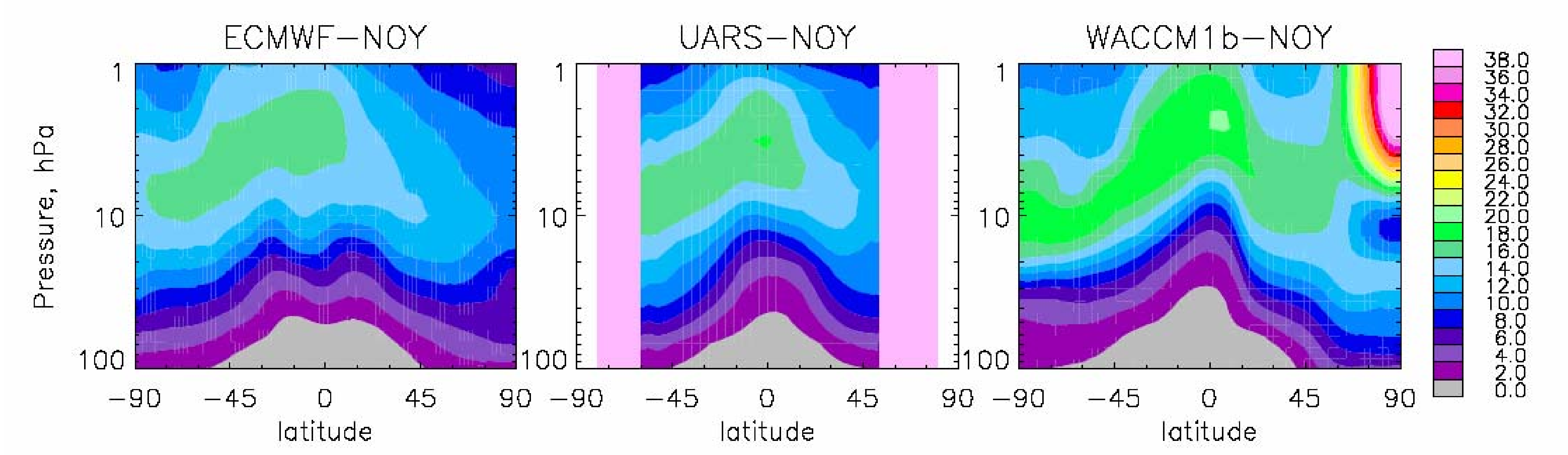
Using MZ3 / MATCH CCM3.6 column physics

Comparison of Long-lived Tracers - H_2O (ppmv)

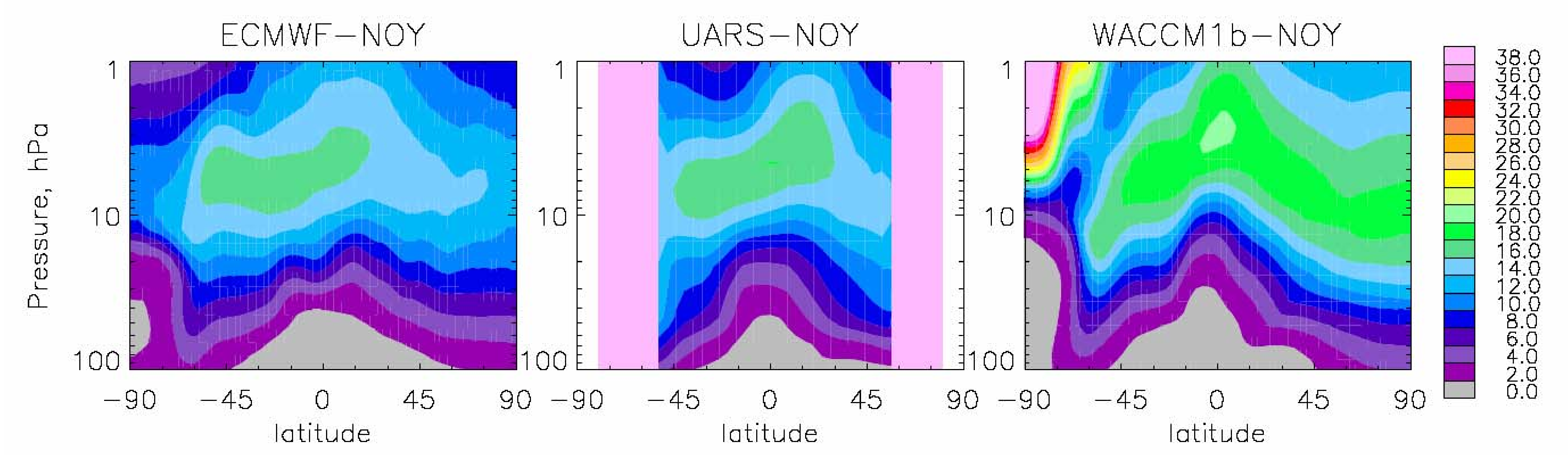


Comparison of Long-lived Tracers - NO_Y (ppbv)

