



Ultraviolet and visible trace gas measurements from satellites

Kelly Chance

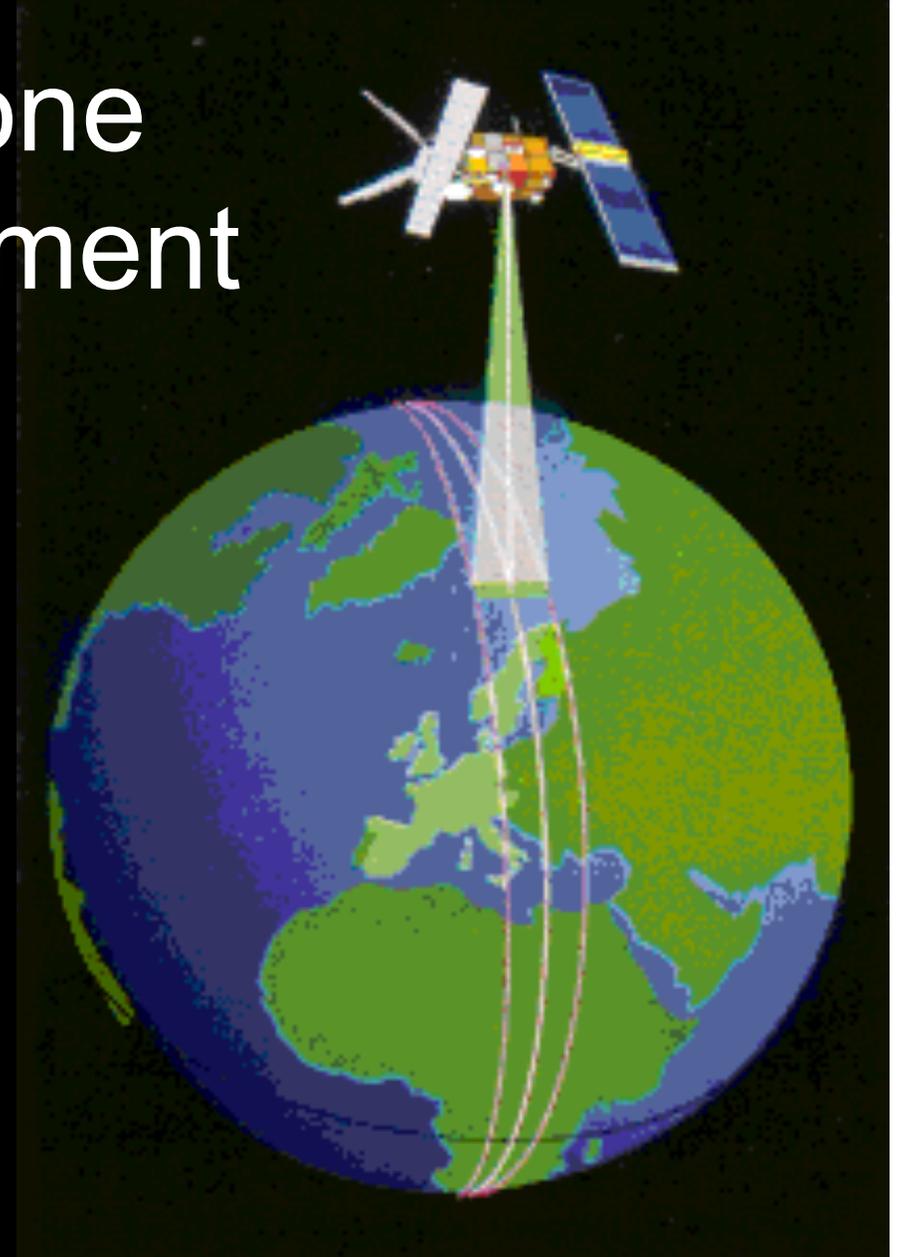
Smithsonian Astrophysical Observatory
Harvard-Smithsonian Center for Astrophysics

July 28, 2016



ESA Global Ozone Monitoring Experiment

- Nadir-viewing UV/vis/NIR
 - 240-400 nm @ 0.2 nm
 - 400-790 nm @ 0.4 nm
- Launched April 1995, turned off July 2011
- Footprint $320 \times 40 \text{ km}^2$
- 10:30 am cross-equator time, descending node
- Global coverage in 3 days





Sun-synchronous nadir heritage*

Instrument	Detectors	Spectral Coverage [nm]	Spectral Resolution [nm]	Ground Pixel Size [km ²]	Global Coverage
GOME (1995-2011)	Linear Arrays	240-790	0.2-0.4	40×320 (40×80 zoom)	3 days
SCIAMACHY (2002-2012)	Linear Arrays	240-2380	0.2-1.5	30×30/60/90 30×120/240 (depending on product)	6 days
OMI (2004)	2-D CCD	270-500	0.42-0.63	15×30 - 42×162 (depending on swath position)	daily
GOME-2a,b (2006, 2012)	Linear Arrays	240-790	0.24-0.53	40×40 (40×80 wide swath; 40×10 zoom)	near-daily
OMPS-1 (2011)	2-D CCDs	250-380	0.42-1.0	50×50 250×250 (depending on product)	daily

***Thanks to the late Dieter Perner of MPI**

Previous experience (since 1985 at SAO and MPI)

Scientific and operational measurements of pollutants O₃, NO₂, SO₂, H₂CO, C₂H₂O₂ (& CO, CH₄, BrO, OCIO, ClO, IO, H₂O, O₂-O₂, Raman, aerosol,)



Low Earth orbit (LEO) measurement capability

A full, minimally-redundant, set of polluting gases, plus aerosols and clouds is now measured to very high precision from satellites. Ultraviolet and visible spectroscopy of backscattered radiation provides O_3 (including profiles and tropospheric O_3), NO_2 (for NO_x), H_2CO and $C_2H_2O_2$ (for VOCs), SO_2 , H_2O , O_2-O_2 , N_2 and O_2 Raman scattering, and halogen oxides (BrO, ClO, IO, OClO). Satellite spectrometers planned since 1985 began making these measurements in 1995.

Air quality requirements from the GEO-CAPE Science Traceability Matrix

7/12/16

11-28-2011 DRAFT GEO-CAPE aerosol-atmospheres Science Traceability Matrix BASELINE and THRESHOLD

Science Questions	Measurement Objectives (color flag maps to Science Questions)	Measurement Requirements (mapped to Measurement Objectives)	Measurement Rationale																																																																															
<p>1. What are the temporal and spatial variations of emissions of gases and aerosols important for air quality and climate?</p> <p>2. How do physical, chemical, and dynamical processes determine tropospheric composition and air quality over scales ranging from urban to continental, diurnally to seasonally?</p> <p>3. How does air pollution drive climate forcing and how does climate change affect air quality on a continental scale?</p> <p>4. How can observations from space improve air quality forecasts and assessments for societal benefit?</p> <p>5. How does intercontinental transport affect air quality?</p> <p>6. How do episodic events, such as wild fires, dust outbreaks, and volcanic eruptions, affect atmospheric composition and air quality?</p>	<p>Baseline measurements¹: O₃, NO₂, CO, SO₂, HCHO, CH₄, NH₃, CHOCHO, different temporal sampling frequencies, 4 km x 4 km product horizontal spatial resolution at the center of the domain; and AOD, AAOD, AI, aerosol optical centroid height (AOCH), hourly for SZA<70 and 8 km x 8 km product horizontal spatial resolution at the center of the domain.</p> <p>Threshold measurements¹: CO hourly day and night; O₃, NO₂ hourly when SZA>70; AOD hourly (SZA<50); at 8 km x 8 km product horizontal spatial resolution at the center of the domain.</p>	<p>Geostationary Observing Location: 100 W +/-10</p> <p>Column measurements: [A to K] All the baseline and threshold species</p> <p>Cloud Camera 1 km x 1km horizontal spatial resolution, two spectral bands, baseline only</p> <p>Vertical information: [A to K] Two pieces of information in the troposphere in daylight with sensitivity to the lowest 2 km</p> <p>Altitude (+/- 1km)</p> <p>Product horizontal spatial resolution at the center of the domain, (nominally 100W, 35 N): [A to H] 4 km x 4 km (baseline), 8 km x 8 km (threshold) 8 km x 8 km (baseline, threshold) 16 km x 16 km (baseline only)</p> <p>Spectral region : [A to F] UV-Vis or UV-TIR SWIR, MWIR UV SWIR TIR Vis UV-deep blue UV-deep blue Vis-NIR</p>	<p>Provides optimal view of North America.</p> <p>Continue the current state of practice in vertical; add temporal resolution.</p> <p>Improve retrieval accuracy, provide diagnostics for gases and aerosol</p> <p>Separate the lower-most troposphere from the free troposphere for O₃, CO.</p> <p>Detect aerosol plume height; improve retrieval accuracy.</p> <p>Capture yield/temporal variability; obtain better spatial/temporal variability; obtain better yields of products.</p> <p>Inherently larger spatial scales, sufficient to link to LEO observations</p> <p>Typical use</p> <p>Provide multispectral retrieval information in daylight</p> <p>Retrieve gas species from their atmospheric spectral signatures (typical)</p> <p>Obtain spectral-dependence of AOD for particle size and type information</p> <p>Obtain spectral-dependence of AAOD for aerosol type information</p> <p>Provide absorbing aerosol information</p> <p>Retrieve aerosol height²</p>																																																																															
	<p>A. Measure the threshold or baseline species or properties with the temporal and spatial resolution specified (see next column) to quantify the underlying emissions, understand emission processes, and track transport and chemical evolution of air pollutants [1, 2, 3, 4, 5, 6]</p> <p>B. Measure AOD, AAOD, and NH₃ to quantify aerosol and nitrogen deposition to land and coastal regions [2, 4]</p> <p>C. Measure AOD, AAOD, and AOCH to relate surface PM concentration, UV-B level and visibility to aerosol column loading [1, 2, 3, 4, 5, 6]</p> <p>D. Determine the instantaneous radiative forcings associated with ozone and aerosols on the continental scale and relate them quantitatively to natural and anthropogenic emissions [3, 4, 6]</p> <p>E. Observe pulses of CH₄ emission from biogenic and anthropogenic releases; CO anthropogenic and wildfire emissions; AOD, AAOD, and AI from fires; AOD, AAOD, and AI from dust storms; SO₂ and AOD from volcanic eruptions [4, 5, 6]</p> <p>F. Quantify the inflows and outflows of O₃, CO, SO₂, and aerosols across continental boundaries to determine their impacts on surface air quality and on climate [2, 3, 5]</p> <p>G. Characterize aerosol particle size and type from spectral dependence measurements of AOD and AAOD [1, 2, 3, 4, 5, 6]</p> <p>H. Acquire measurements to improve representation of processes in air quality models and improve data assimilation in forecast and assessment models [4]</p> <p>I. Synthesize the GEO-CAPE measurements with information from in-situ and ground-based remote sensing networks to construct an enhanced observing system [1, 2, 3, 4, 5, 6]</p> <p>J. Leverage GEO-CAPE observations into an integrated observing system including geostationary satellites over Europe and Asia together with LEO satellites and suborbital platforms for assessing the hemispheric transport [1, 2, 3, 4, 5, 6]</p> <p>K. Integrate observations from GEO-CAPE and other platforms into models to improve representation of processes in the models and to link the observed composition, deposition, and radiative forcing to the emissions from anthropogenic and natural sources [1, 2, 3, 4, 5, 6]</p>	<p>Over open ocean</p> <p>Gases</p> <p>Aerosol properties</p> <p>Over open ocean</p>	<p>Obtain spectral-dependence of AOD for particle size and type information</p> <p>Obtain spectral-dependence of AAOD for aerosol type information</p> <p>Inherently larger spatial scales, sufficient to link to LEO observations</p>																																																																															
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AOD=Aerosol optical depth, AAOD=Aerosol absorption optical depth, AI=Aerosol index. See next page for footnotes.

Infrared species

**Ultraviolet/
visible species
(GOME,
TEMPO,
etc.)**

7/12/16

Atmospheric measurements over Land/Coastal areas, baseline and threshold: [A to K]

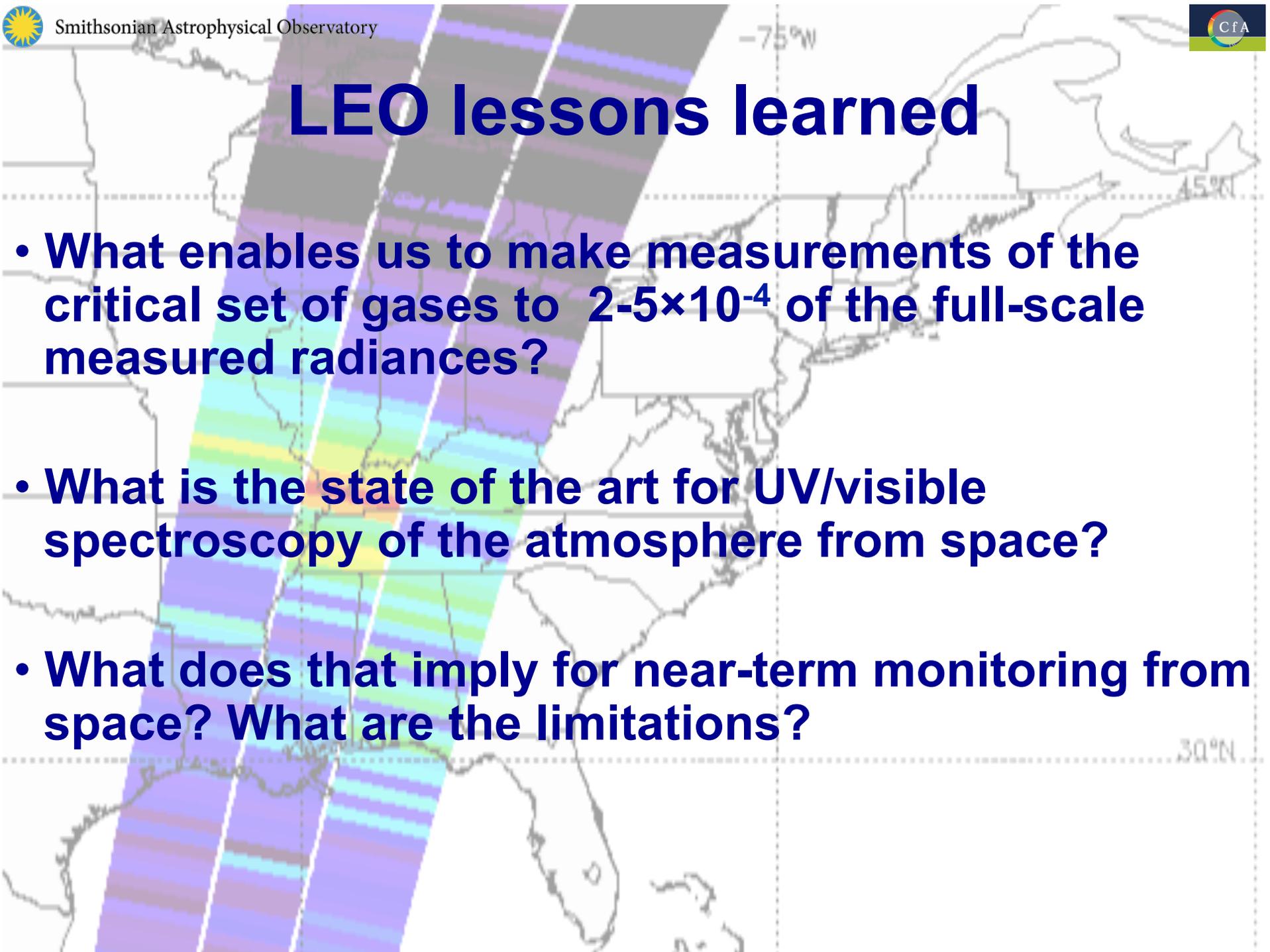
Species	Time resolution	Typical value ²	Precision ²	Description
O ₃	Hourly, SZA<70	9 x 10 ¹⁸	0-2 km: 10 ppbv 2km–tropopause: 15 ppbv Stratosphere: 5%	Observe O ₃ with two pieces of information in the troposphere with sensitivity to the lowest 2 km for surface AQ; also transport, climate forcing
CO	Hourly, day and night	2 x 10 ¹⁸	0-2 km: 20ppbv 2km–tropopause: 20 ppbv	Track anthropogenic and biomass burning plumes; observe CO with two pieces of information in the vertical with sensitivity to the lowest 2 km in daylight
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Additional atmospheric measurements over Land/Coastal areas, baseline only: [A to K]

Species	Time resolution	Typical value ²	Precision ²	Description
HCHO ⁺	3/day, SZA<50	1.0x10 ¹⁶	1x10 ¹⁶	Observe biogenic VOC emissions, expected to peak at midday; chemistry
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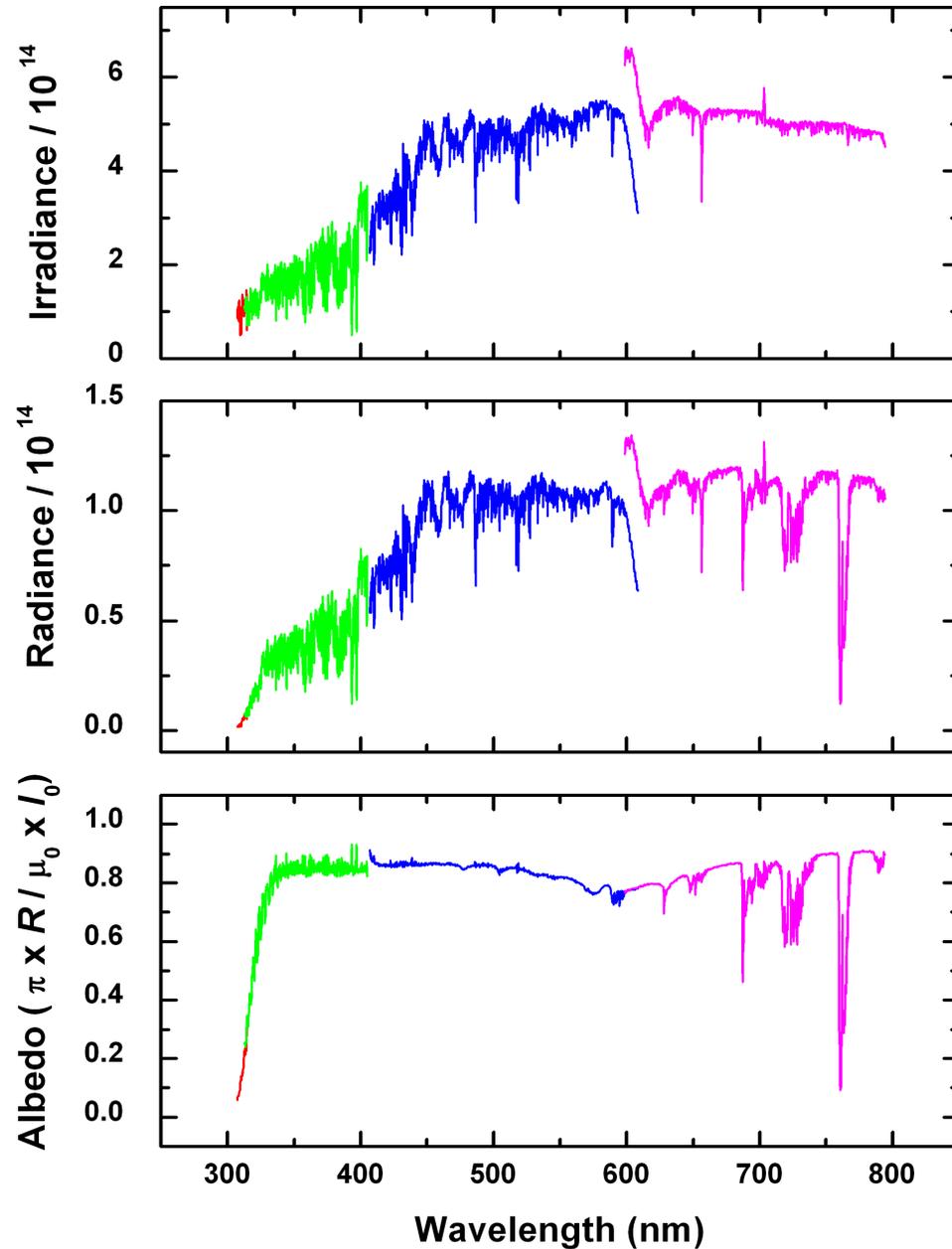
LEO lessons learned

- What enables us to make measurements of the critical set of gases to $2-5 \times 10^{-4}$ of the full-scale measured radiances?
- What is the state of the art for UV/visible spectroscopy of the atmosphere from space?
- What does that imply for near-term monitoring from space? What are the limitations?

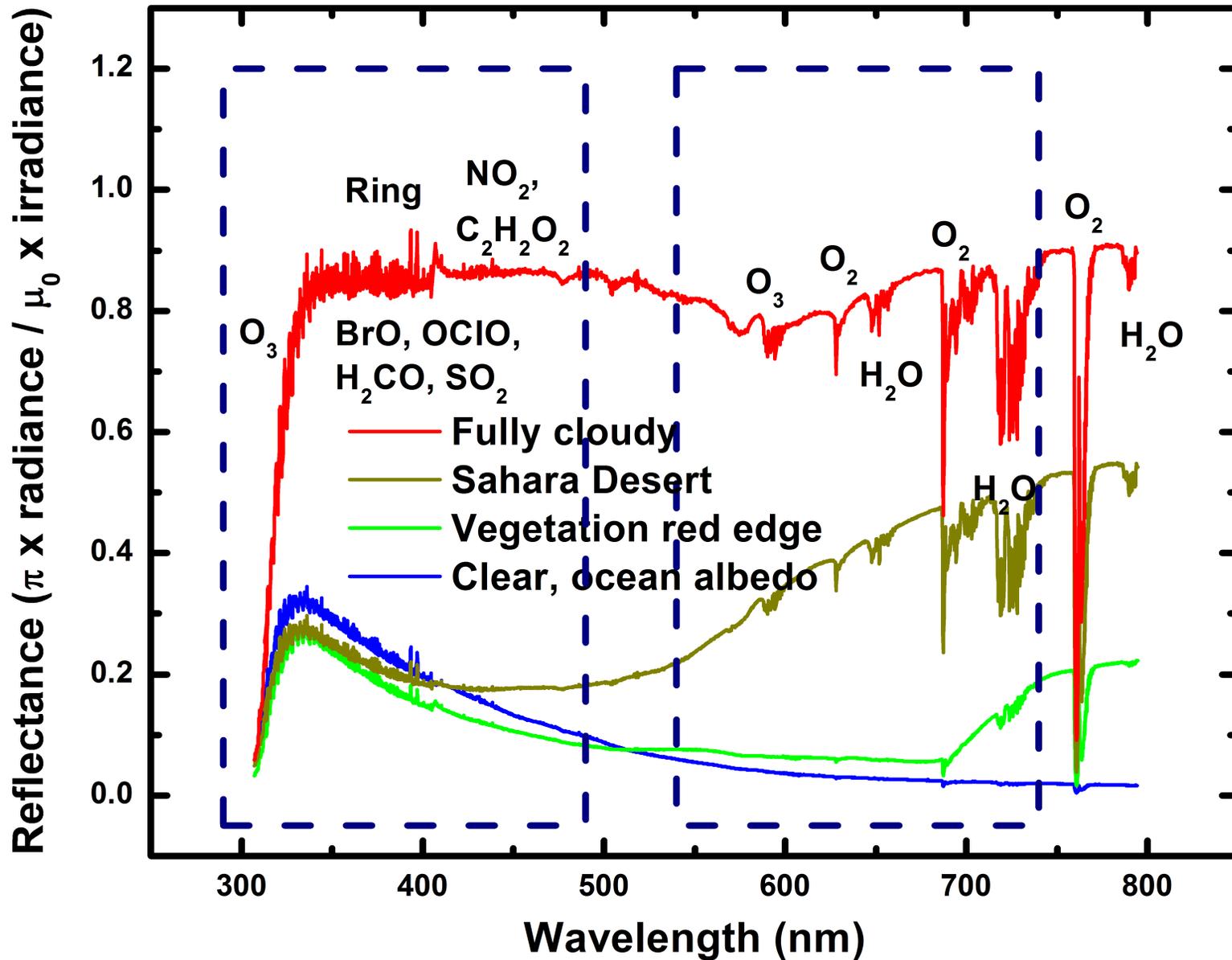


What do we measure?

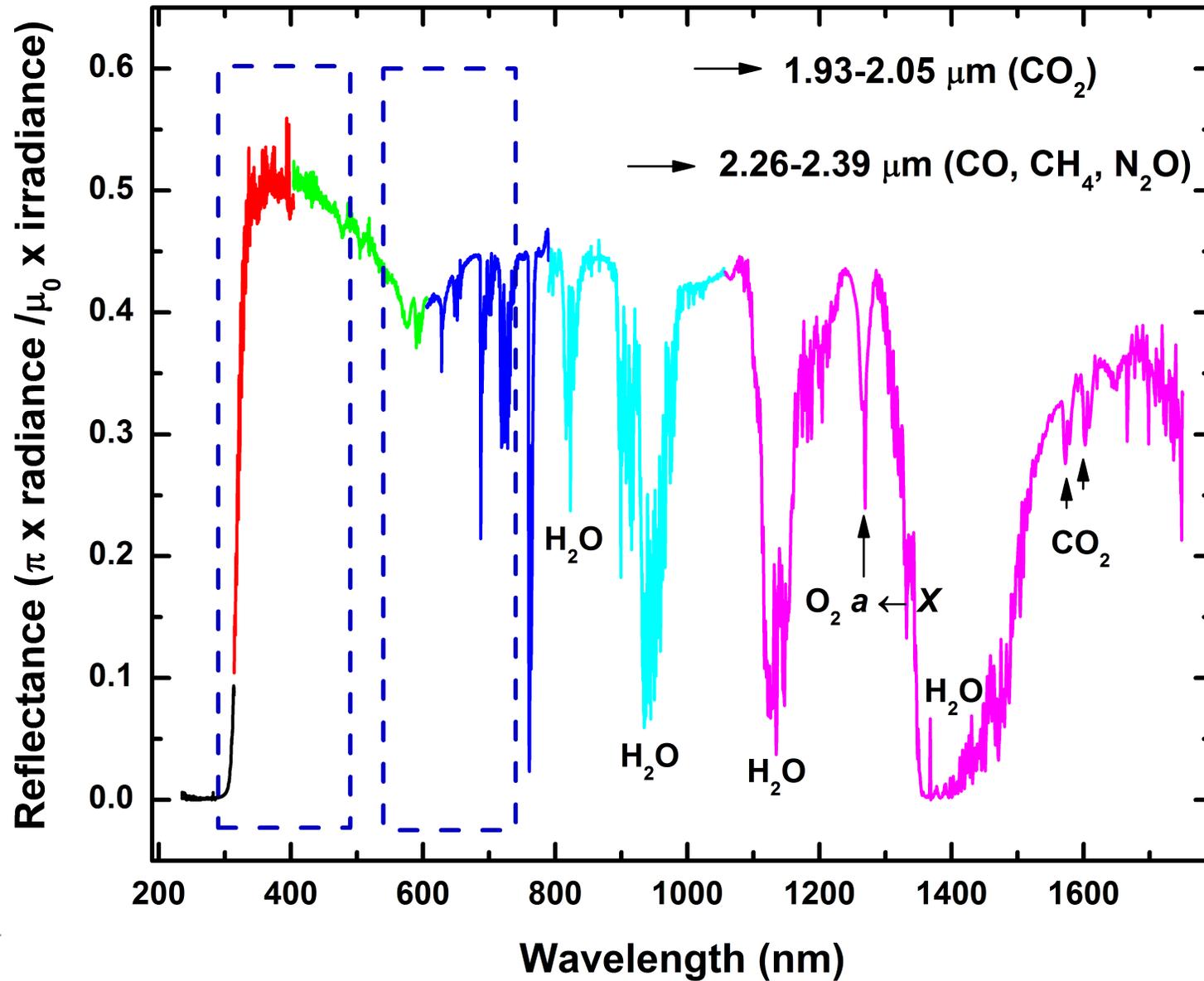
GOME irradiance, radiance, and albedo spectrum for high-albedo (fully cloudy) ground pixel



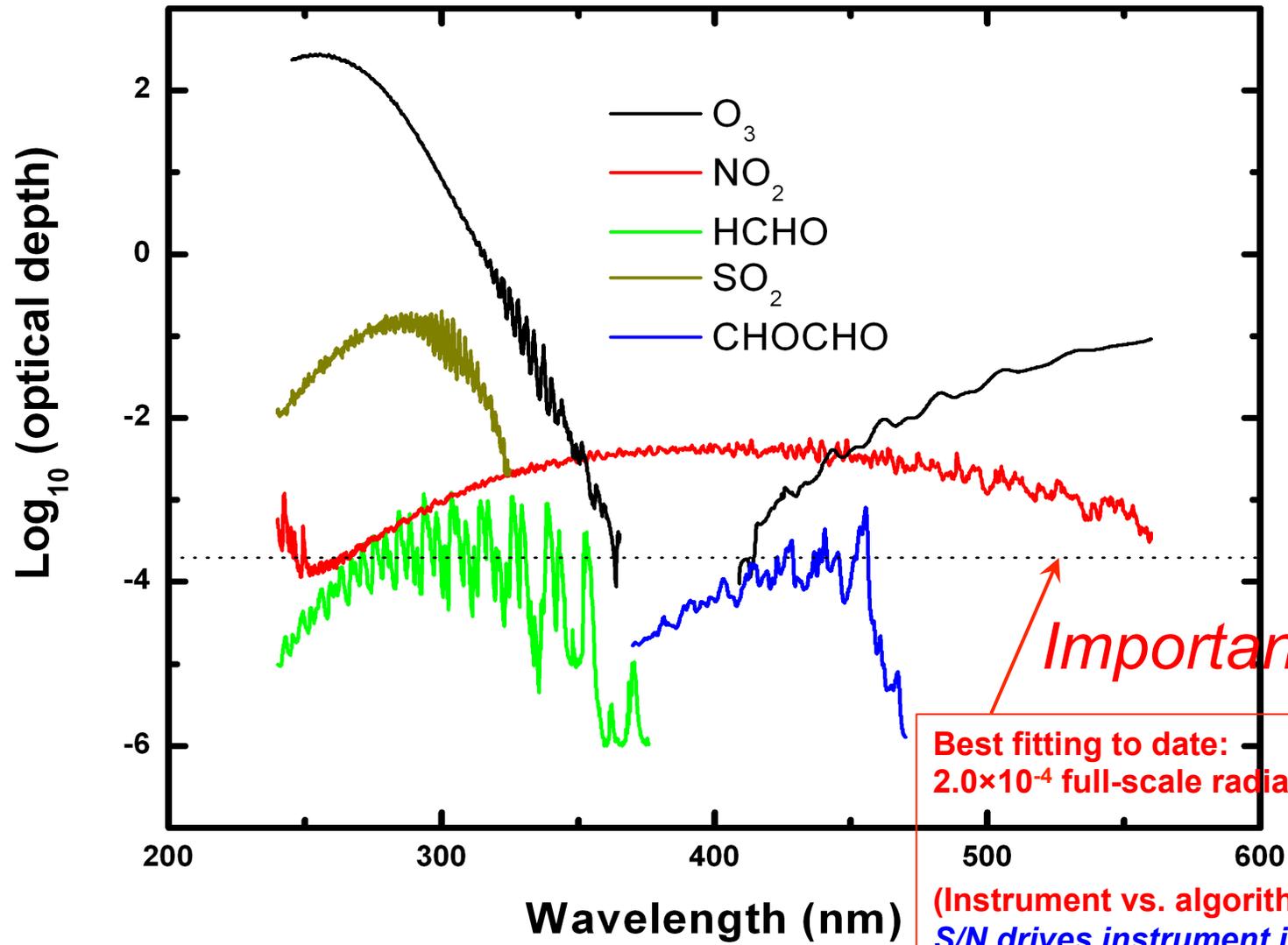
Typical TEMPO-range spectra (from ESA GOME-1)



Typical TEMPO-range spectra (from SCIAMACHY, 2002-2012)