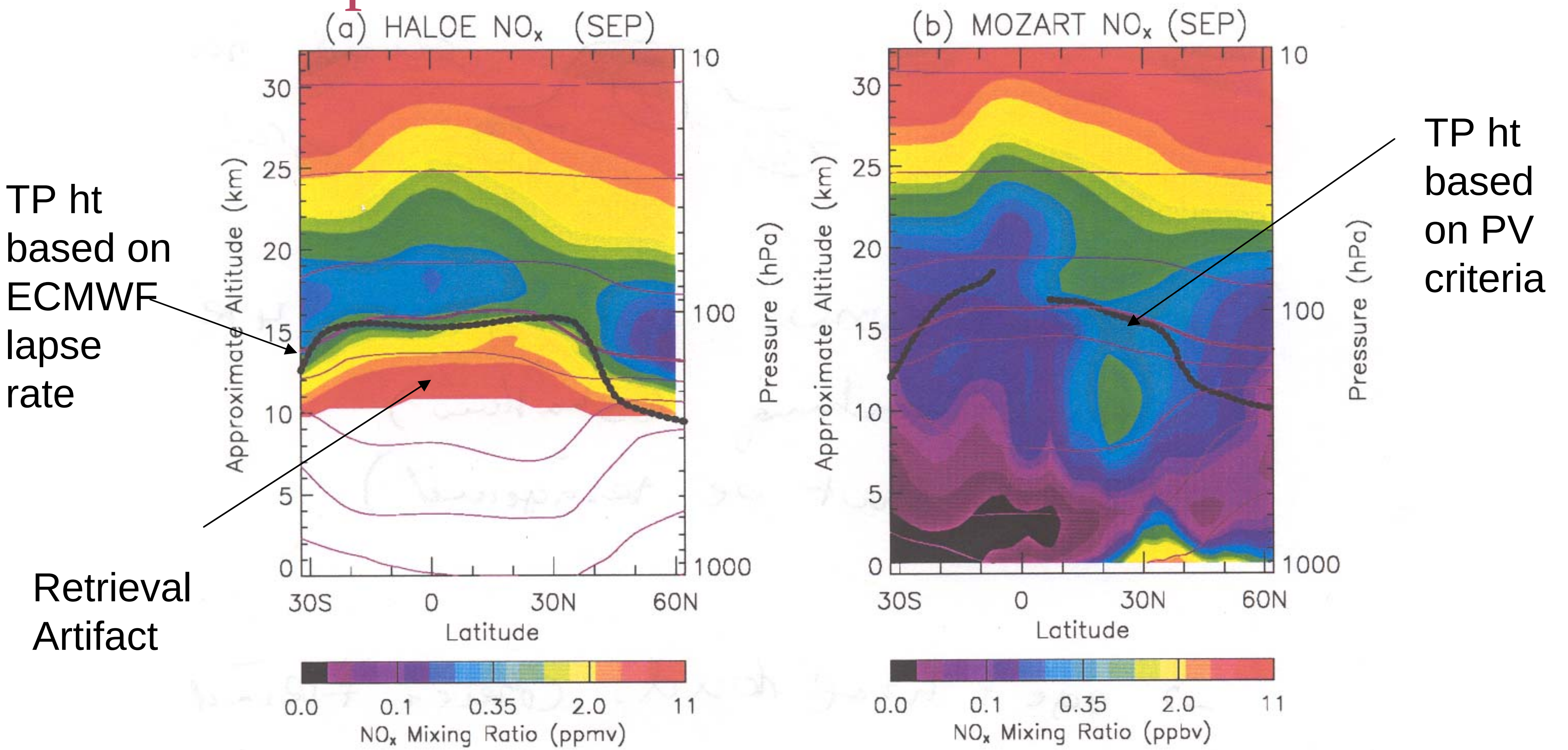
January



July



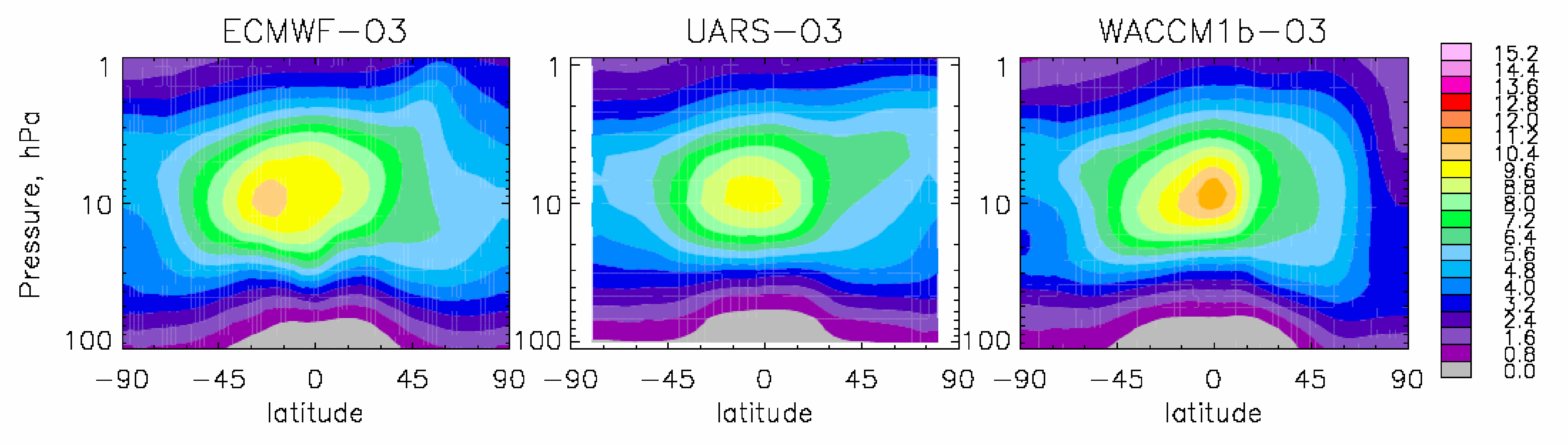
Meridional Cross Section of NOx in the South Asian Monsoon Region (60-120E), Sept



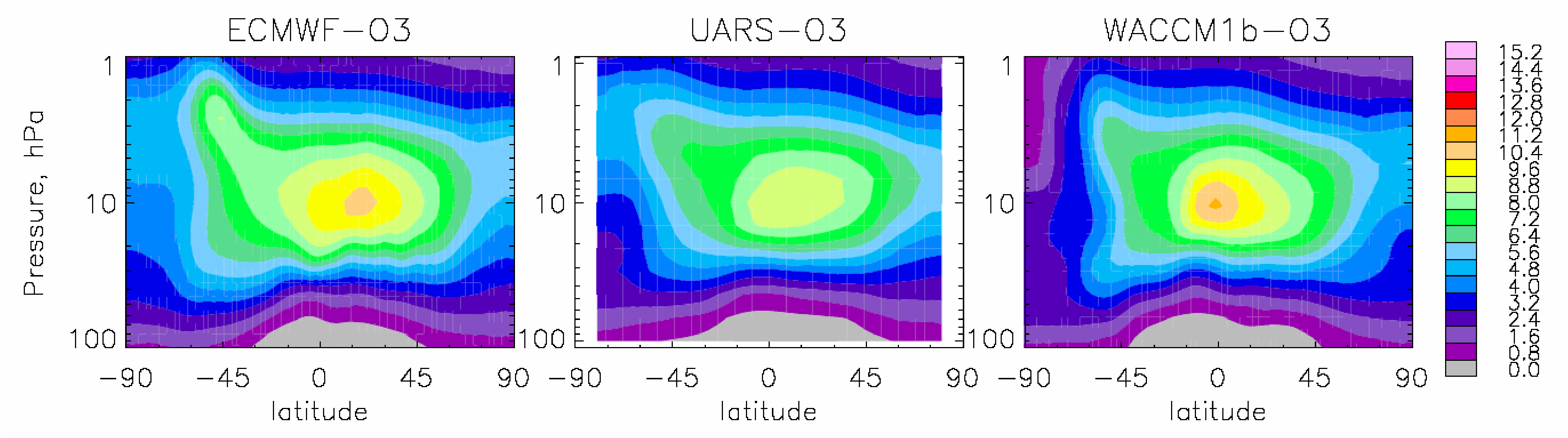
Lightning NOx Penetration into the LS??