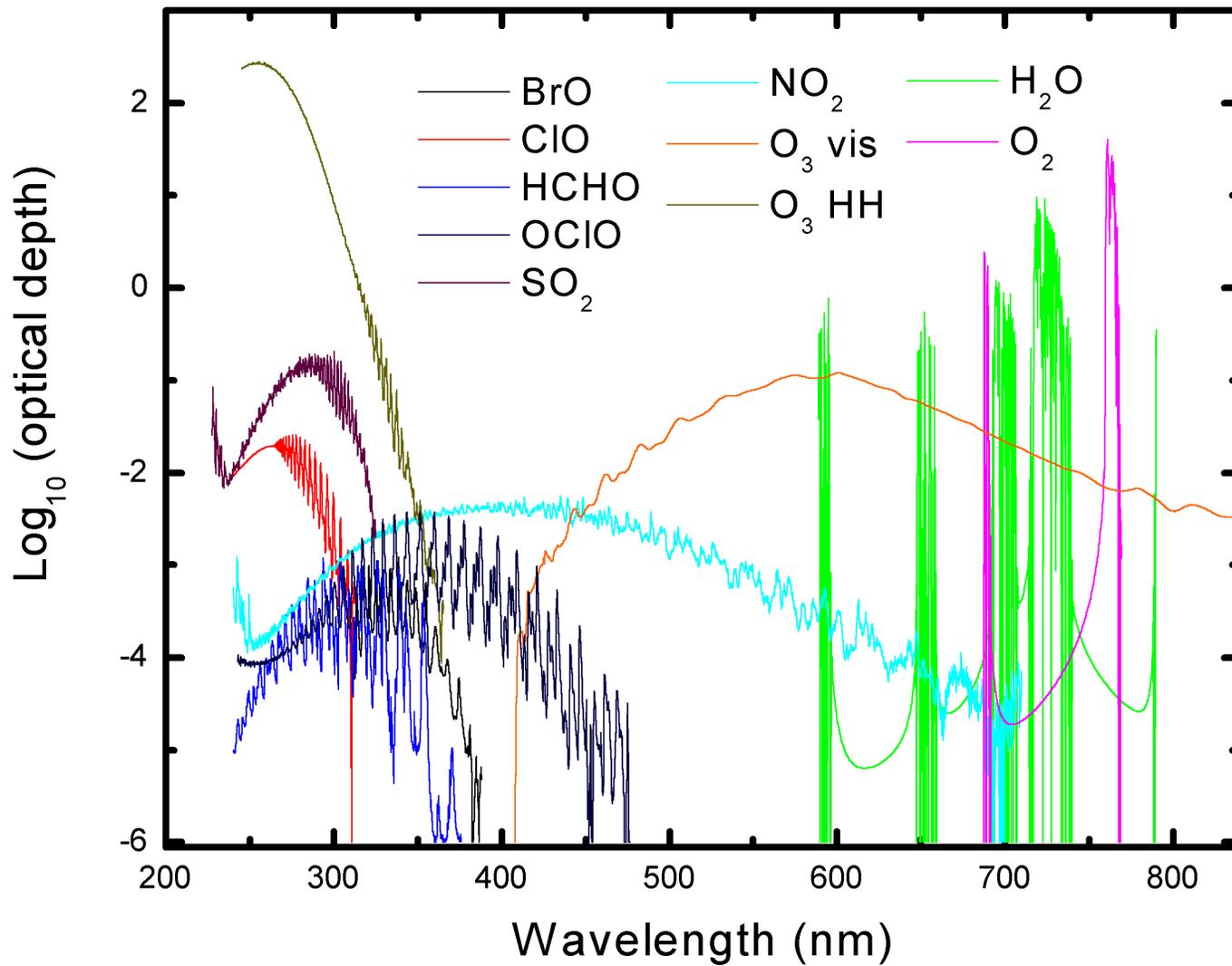


Optical Depths for Typical GEO Measurement Geometry



Important!
Best fitting to date:
 2.0×10^{-4} full-scale radiance
*(Instrument vs. algorithm: Tied!
S/N drives instrument if meas.
requirements can be met*

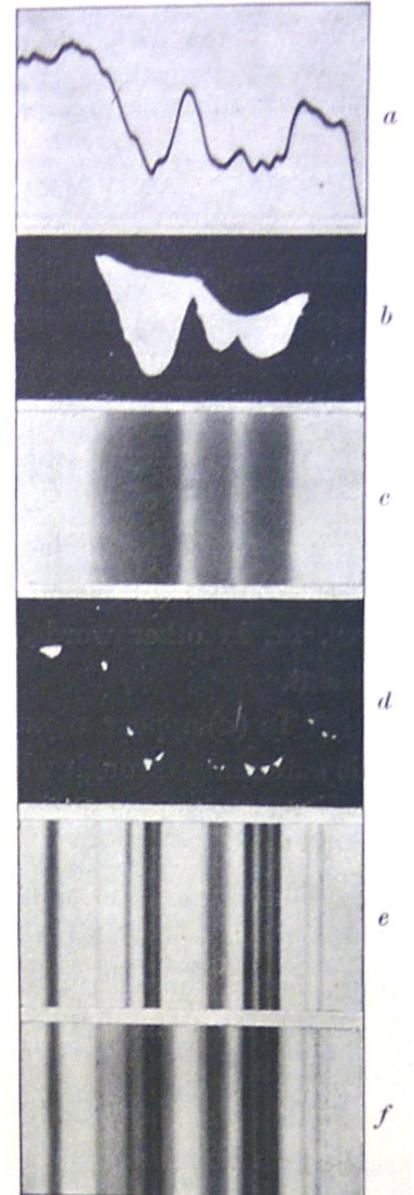
Optical Depths for Typical GOME Measurement Geometry



Why the Smithsonian?

Langley, S.P., and C.G. Abbot, *Annals of the Astrophysical Observatory of the Smithsonian Institution, Volume 1* (1900).

Langley's recently invented bolometer was used to make measurements from the infrared through the near ultraviolet in order to determine the mean value of the solar constant and its variation. Langley and Abbot also developed substantial new experimental techniques (such as an early chart recorder) and various analysis techniques (e.g., the "Langley plot"), including photographic techniques for high and low pass filtering to produce line spectra from "bolographs" (spectra), illustrated, foreshadowing the high pass filtering used today by researchers employing the DOAS technique for analyzing atmospheric spectra.



The Rules

1. Don't define your algorithm in advance
 - *Test all steps for utility and applicability*
 - *Let the physics guide you*
2. No black boxes
 - *You must have and understand all source code, and be able to modify it as necessary*
 - *You must test all assumptions*
3. Fitters must go to bedrock: (Occam's taser): If you didn't do it yourself, it isn't done (and you have to do it down to bedrock and also understand and publish all the reasons why you did it that way)
4. Reference data *as used* must be peer-reviewed, published, and publicly-available (**P³**)
 - *no unexplained shifts in cross sections, for example*
5. A description of the analysis *as performed* must be publicly available.
6. Ecclesiastes 11:1 *Cast thy bread upon the waters: for thou shall find it after many days.*

Spectrum fitting and radiative transfer correction

Frustra fit per plura, quod fieri potest per pauciora.
Essentia non sunt multiplicada praeter necessitatem.

- *William of Occam*





Fitting trace species

- **HCHO is the most challenging** gas to fit for slant columns in GOME spectra (HCHO > CHO-CHO > NO₂ > SO₂ > OCIO > O₃ (depending) > BrO)
- Requires precise (**dynamic**) wavelength calibration, Ring effect correction, undersampling correction, and proper choices of reference spectra (**HITRAN!**)
- Best fitting results come from **direct fitting** of GOME radiances, *I* or *I/E* (except for tropospheric ozone)



Algorithm Overview



- Direct fitting of GOME **radiances** by nonlinear least-squares fitting:
 - Simpler Ring effect formulation (no induced Fraunhofer structure or induced wavelength mismatch)
 - Less distortion of measured data (no high-pass filtering)
- Correction for:
 - Wavelength calibration
 - Ring effect
 - Spectral undersampling
 - Instrument transfer (slit) function
- Division by air-mass factor (**AMF**) using LIDORT radiative transfer model and GEOS-CHEM 3-D tropospheric chemistry and transport model
 - Tropospheric residuals may require further adjustment (e.g., for NO₂)



Fitting approach: Nonlinear least-squares fitting of radiances with lots of optimization



Radiance R is fitted directly (“BOAS fitting”) as:

$$R = A(\lambda)I_0e^{-\sum\tau_n} + Ring + closure(\lambda) \quad \text{N.B. } \Delta\lambda!$$

Further manipulation for Beer’s law fitting gives:

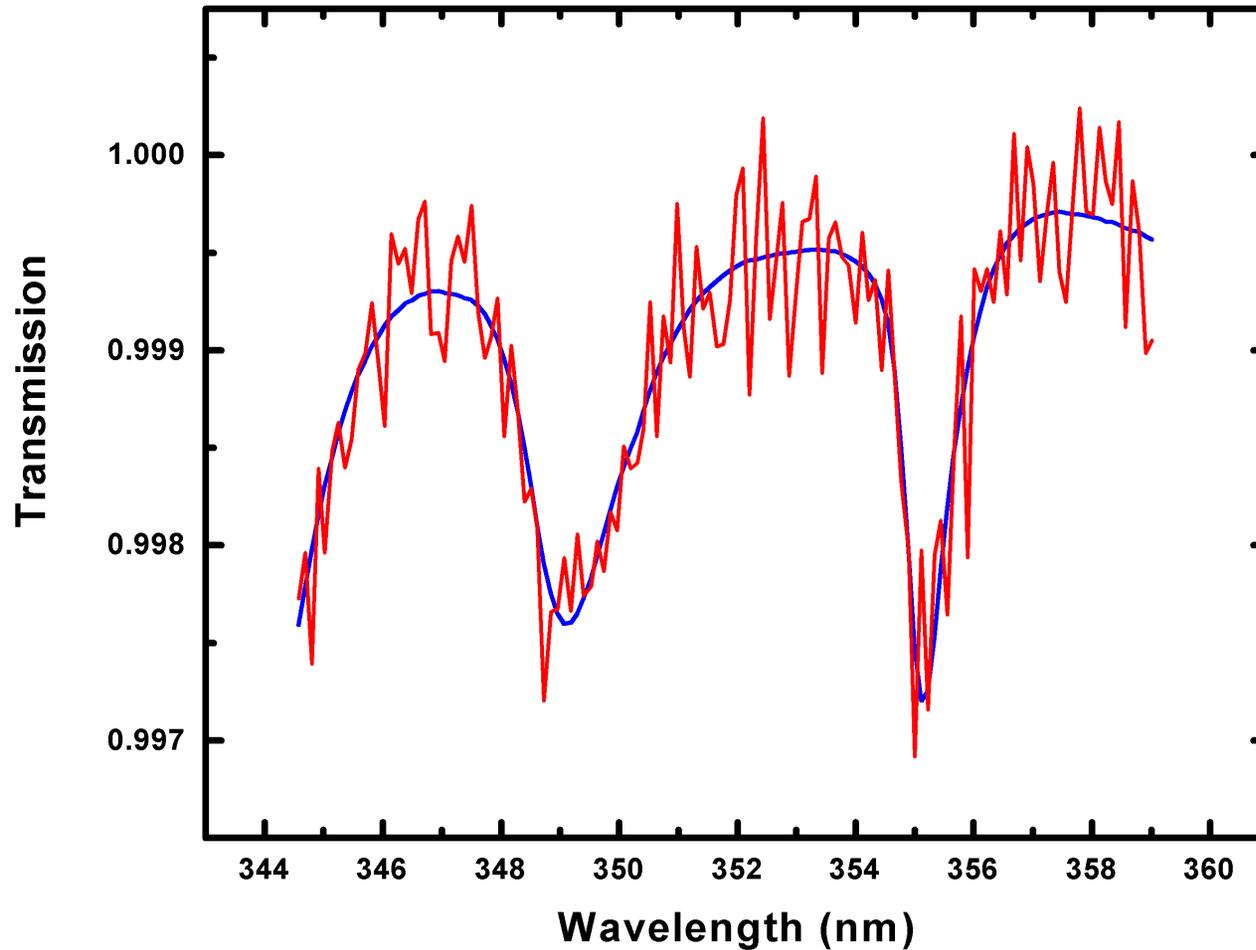
$$\ln \frac{R}{I_0} = -A(\lambda) \sum \tau_n + \frac{Ring}{I_0} + higher - order - Ring + closure(\lambda)$$

But: It’s not a linear fitting problem!

“DOAS” fitting adds high-pass filtering (“ H ”) to give:

$$H\left(\ln \frac{R}{I_0}\right) = -A(\lambda) \sum H(\tau_n) + H\left(\frac{Ring}{I_0}\right) + closure(\lambda)$$

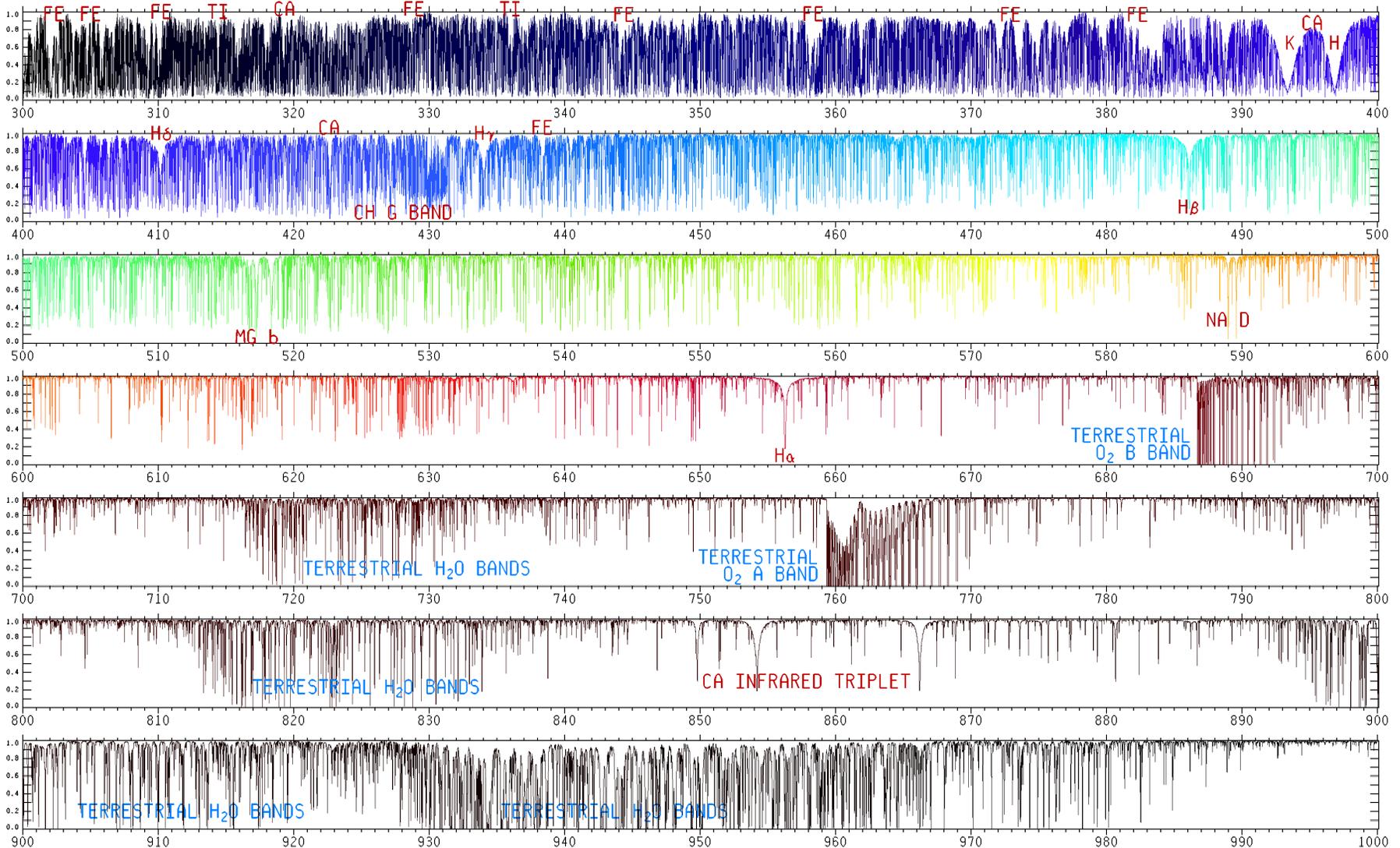
Direct “BOAS” fitting gives a factor of 2-3 improvement!

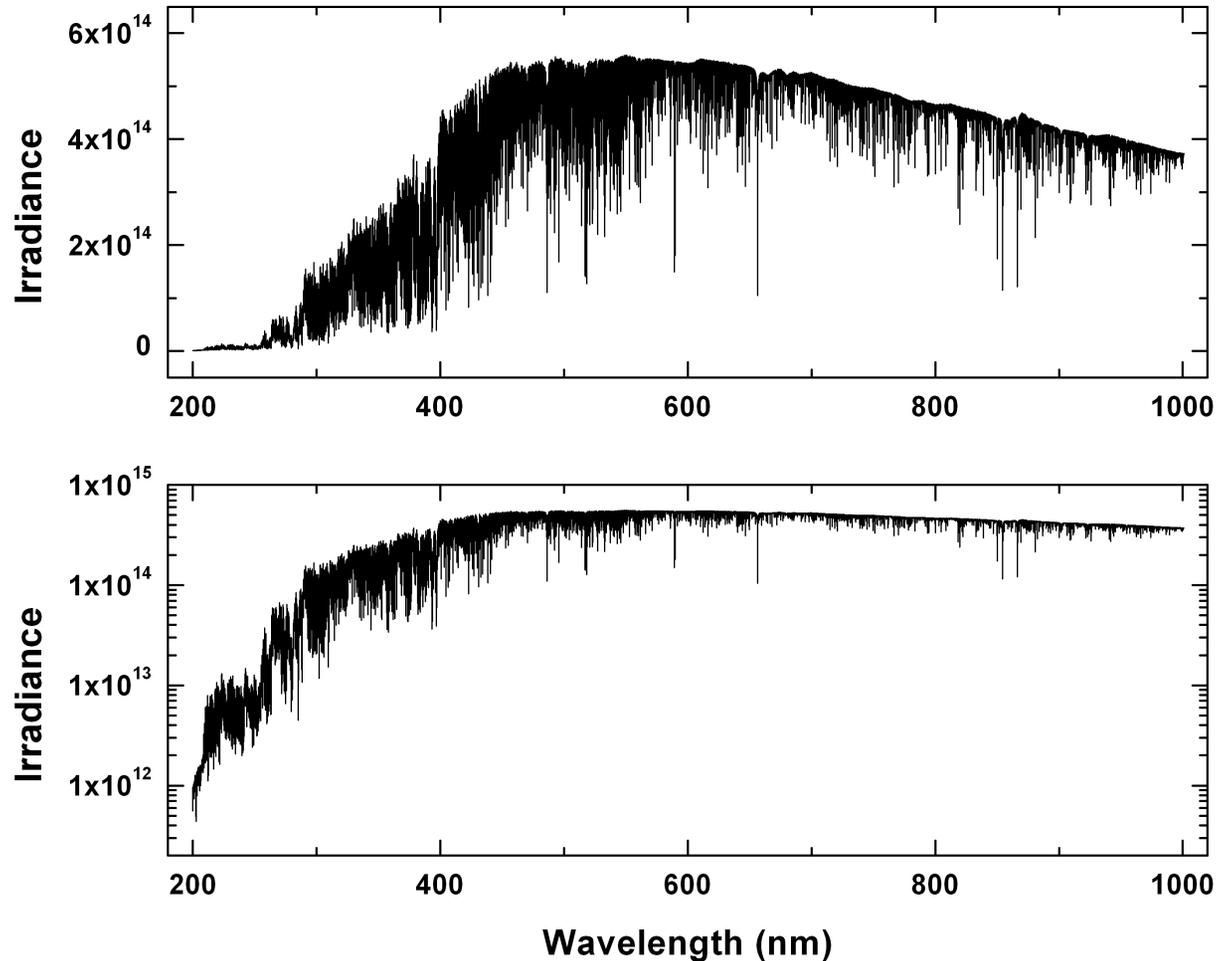


GOME BrO fitting for the FIRS-2 overflight on April 30, 1997. The integration time is 1.5s. The fitting precision is 4.2% and the RMS is 2.7×10^{-4} in optical depth. Fitting and inversion give a vertical BrO column of 9.3×10^{13} cm⁻².

High resolution solar reference spectrum

KITT PEAK SOLAR FLUX ATLAS (KURUCZ, FURENLID, BRAULT, AND TESTERMAN 1984)



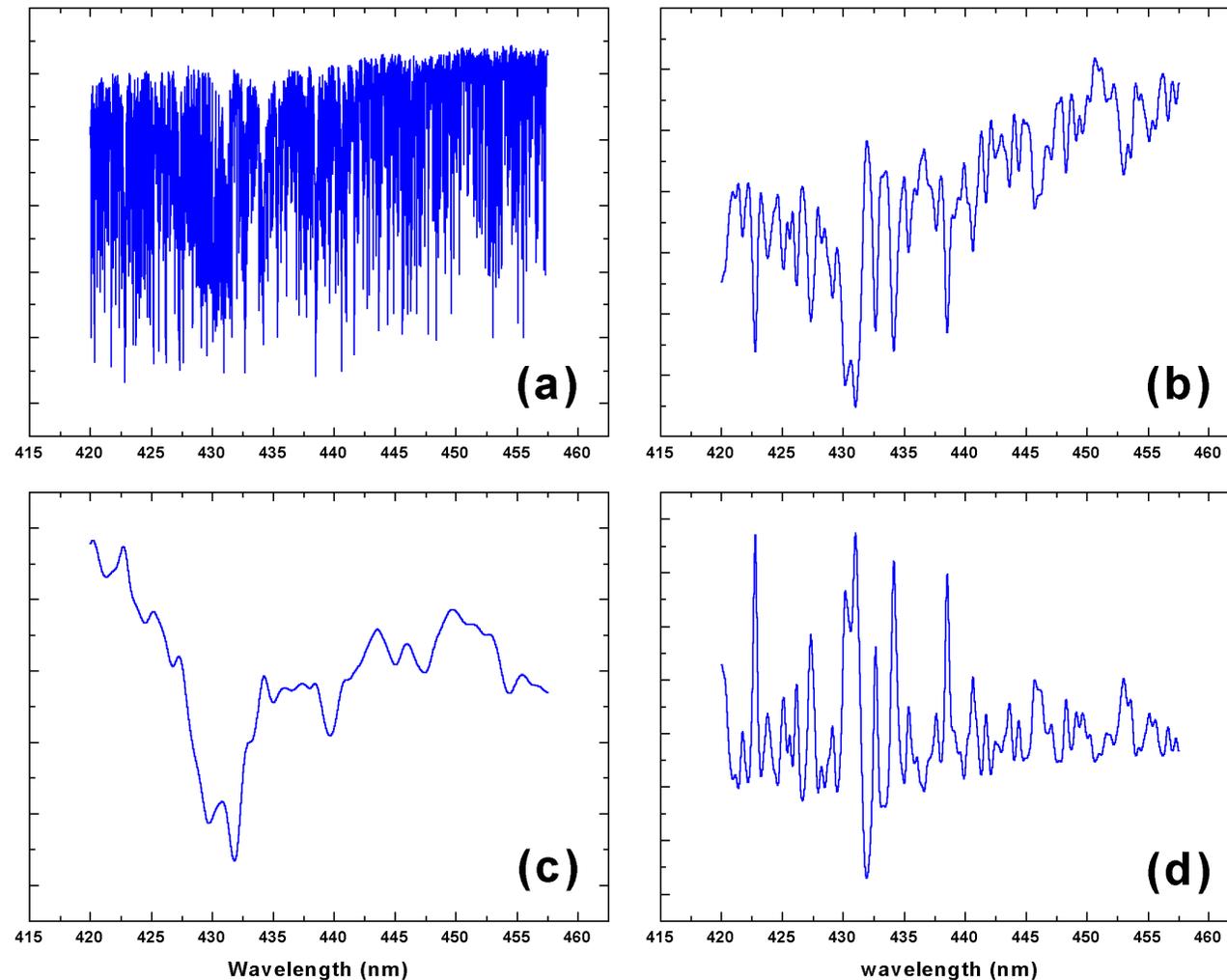


Upper panel: The SAO2010 irradiance reference spectrum (photons $s^{-1} cm^{-2} nm^{-1}$). Lower panel: Irradiance on a logarithmic scale.

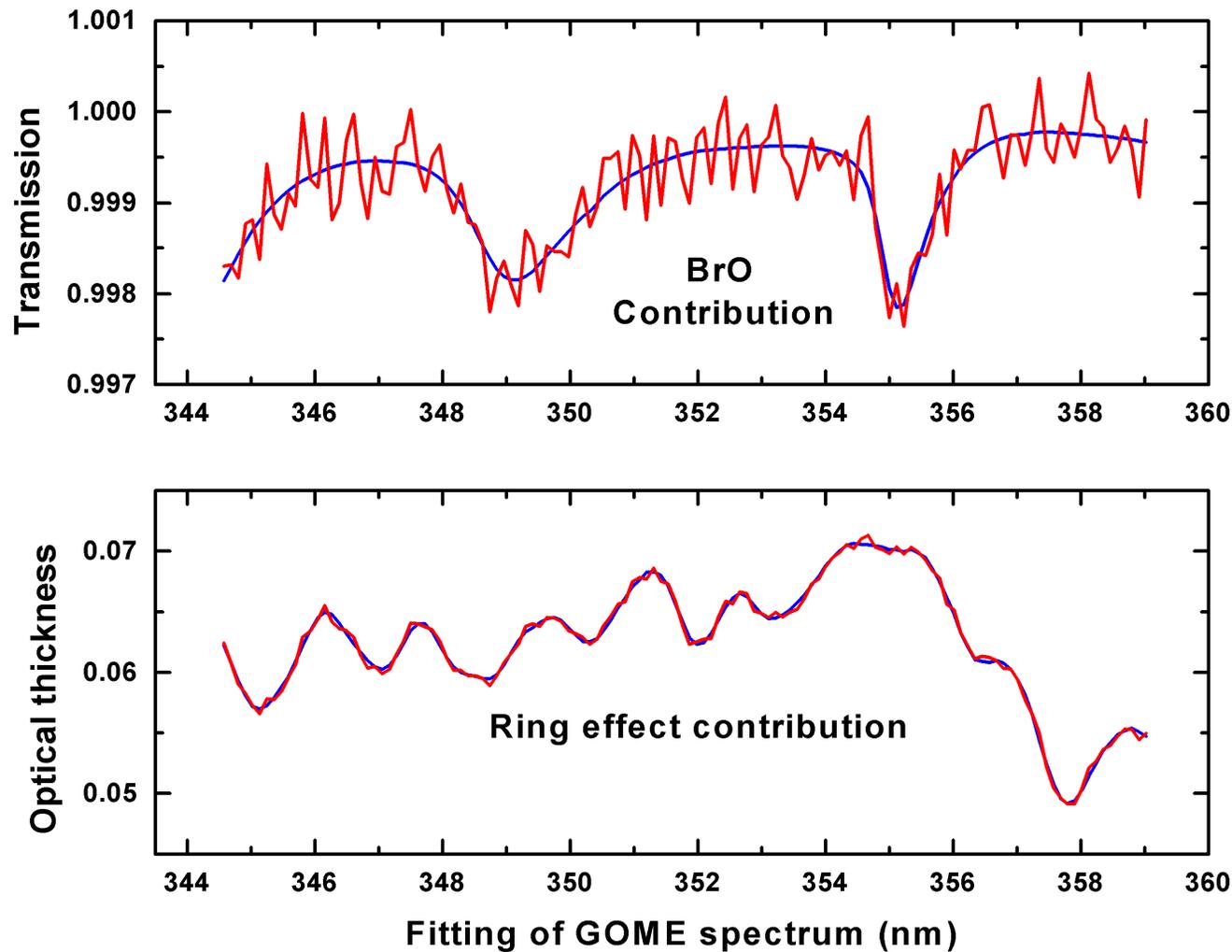
An improved high-resolution solar reference spectrum for Earth's atmosphere measurements in the ultraviolet, visible, and near infrared, K. Chance and R.L. Kurucz, JQSRT, 2010, <http://www.cfa.harvard.edu/atmosphere/publications.html>



Ring effect correction spectrum



(a) Fraunhofer reference spectrum for the NO₂ fitting region; (b) Fraunhofer convolved to GOME spectral resolution; (c) = (b) convolved with rotational Raman cross-sections = Ring effect scattering source per molecule; (d) High-pass filtered version of (c) / (b) = DOAS "Ring effect correction."



GOME BrO fitting: Relative contributions absorption by atmospheric BrO (top) and the **Ring effect** - the inelastic, mostly rotational Raman, part of the Rayleigh scattering – (bottom).

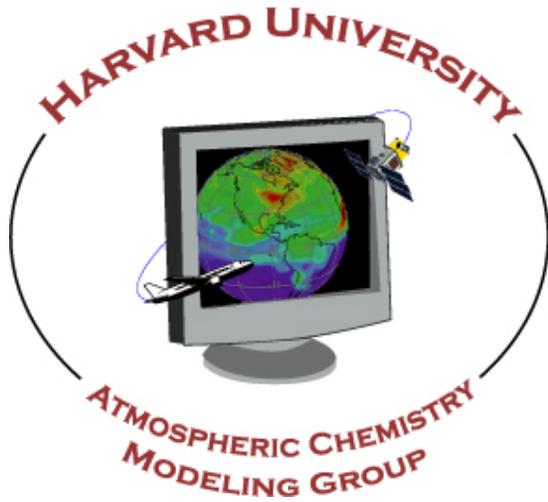
Top-of-atmosphere solar spectral irradiance

The high resolution solar spectral irradiance is critical in analyzing atmospheric trace gases:

- Solar lines are source of accurate wavelength calibration ($\pm 0.0003\text{-}0.0004$ nm for GOME!) – Our method now used operationally on GOME, SCIAMACHY, OMI, and OMPS – Adapted from CfA galactic redshift survey
- Determination of the Ring effect (Inelastic part of Rayleigh, mostly RR)
- Improved knowledge of instrument slit functions
- Correction for spectral undersampling
- Photochemistry of Schumann-Runge system

A space-based determination would be an ideal support mission for 12+ international atmospheric missions!

- Range: 240-1000+ nm
- FWHM: 0.01 nm or better
- Ideal FTS Space Shuttle Canadian European Asian experiment



GEOS-CHEM global 3D tropospheric chemistry and transport model

- **Driven by NASA GMAO met data**
- **$\leq 2 \times 2.5^\circ$ resolution/26 vertical levels**
- **O_3 - NO_x -VOC-halogen chemistry**
- **VOC NO_x , SO_2 emissions**
- **Aerosol scattering**



RT SOLUTIONS

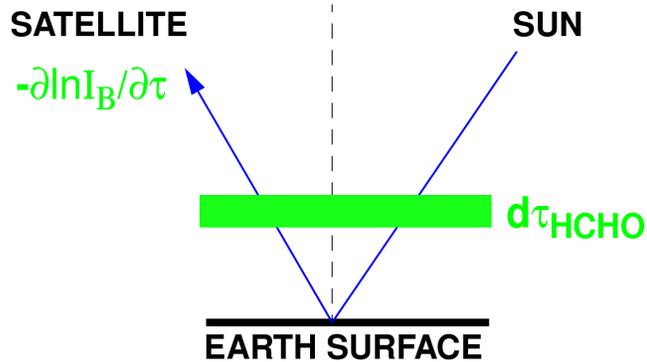
Radiative Transfer Consultancy

LIDORT multiple-scattering radiative transfer code (*R. Spurr*)

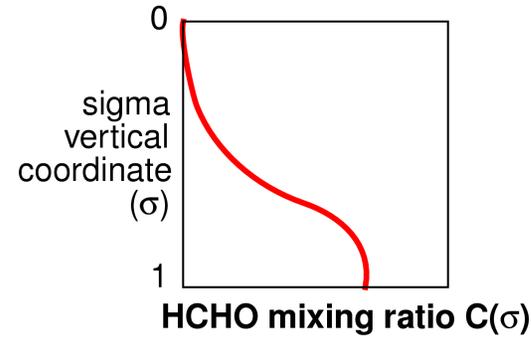
- **Discrete ordinate radiative transfer code**
- **Full analytical perturbation analysis of intensity field:**
 - **Yields radiances and Jacobians (weighting functions) in one pass (no finite-differencing)**
- **Pseudo-spherical and quasi-spherical versions available**
- **Surface BRDF**
- **Vector (polarization) version (VLIDORT) now used**



SAO LIDORT radiative transfer model



GEOS-CHEM global 3-D model



Scattering Weights

$$w(\sigma) = -\frac{1}{AMF_G} \frac{\partial}{\partial \tau} (\ln I/B)$$

Shape Factor

$$S(\sigma) = C(\sigma) \frac{\Omega_{air}}{\Omega_{HCHO}}$$

$$AMF = AMF_G \int_0^1 w(\sigma) S(\sigma) d\sigma$$

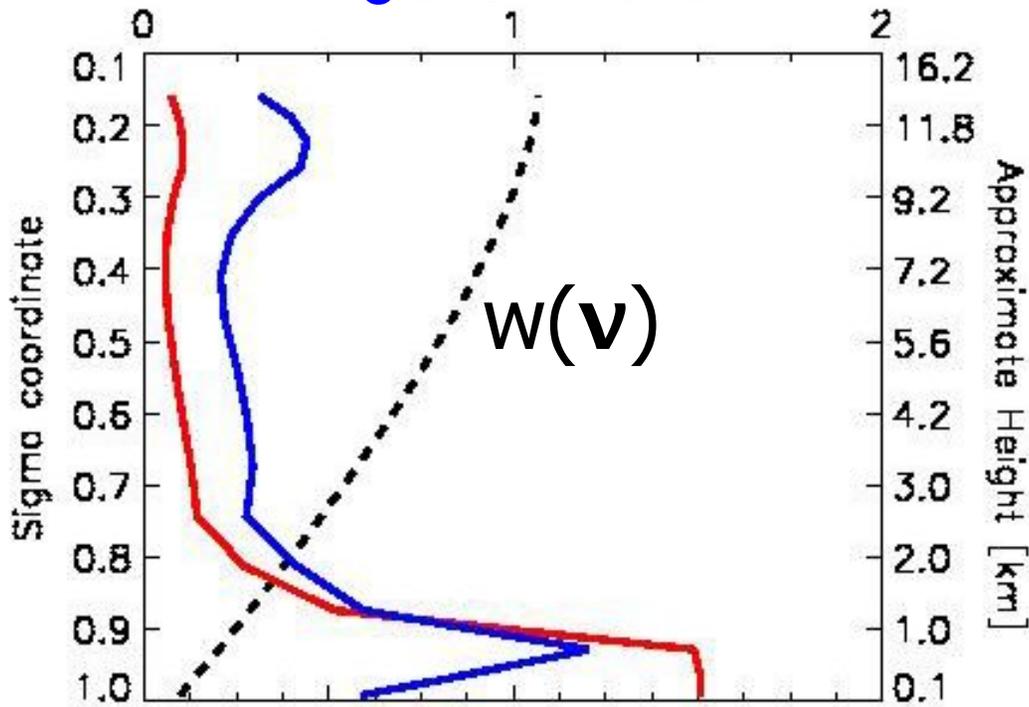
Determination of **air mass factors (AMFs)**, for converting measured slant column abundances in vertical column abundances, for absorption by atmospheric gases. In the optically thin case, the air mass factor calculation is separable into a radiative transfer part (“scattering weights”) and a normalized atmospheric loading (“shape factor”).