Comparison of Long-lived Tracers - O_3 (ppmv)

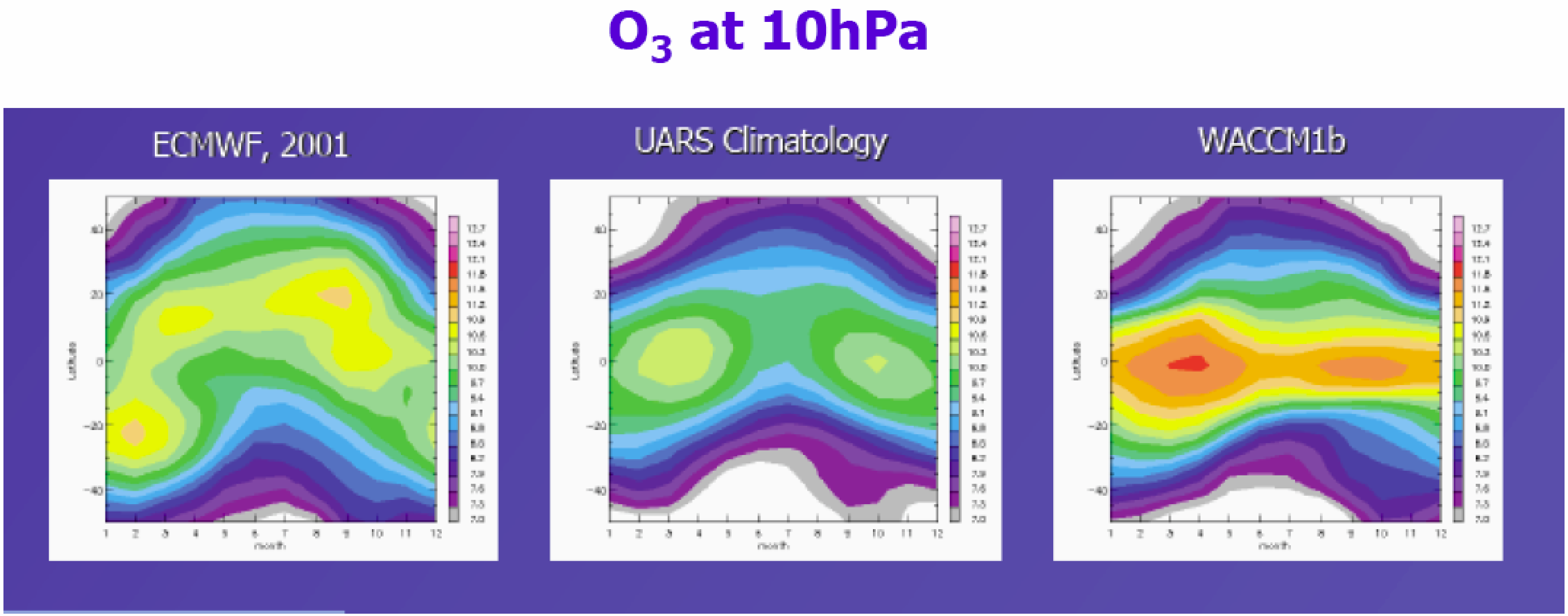
January



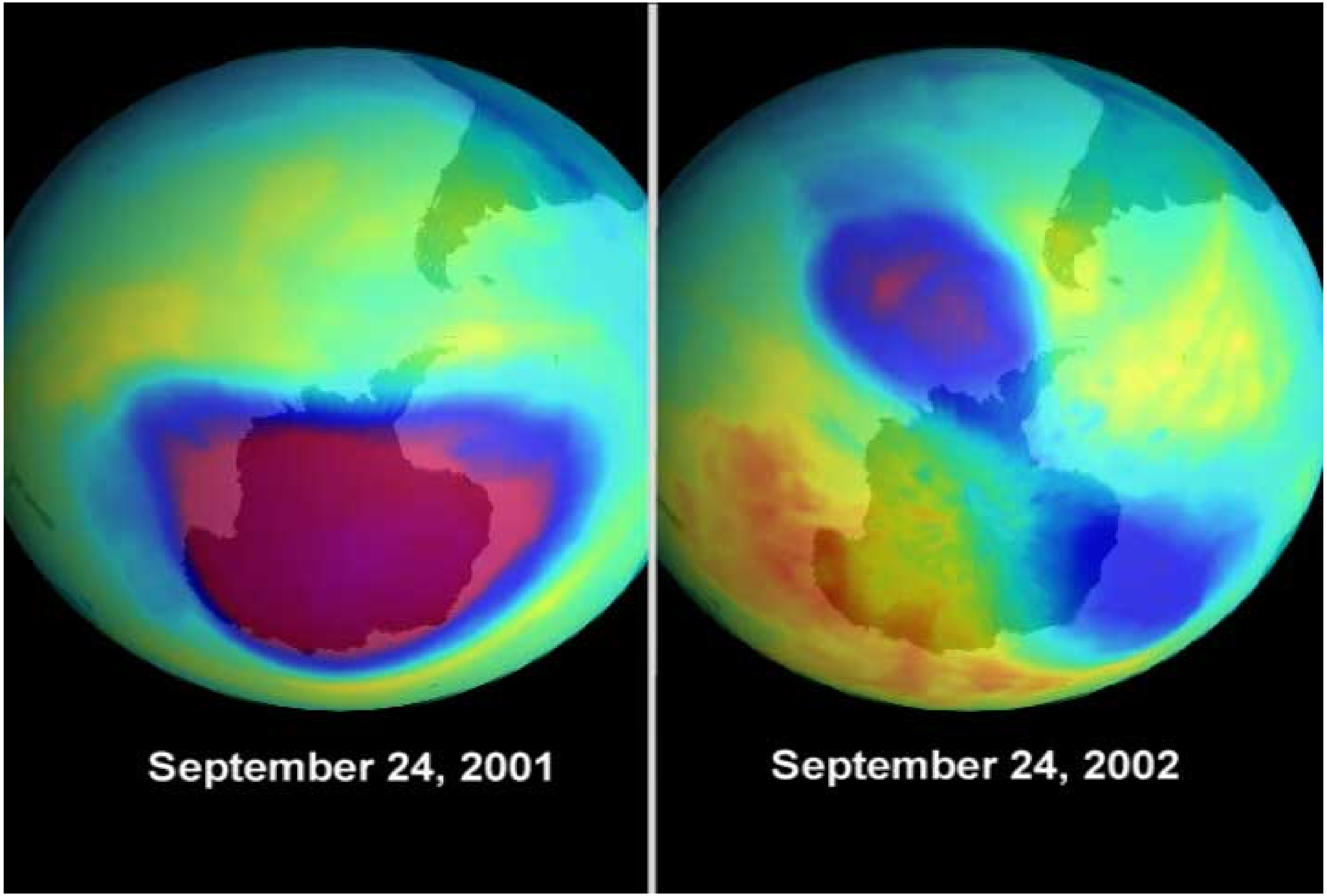
July



Comparison of Long-lived Tracers - O_3 (ppmv)