AMF example – HCHO over Tennessee



$S_{\sigma}(\mathbf{v})$ $w(\mathbf{v})$



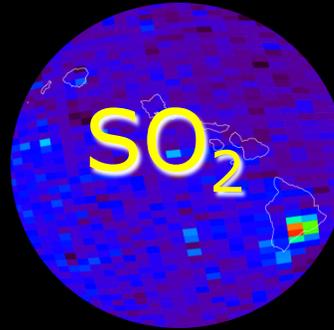
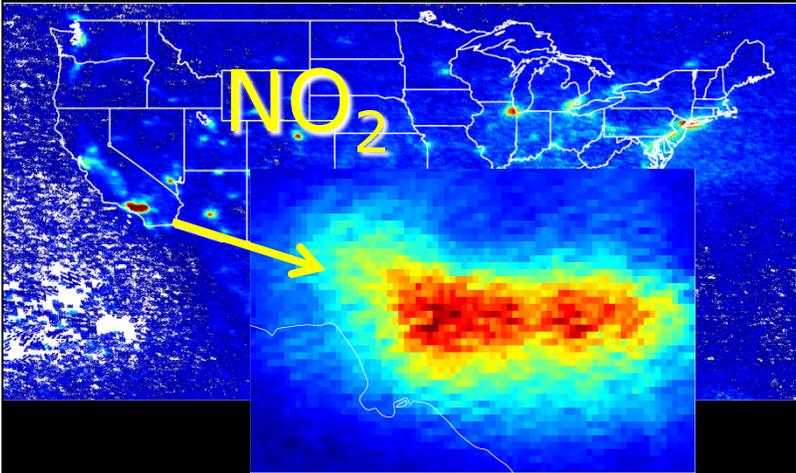
GEOS-CHEM $S_{\sigma}(\mathbf{v})$

AMF=0.71

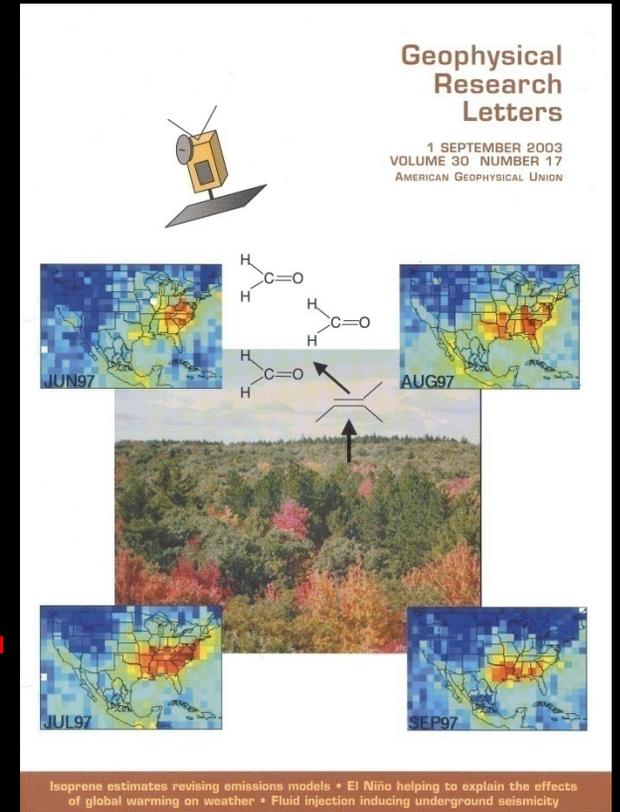
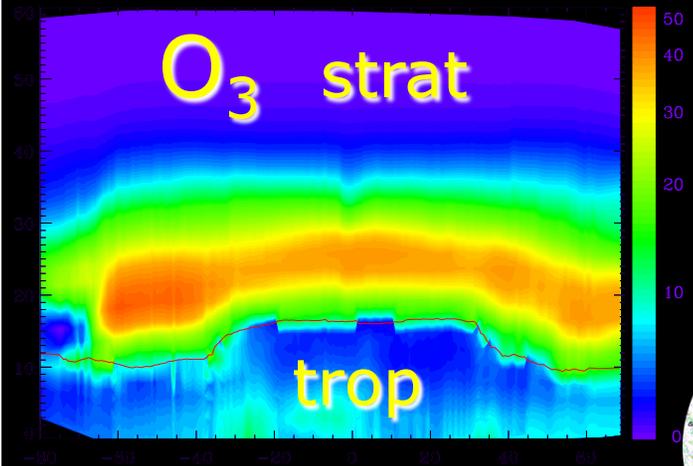
AMF_G=2.08

An AMF calculation should be done for every scene.

GOME, SCIAMACHY, and OMI measurement examples

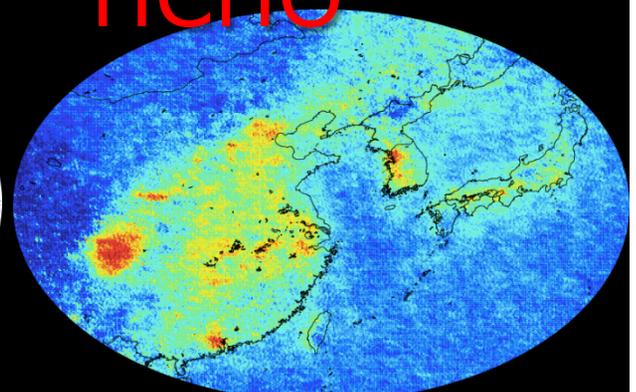


Kilauea activity, source of the VOG event in Honolulu on 9 November 2004

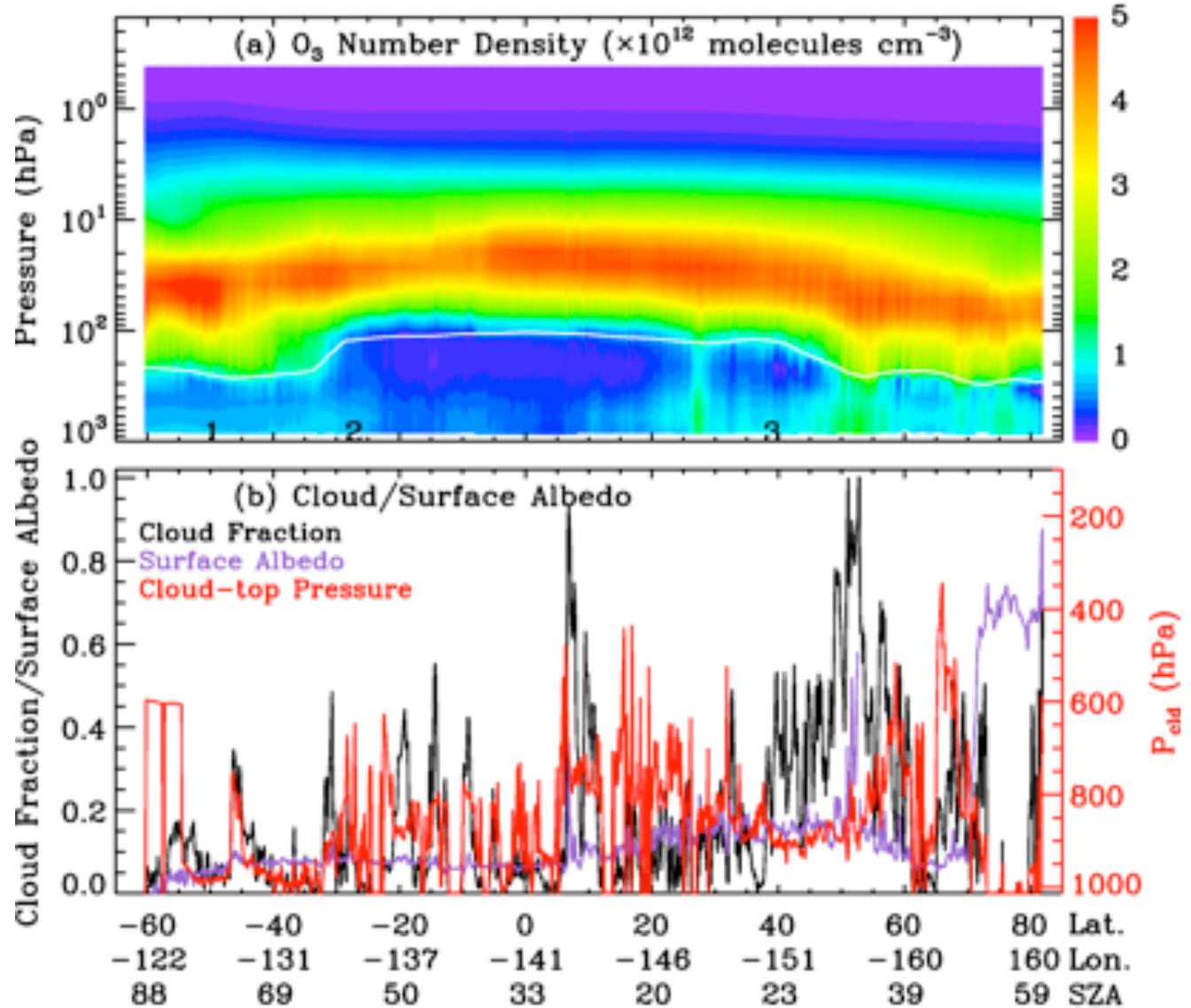


Isoprene estimates revising emissions models • El Niño helping to explain the effects of global warming on weather • Fluid injection inducing underground seismicity

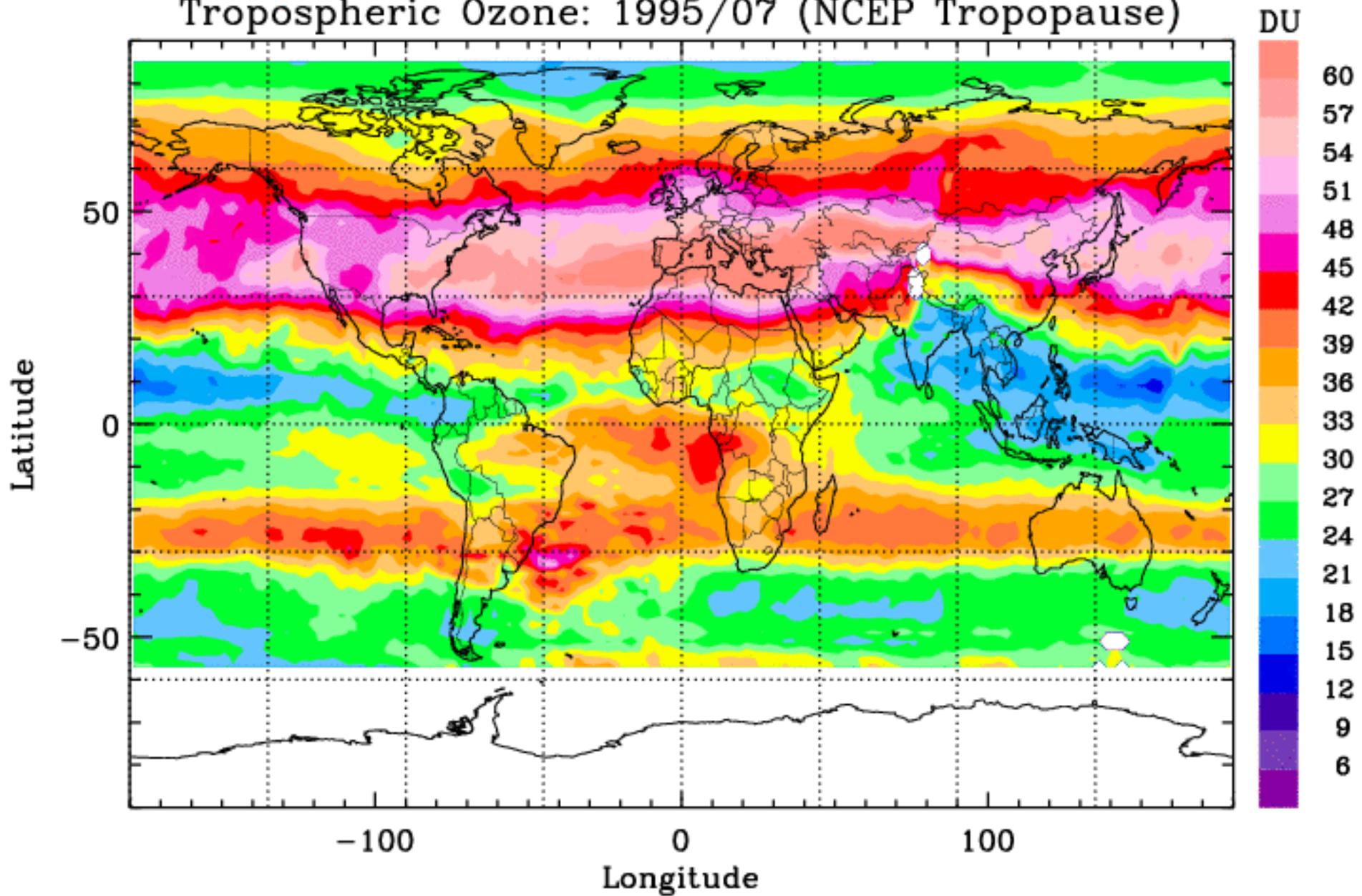
HCHO



An orbit of retrievals at OMI across-track position 16 (in the UV-1 channel) for July 11, 2006 as a function of latitude, longitude, and solar zenith angle. (a) Ozone profiles in number density, and (b) the effective cloud fraction (black), fitted surface albedo (purple) for the UV-2 channel, and effective cloud-top pressure (red) used in the retrievals. The white line in (a) indicates the NCEP thermal tropopause.