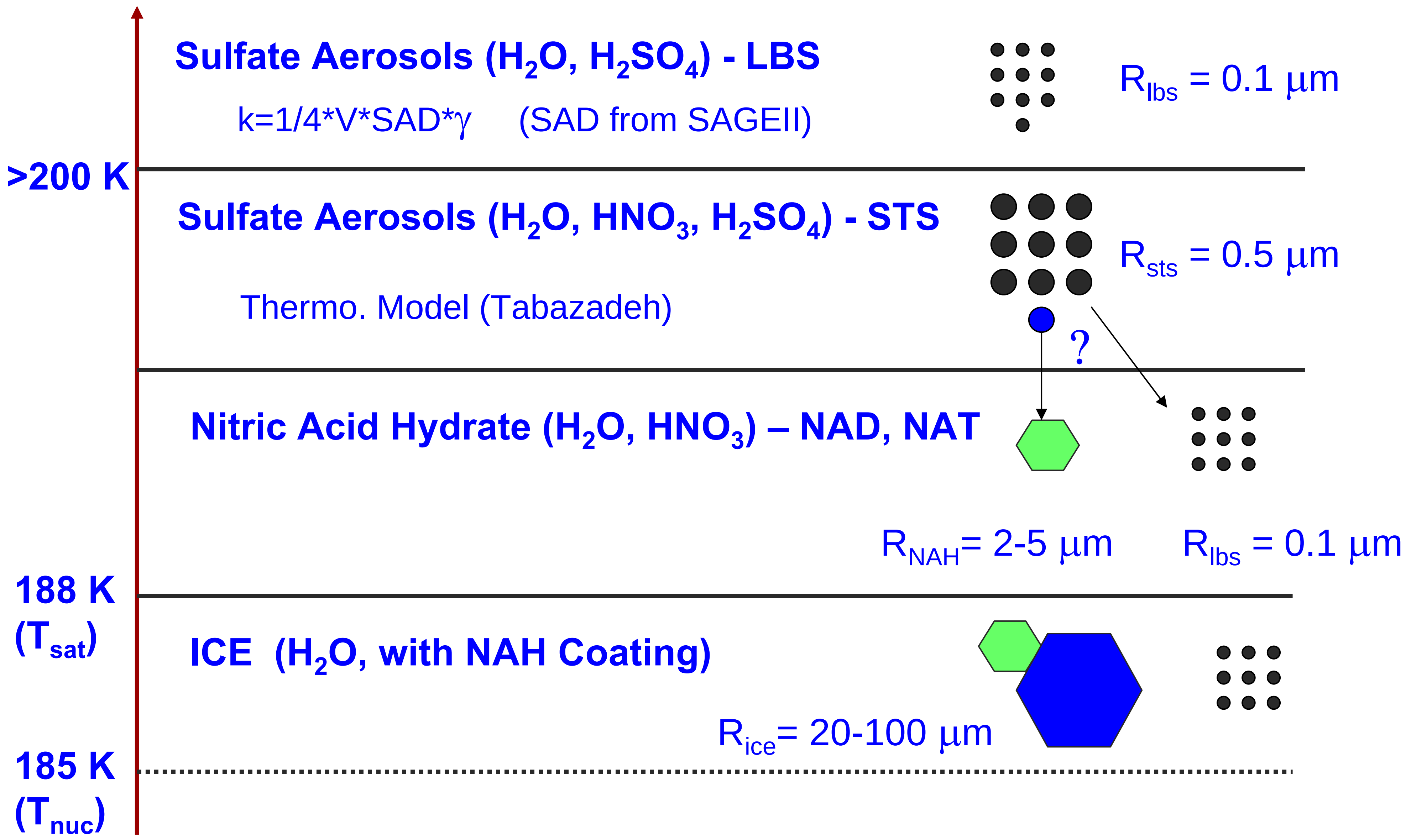


Modeling the Antarctic ozone hole 2001/2002



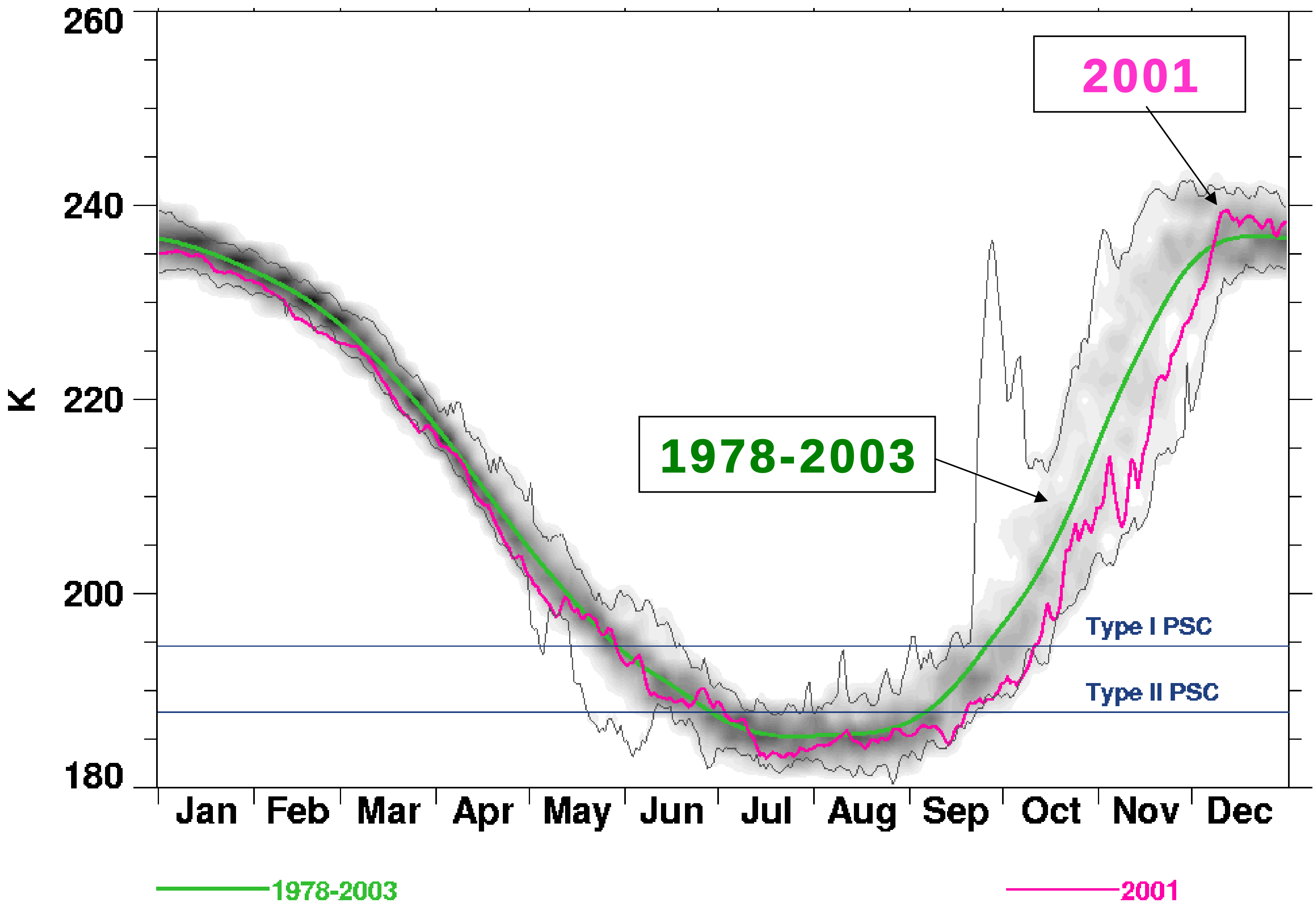
[GSFC, NASA]