Tropospheric Ozone: 1995/07 (NCEP Tropopause)

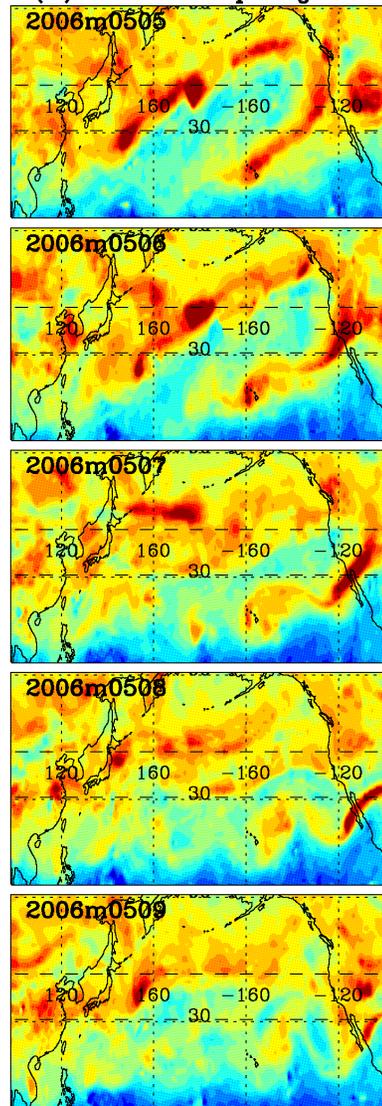


An event of transpacific transport of pollution from East Asia across the North Pacific Ocean to the United States on 5-9 May, 2006

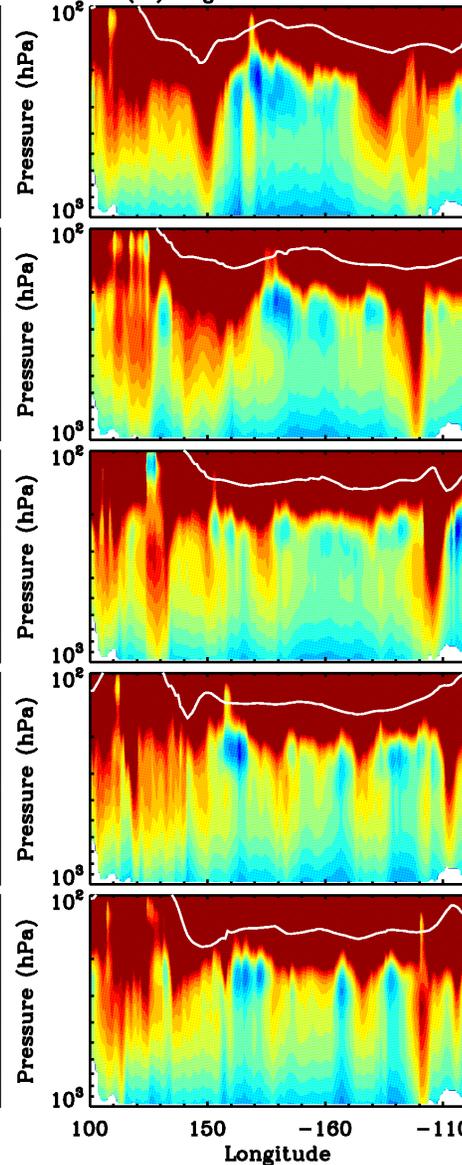
“eXceL” method



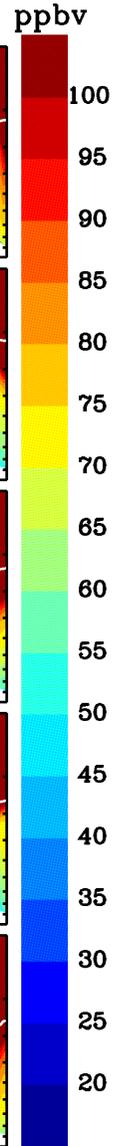
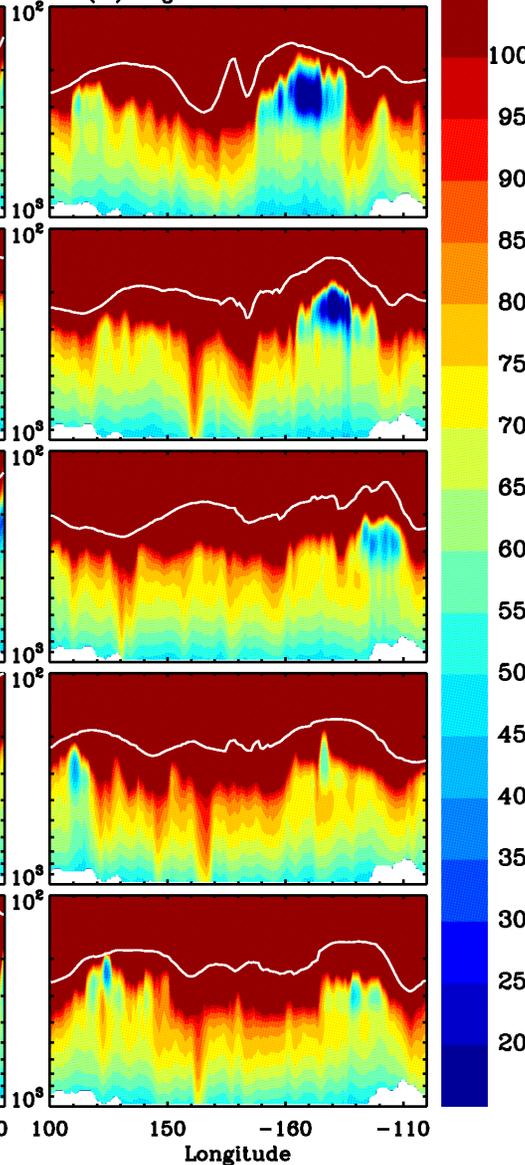
(a) Mean Trop. O₃ MR



(b) O₃ MR at 31.5 N



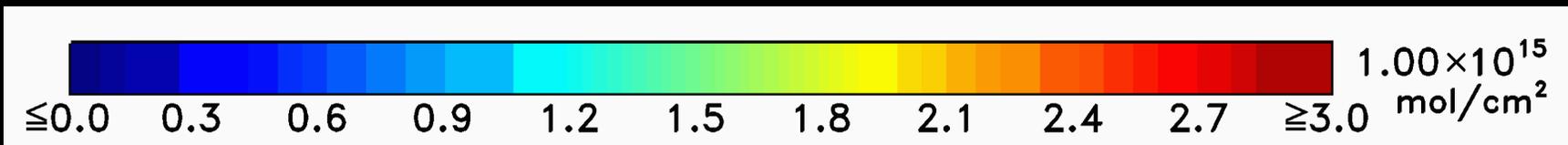
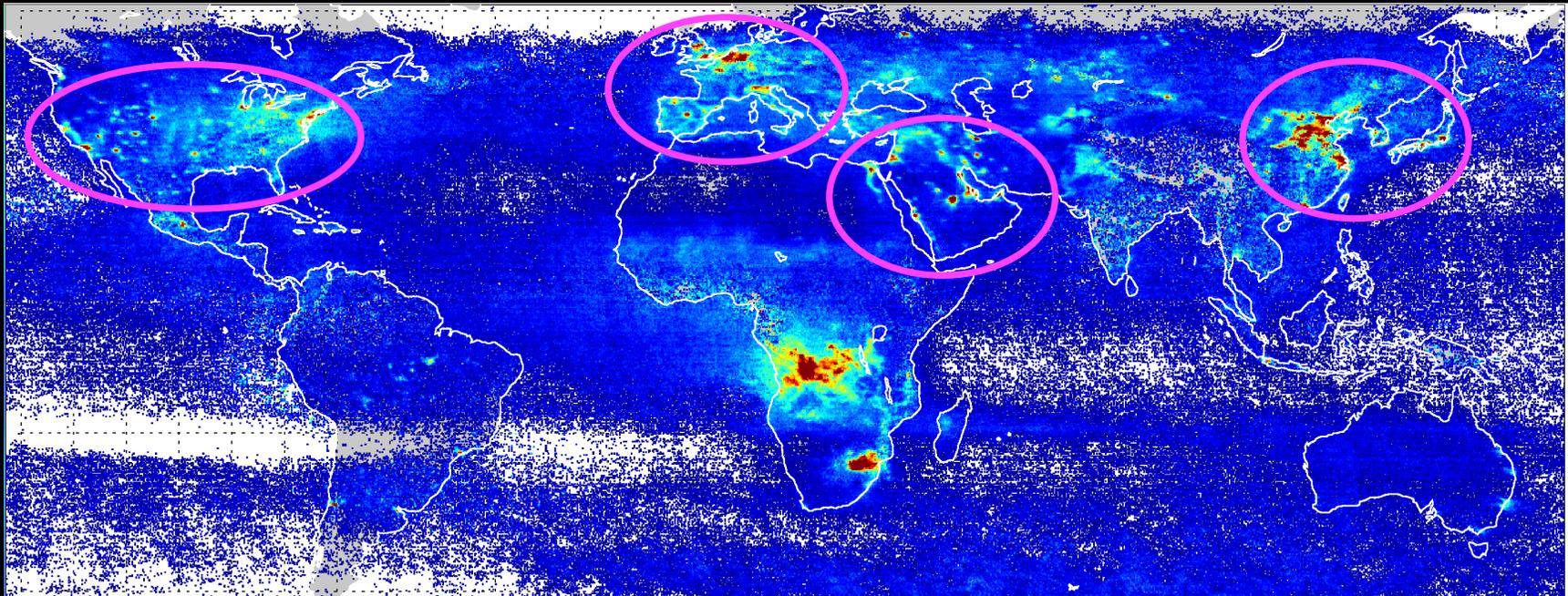
(c) O₃ MR at 41.5 N



Ozone Profile Retrievals from the Ozone Monitoring Experiment, X. Liu, P.K. Bhartia, K. Chance, R.J.D. Spurr, and T.P. Kurosu, *ACP*, 10, 2521-2537, 2010.

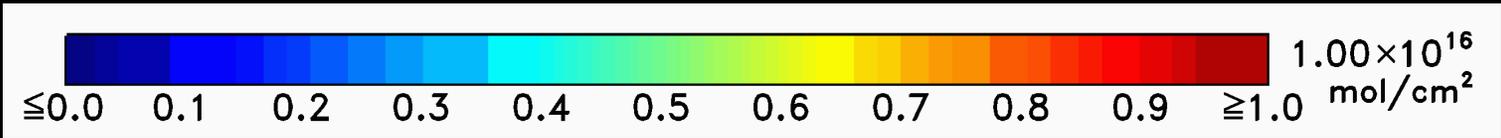
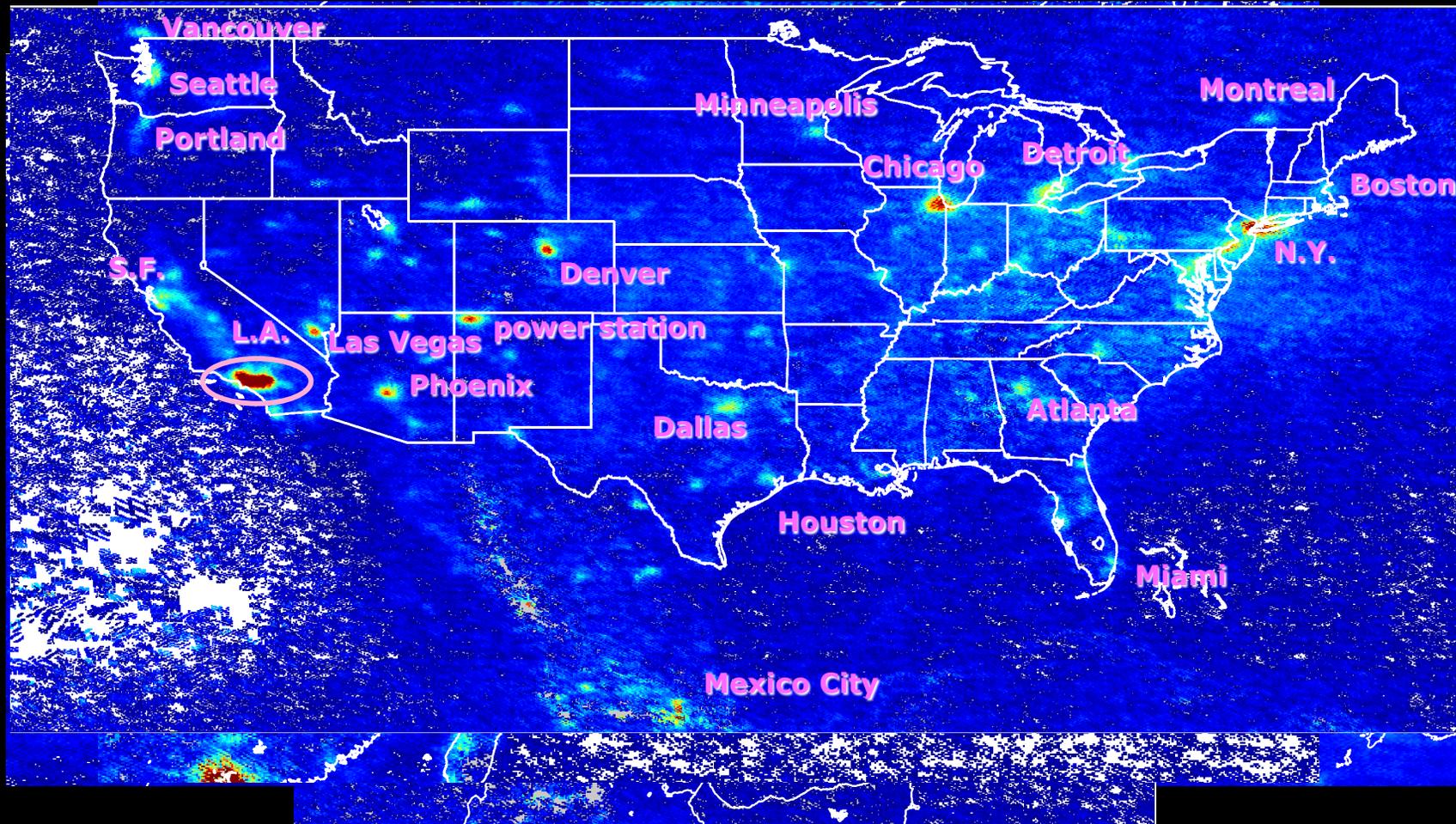
NO₂ — Global Picture (here from OMI)