Heterogeneous Chemistry Module



NCEP CPC Temperatures, 2001

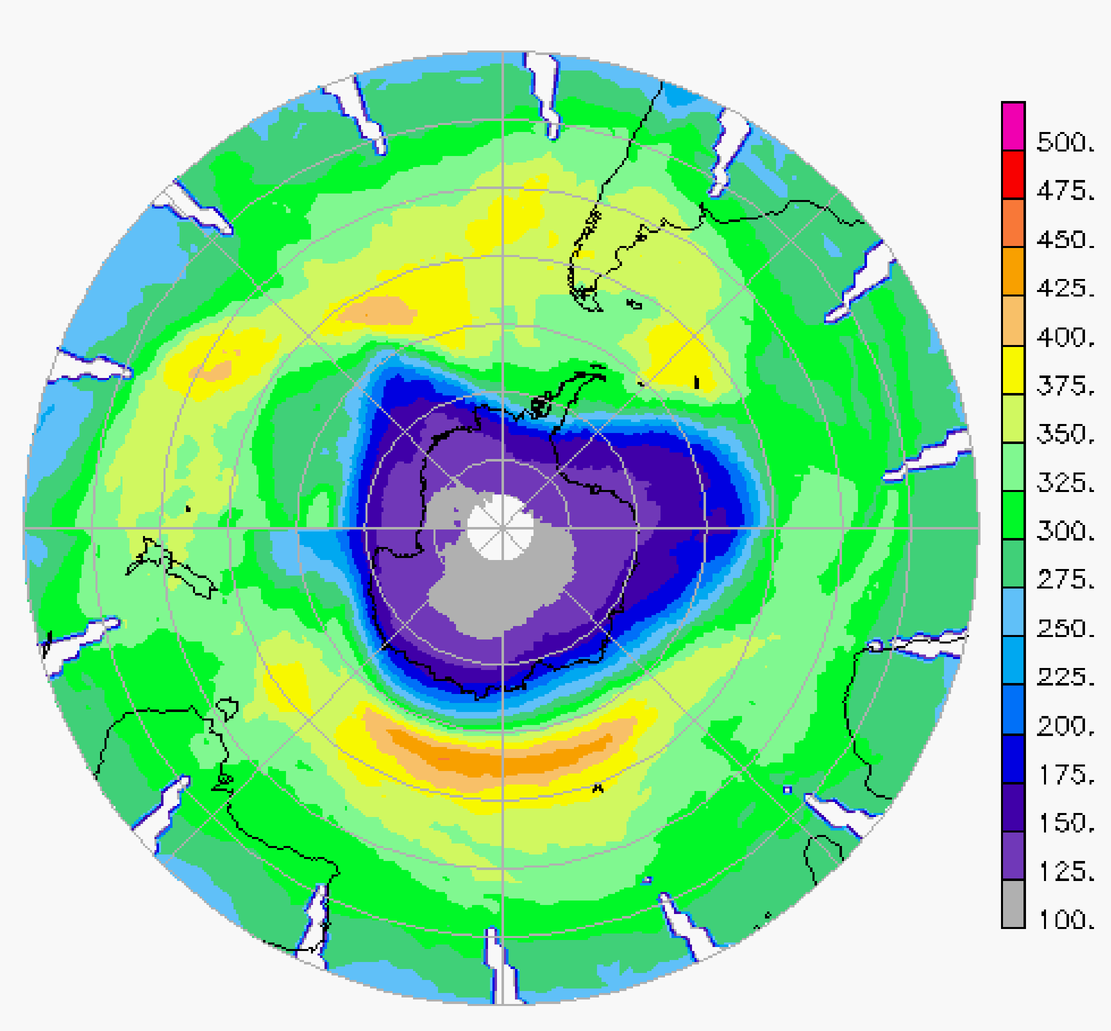
80S, Zonal Mean, 50hPa



P. Newman (NASA), E. Nash (SSAI), R. Nagatani (NCEP CPC)

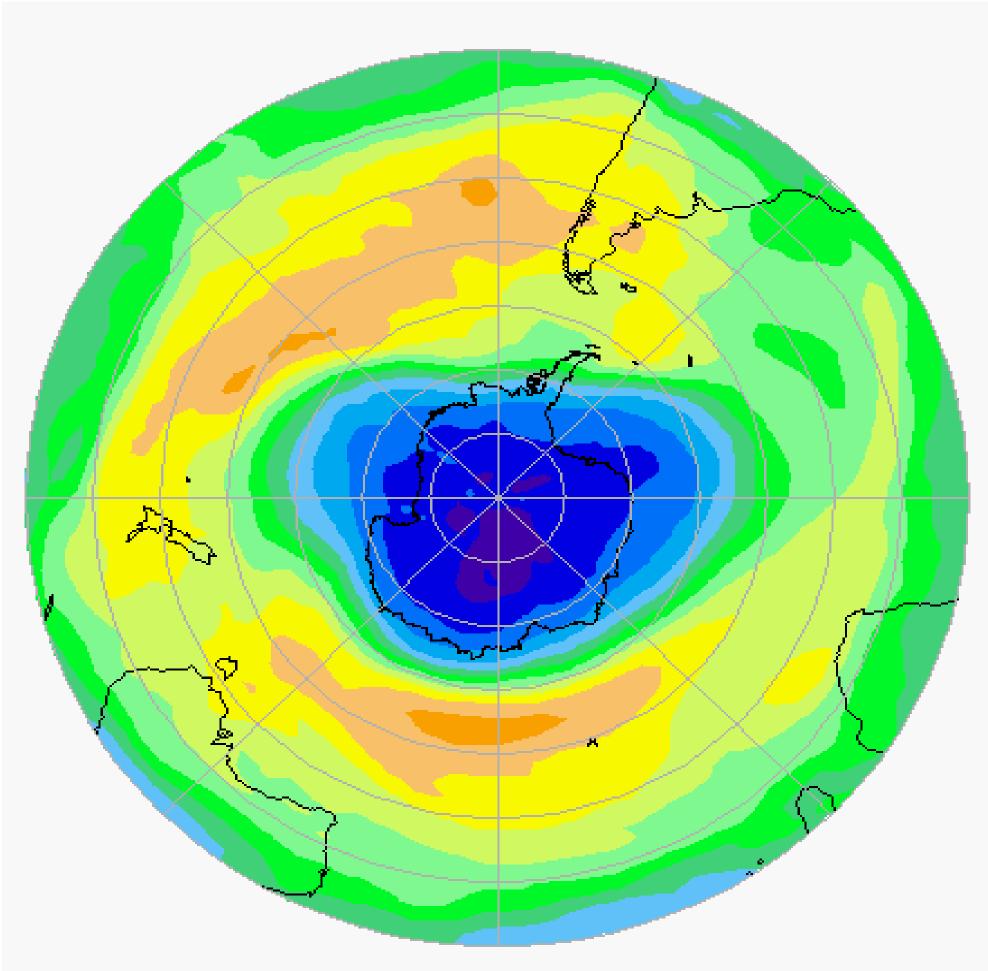
Total Column Ozone (DU) September 25, 2001