Tropospheric Column NO₂ (geometric method) July 2003

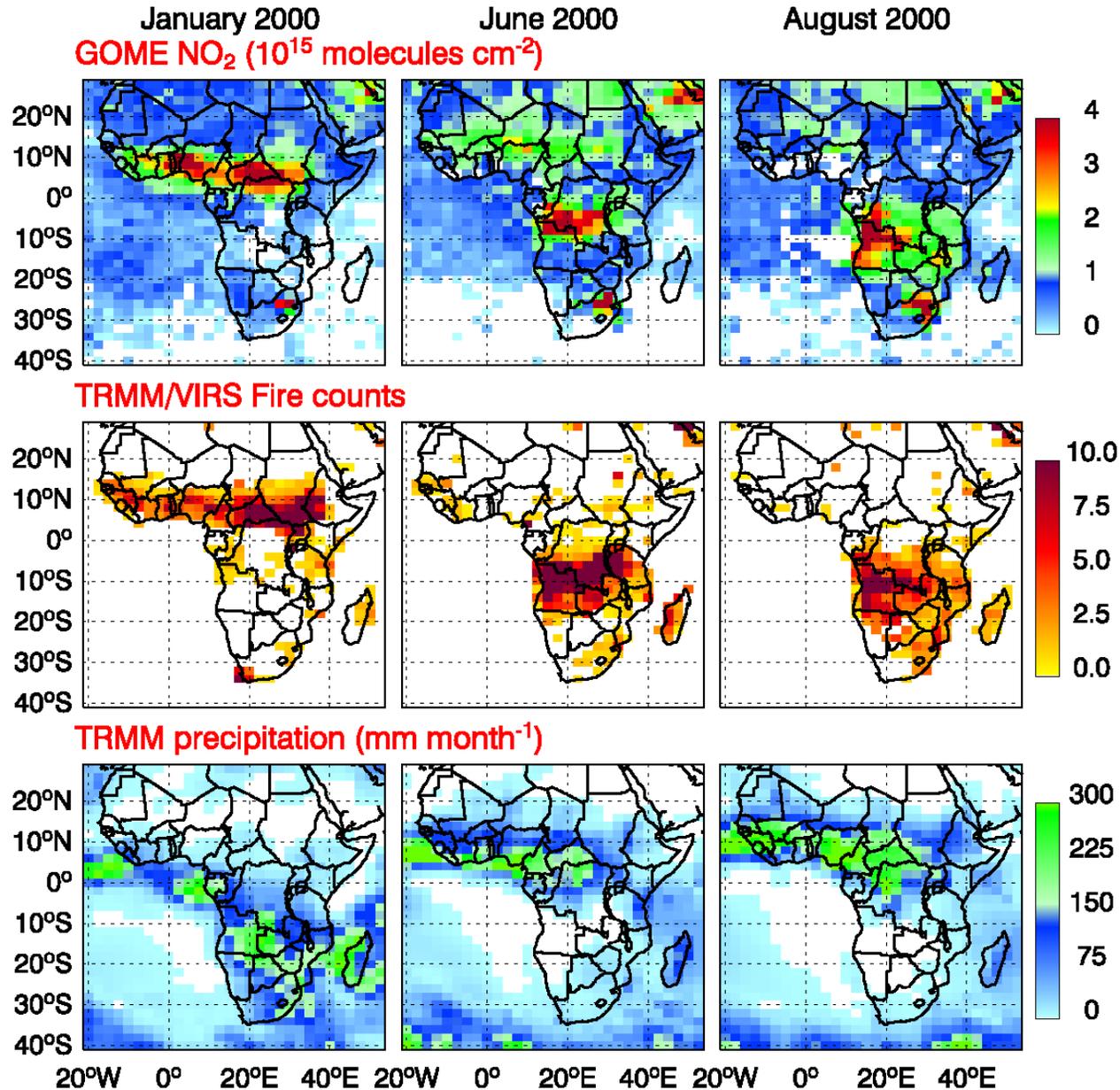


Cloud screening: cloud fraction ≤ 20%

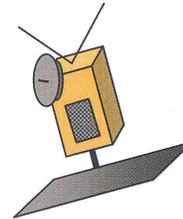
NO₂



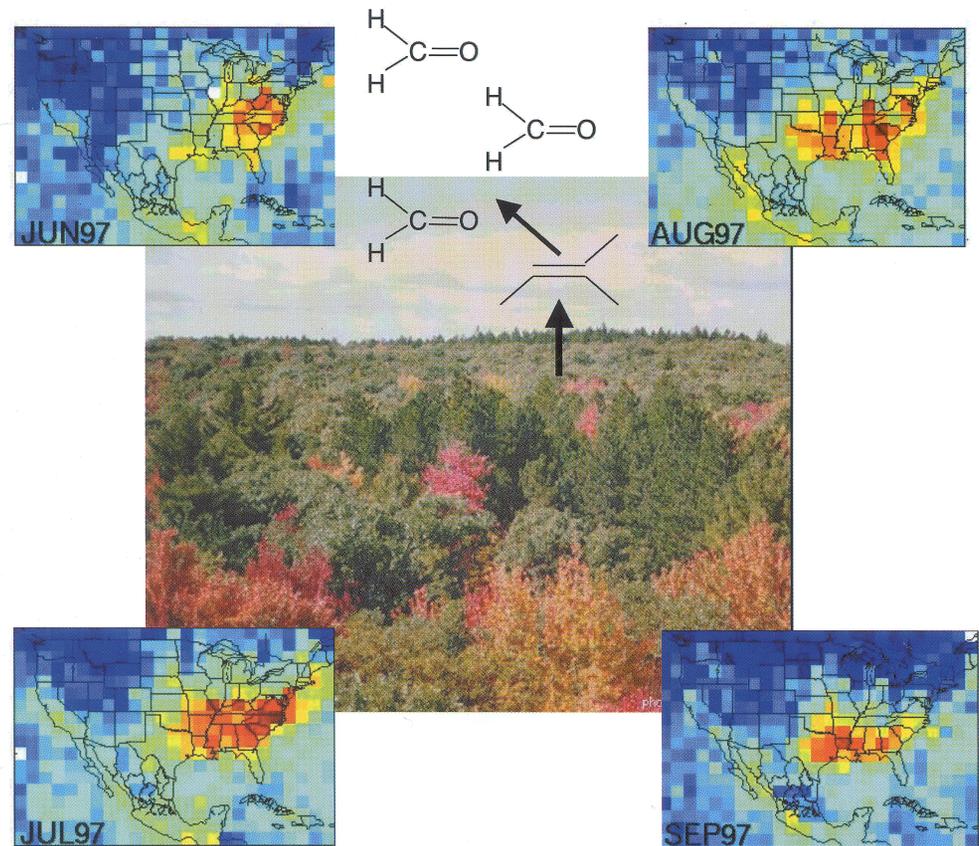
Soil NO_x (Lyatt Jaeglé *et al.*)



VOC emission inventories derived from H_2CO measurements

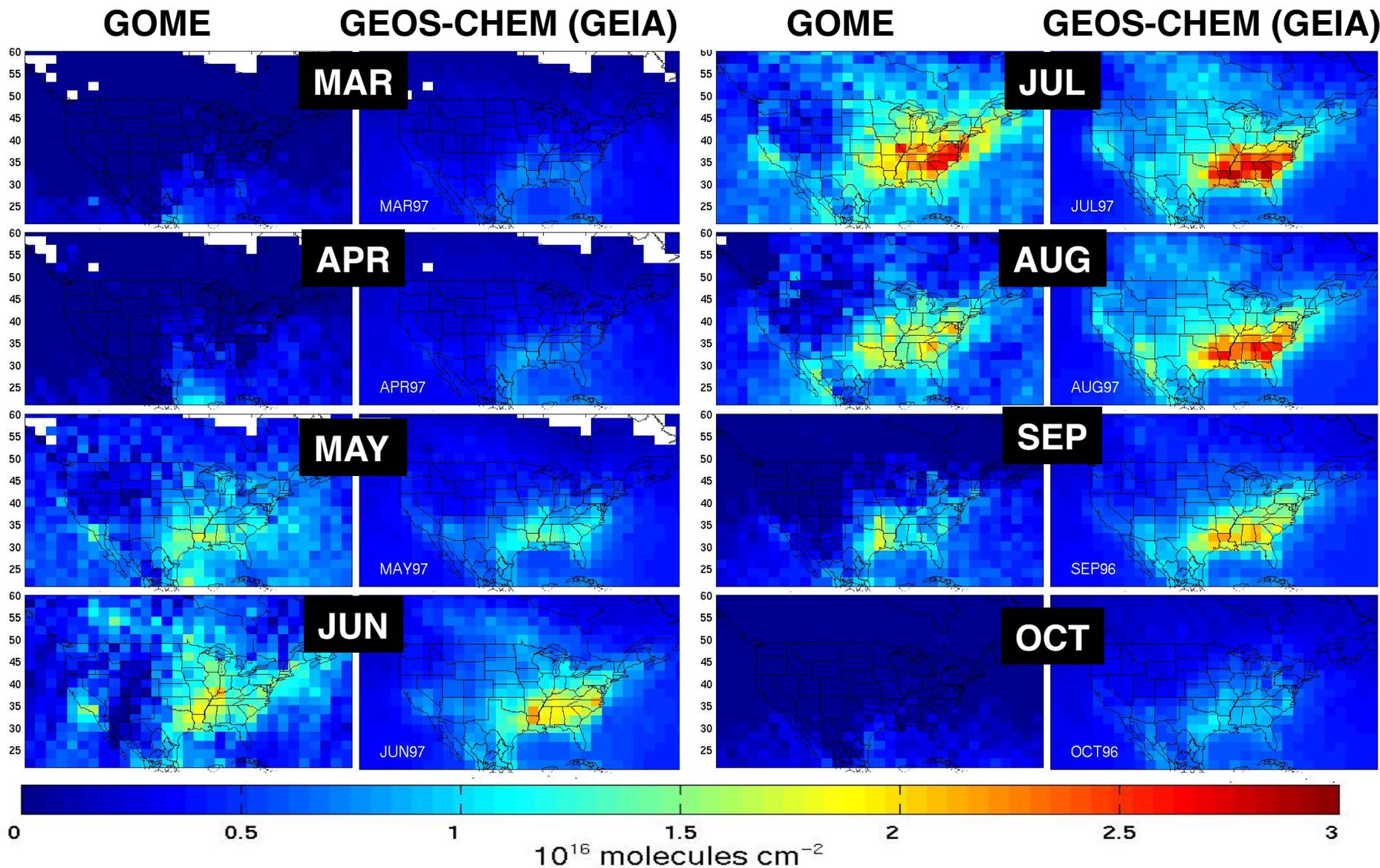


- Volatile Organic Compound
- Produced from Methane oxidation, isoprene emissions
- Indicator for Air Quality
- Average lifetime: ~1.5 h, against photolysis, OH

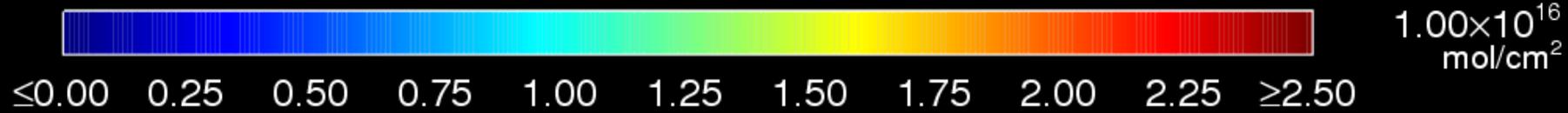
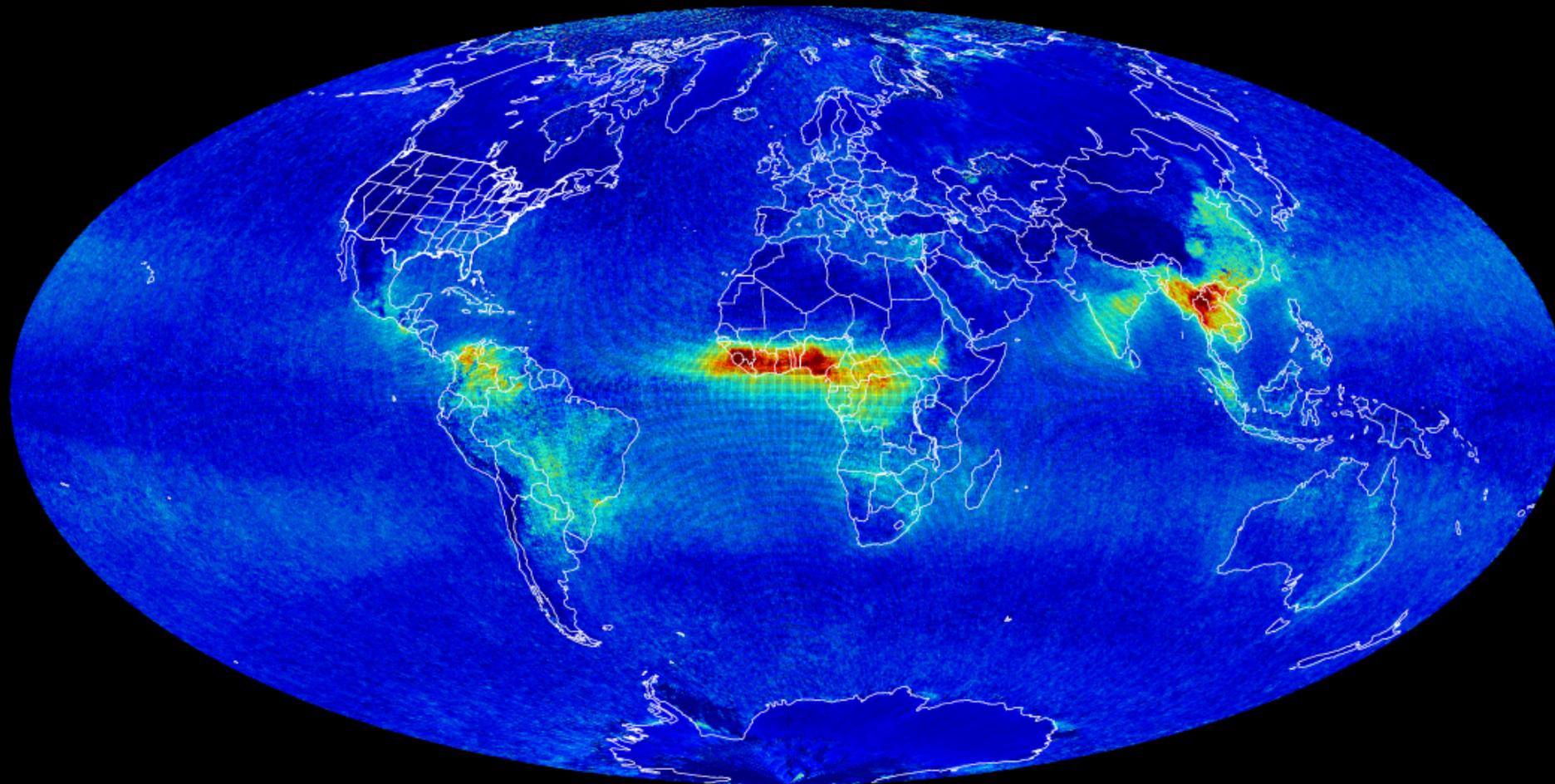


SEASONALITY OF GOME HCHO COLUMNS (9/96-8/97)

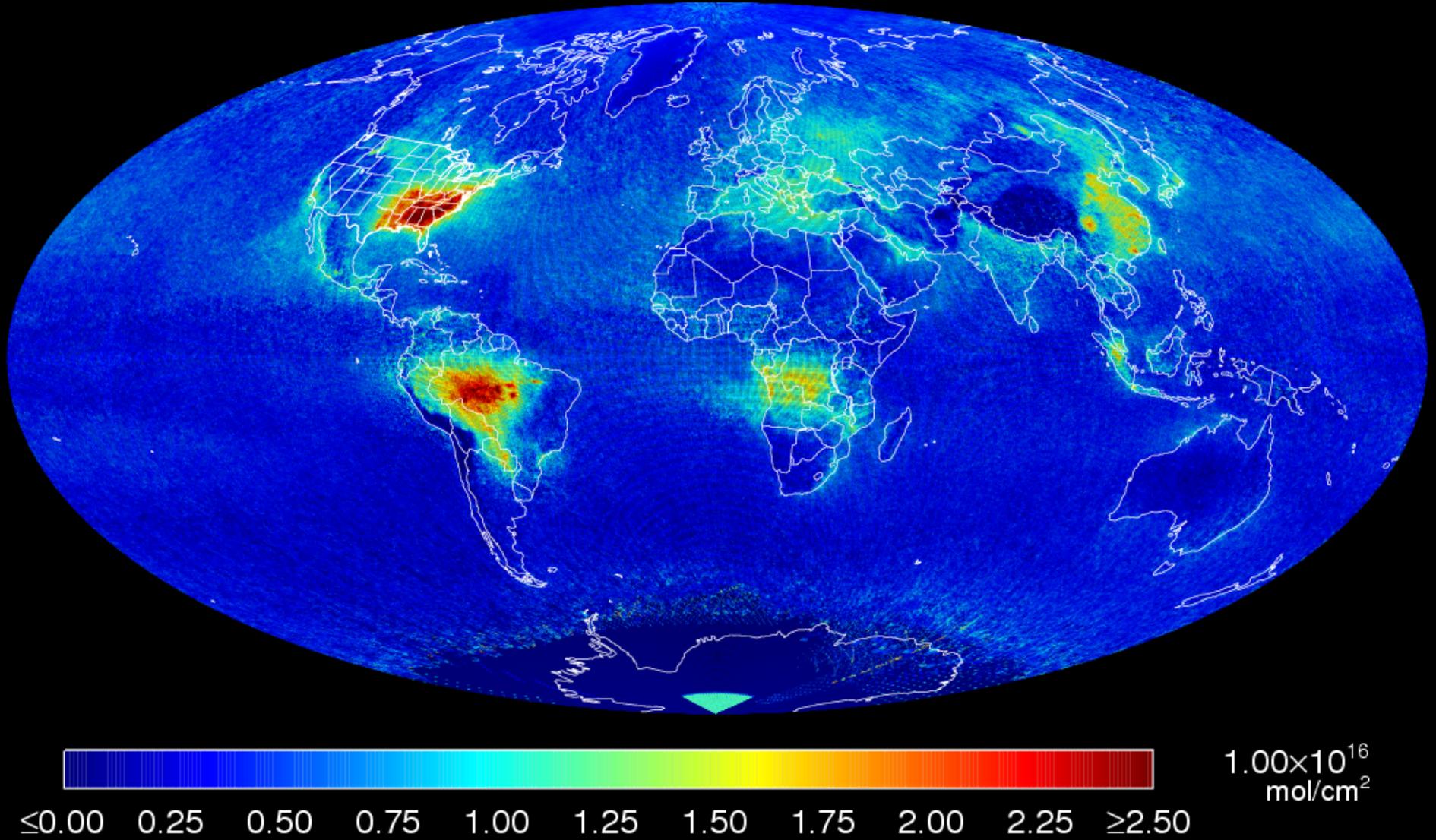
Largely reflects seasonality of isoprene emissions;
general consistency with GEIA but also some notable differences



OMI HCHO March 2007 ($\leq 40\%$ Cloud Cover)



OMI HCHO August 2007 ($\leq 40\%$ Cloud Cover)