1.25° lon x 1.0° lat



EPTOMS

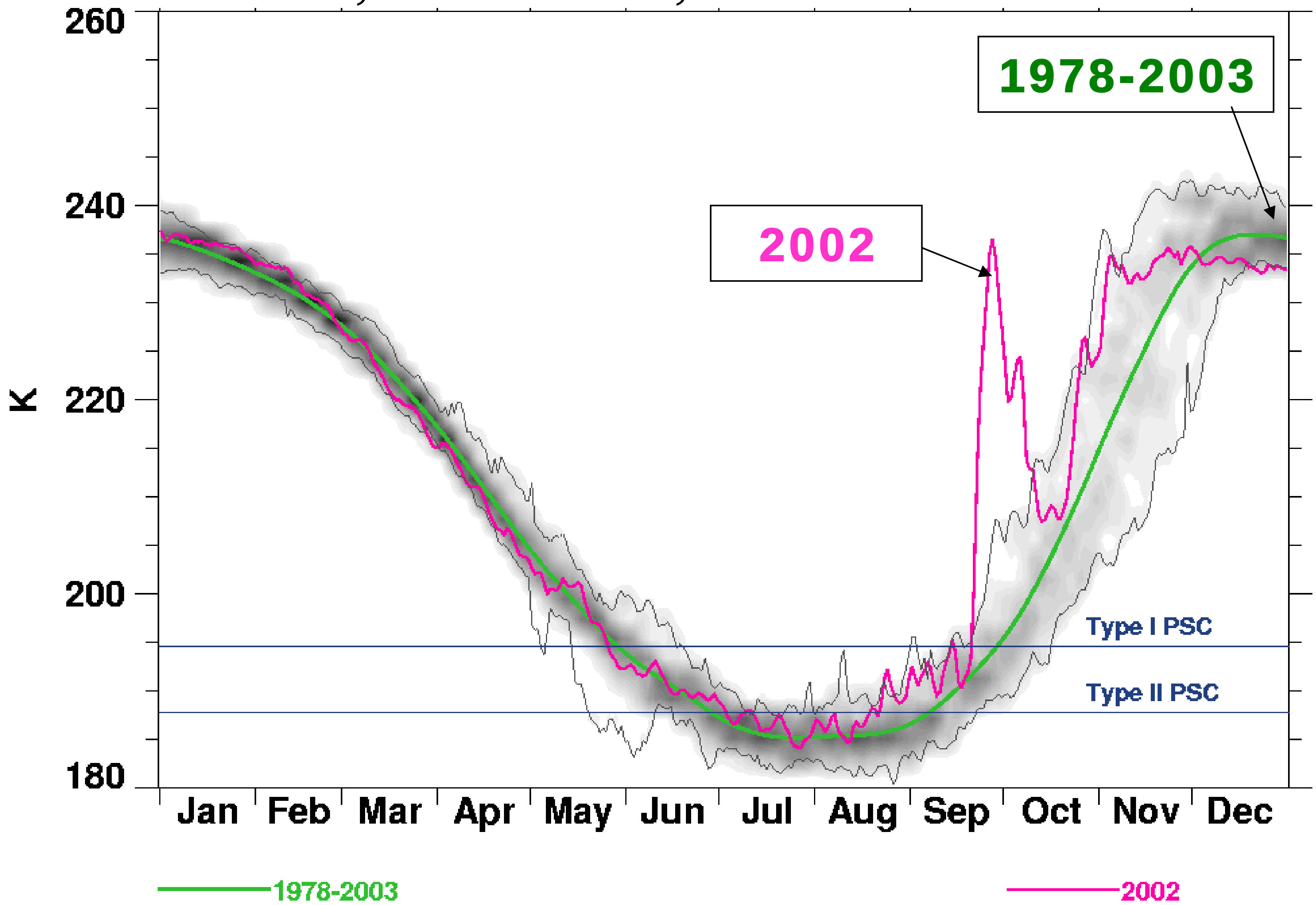
1.9° lon x 1.9° lat



MZ3/ECMWF

NCEP CPC Temperatures, 2002

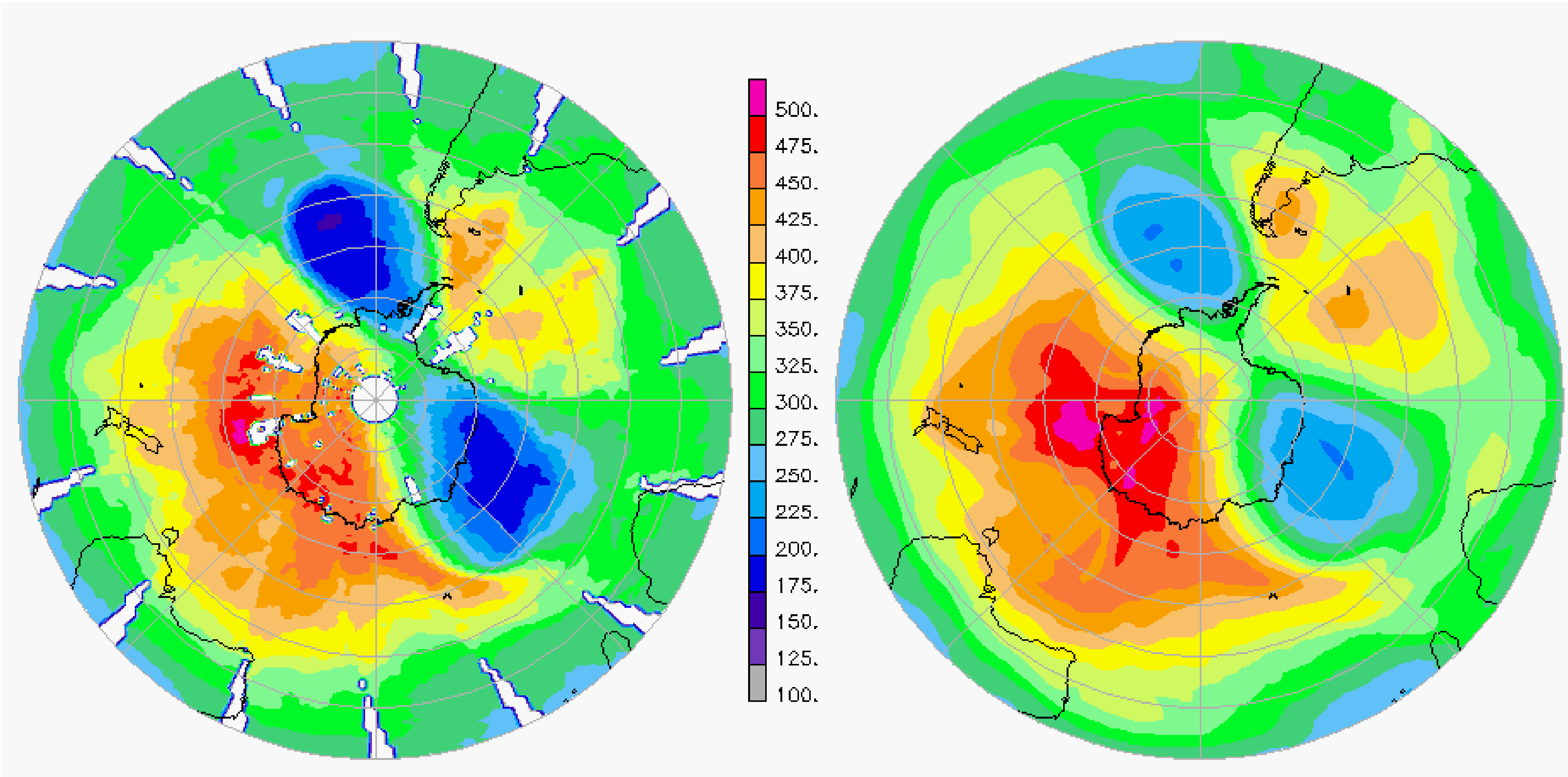
80S, Zonal Mean, 50hPa



P. Newman (NASA), E. Nash (SSAI), R. Nagatani (NCEP CPC)

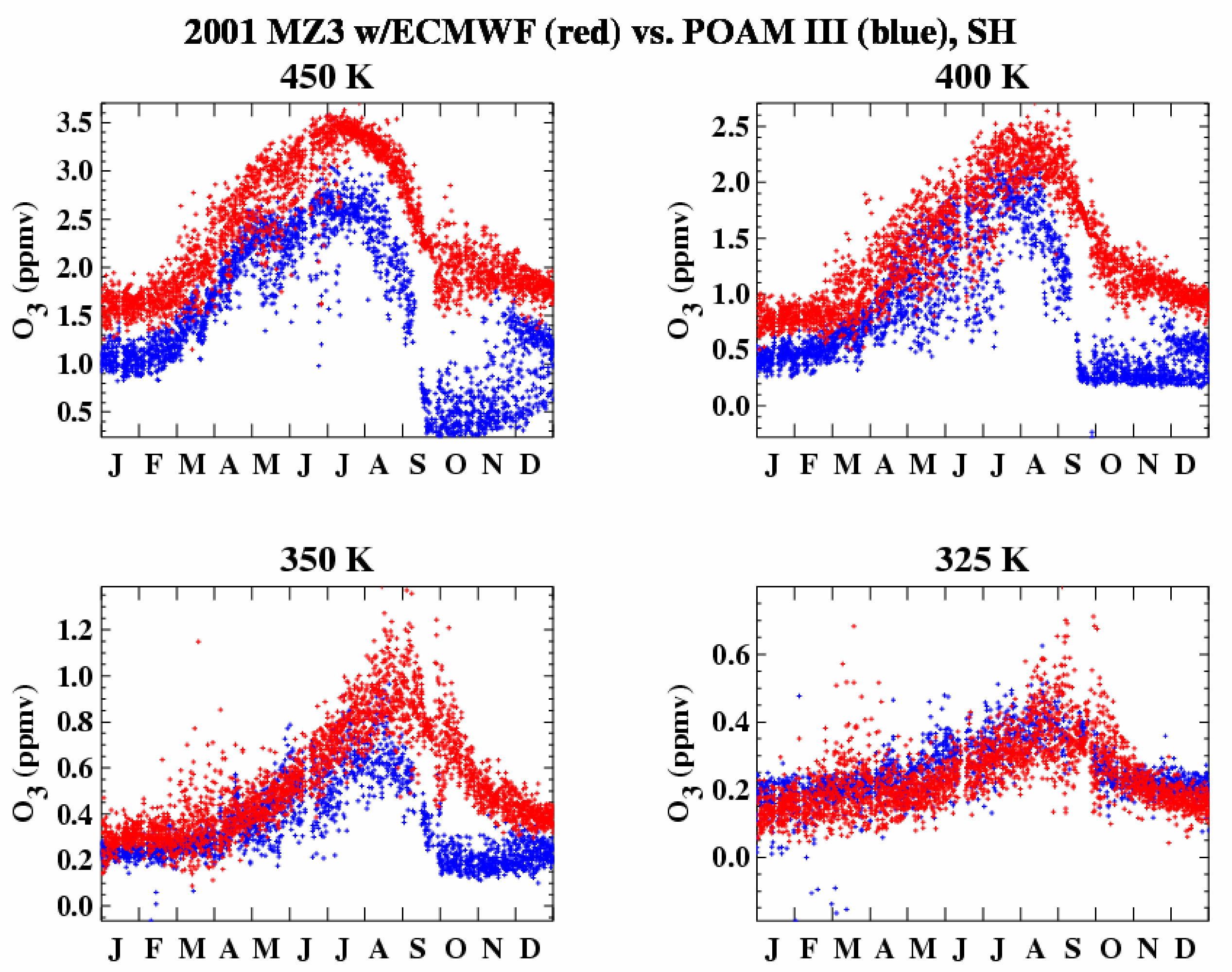
Total Column Ozone (DU) September 25, 2002

1.25° lon x 1.0° lat — 1.9° lon x 1.9° lat



EPTOMS — MZ3/ECMWF

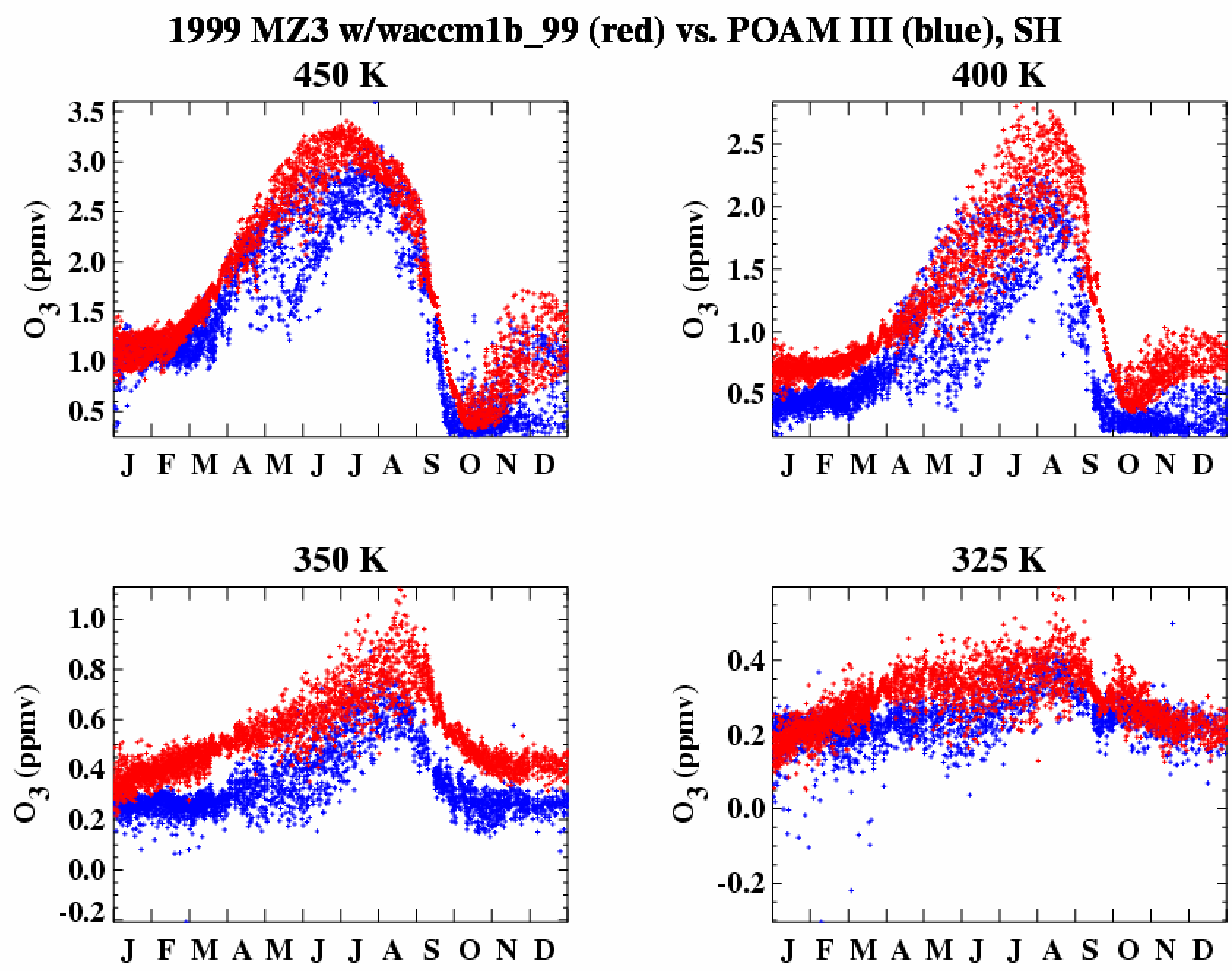
OZONE: Point-by-point time series, lower strat, SH



OZONE: With ECMWF winds and temperature, the model underestimates ozone depletion at 350-450 K. Ozone destruction starts too late in the season.

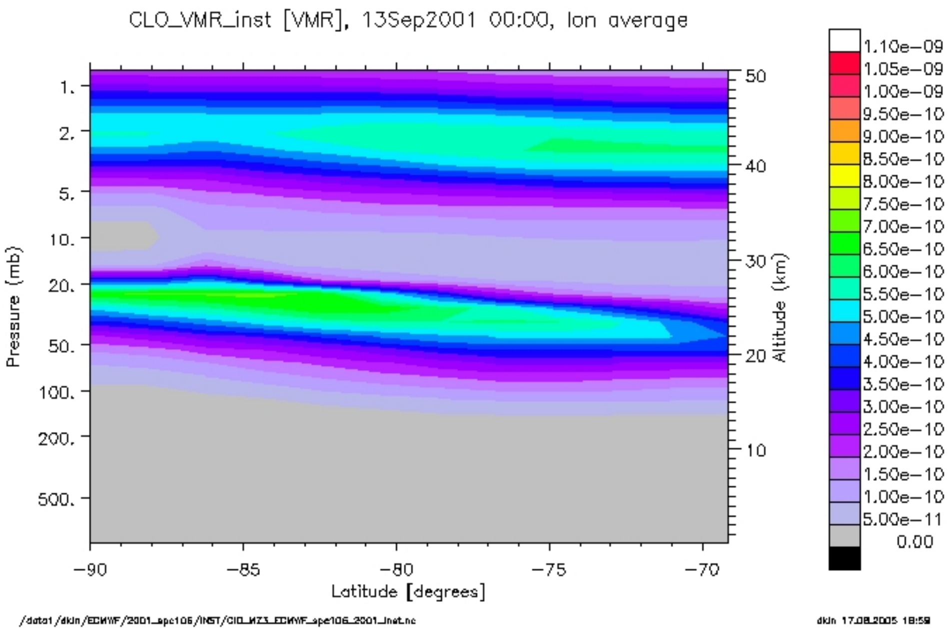
Model at 325 K agrees well with the observations – but the large variability seen in the model in March at 325 & 350 K is not observed in the data.

OZONE: Point-by-point time series, lower strat, SH

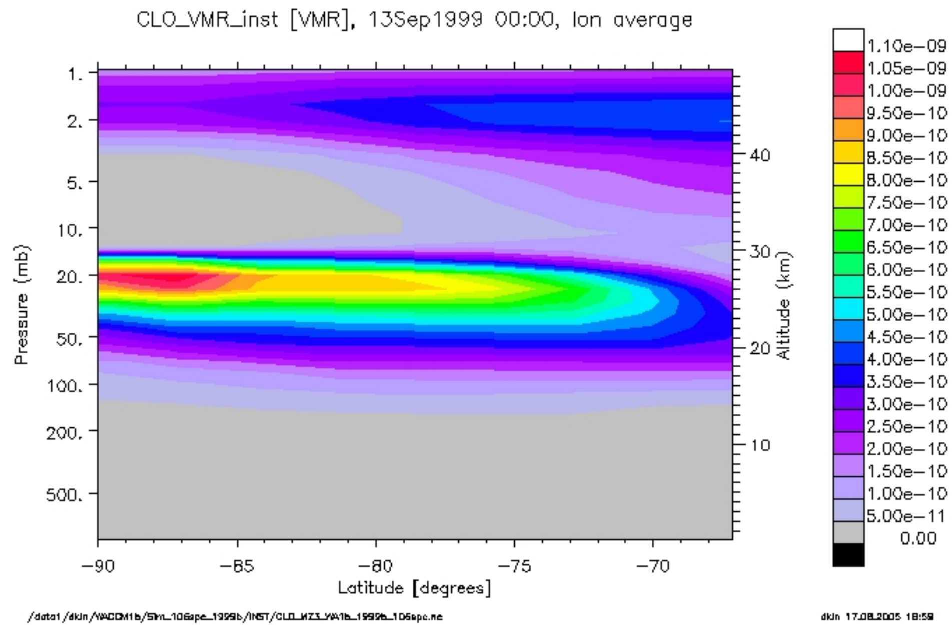


OZONE: With winds and temperature taken from the WACCM model, MOZART-3 ***does*** capture the ozone depletion at 400-450 K.

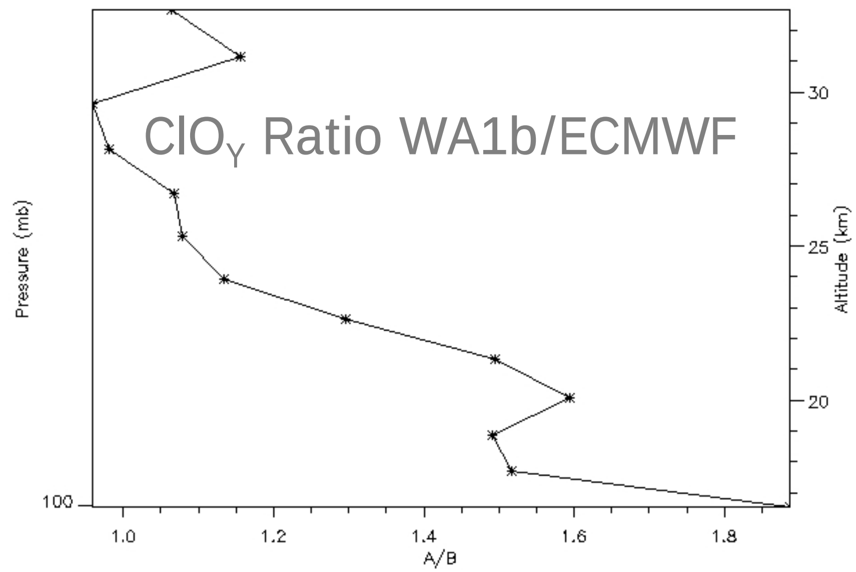
Inorganic Chlorine (ppbv)



ECMWF dynamics



WACCM dynamics



Mozart

The End: Thank You.