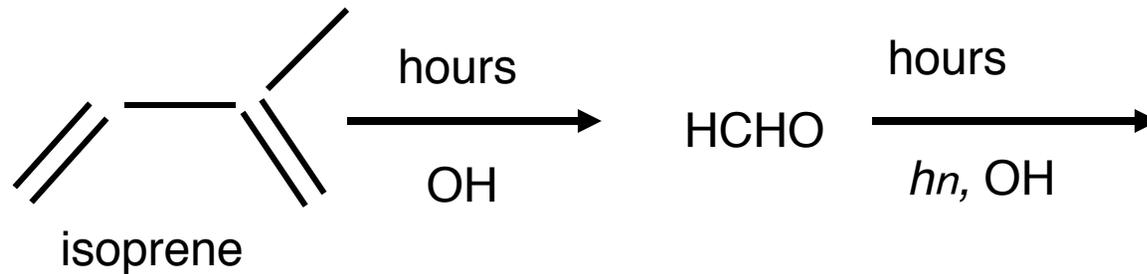


HCHO columns can be used to map isoprene emissions

Displacement/smearing length scale 10-100 km



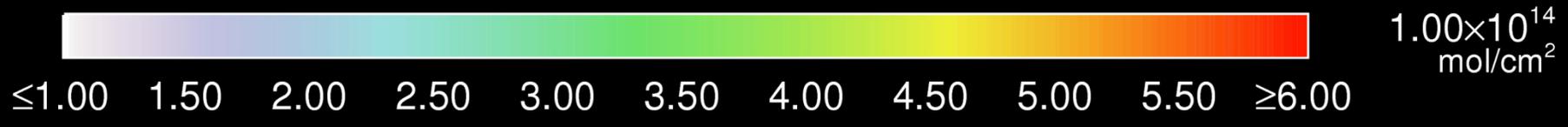
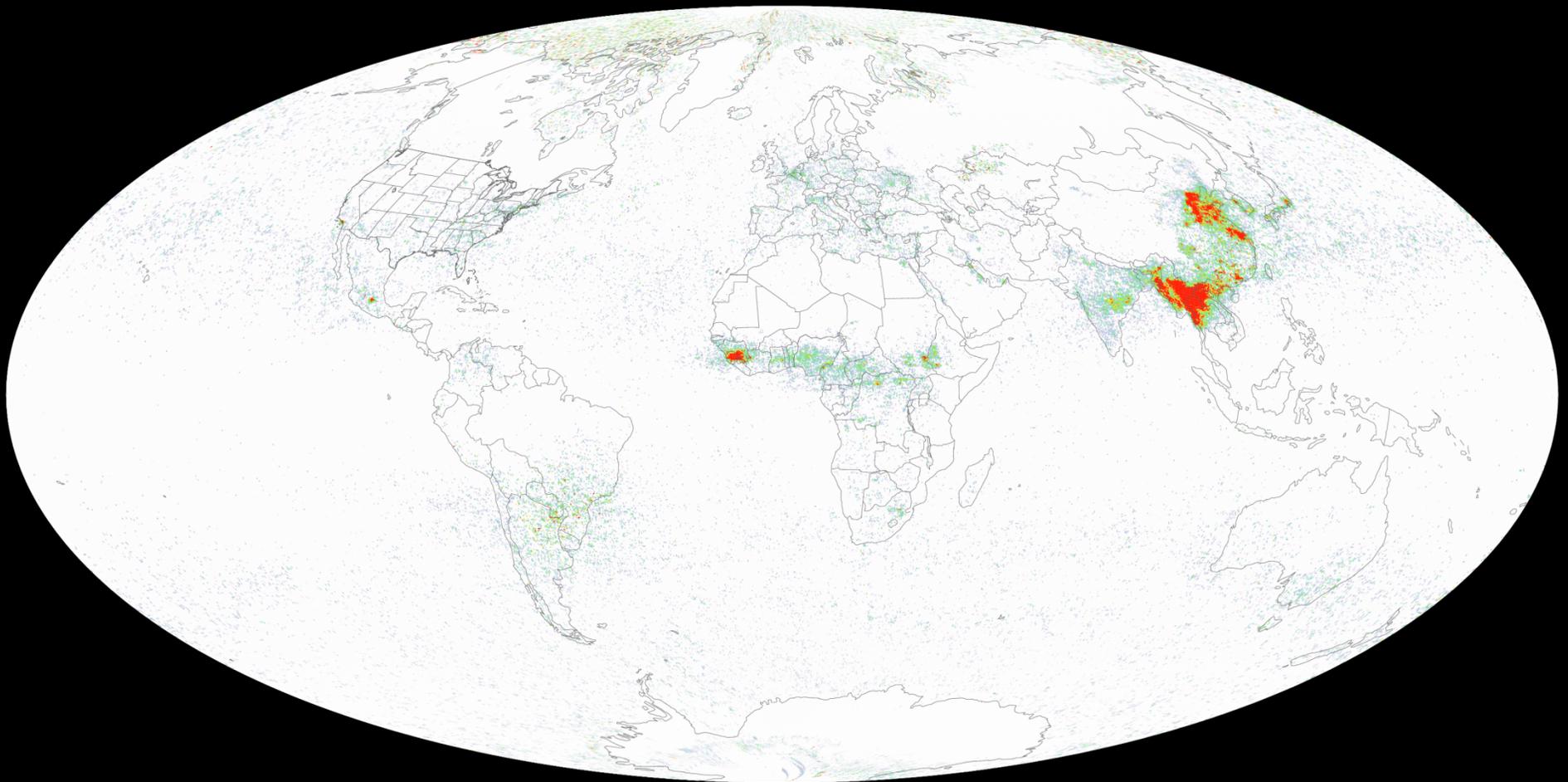
N.B. TEMPO



$$E_{ISOP} = \frac{k_{HCHO} \Omega_{HCHO}}{Yield_{ISOP \rightarrow HCHO}}$$

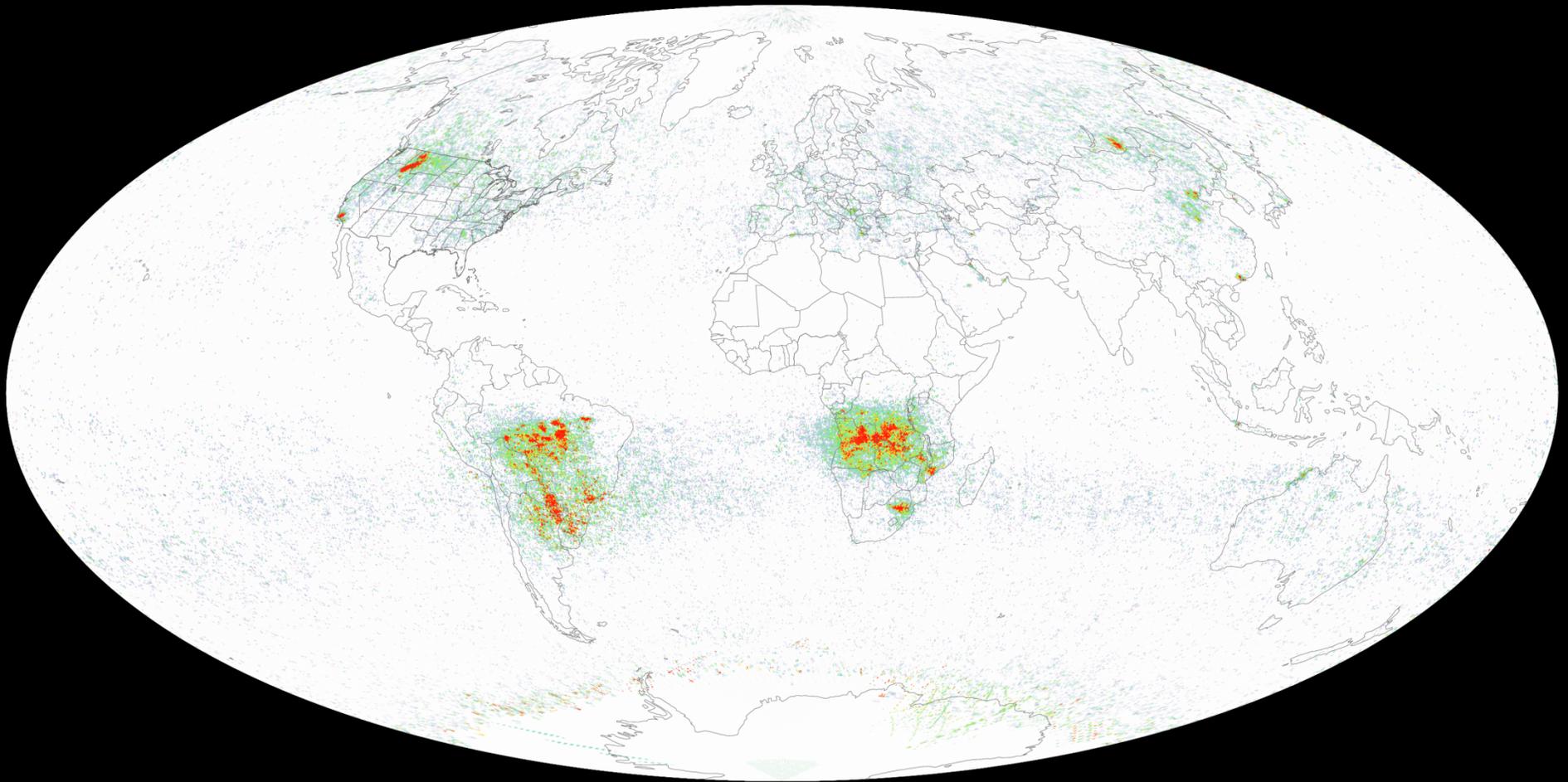


OMI $C_2H_2O_2$, March 2007 (<40% cloud cover)

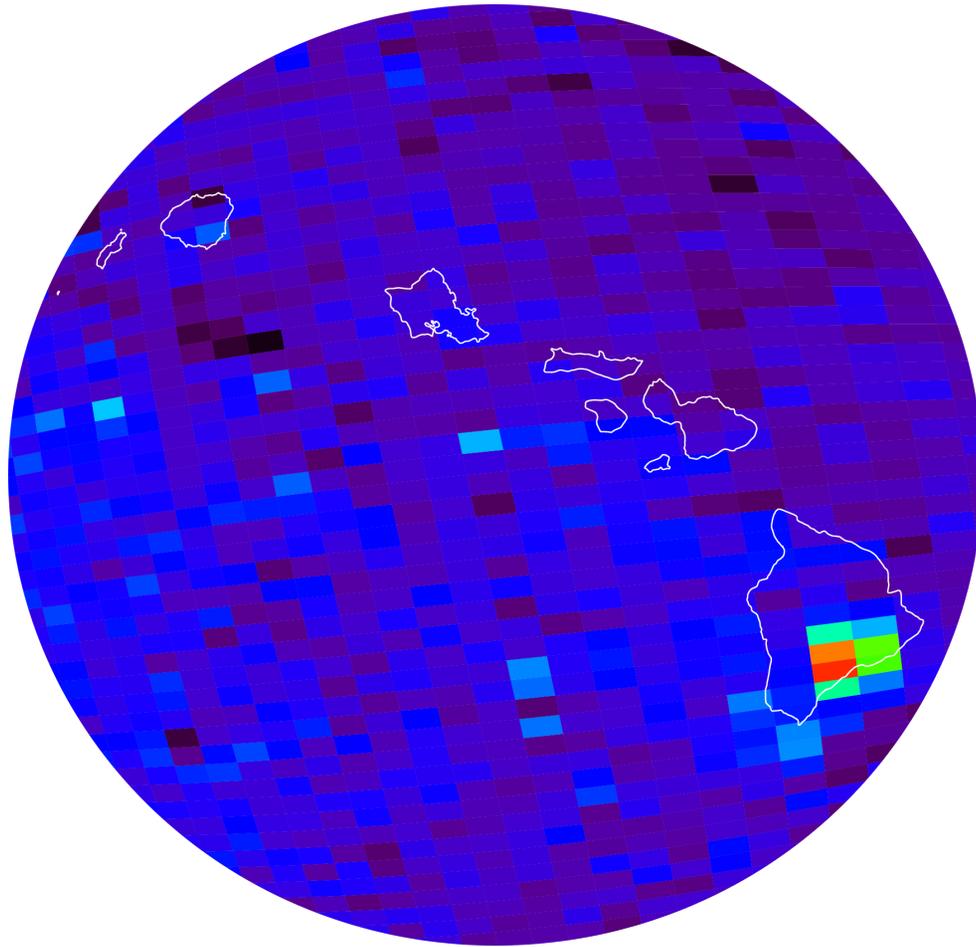




OMI C₂H₂O₂, August 2007 (<40% cloud cover)



Volcanic (and anthropogenic) SO₂

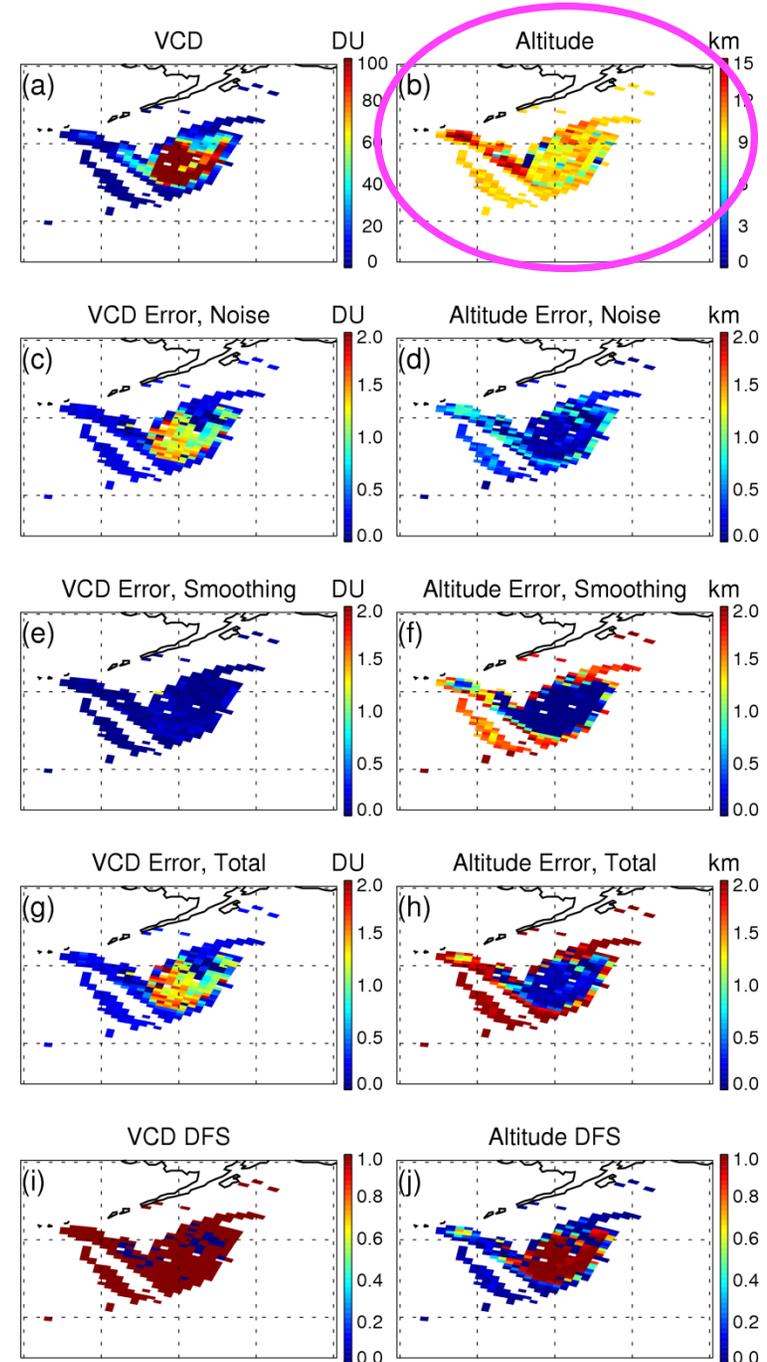


Kilauea activity, source of the VOG event in Honolulu on 9 November 2004

→ Air quality forecasting

C. Nowlan *et al.*, JGR 2011: GOME-2 SO₂ from optimal estimation

Figure 7. (a, b) SO₂ vertical column density and retrieved SO₂ plume altitude; and their (c, d) measurement noise error; (e, f) smoothing error, (g, h) total solution error; and (i, j) the retrieval degrees-of-freedom for signal (DFS) for the Mt. Kasatochi SO₂ plume on 9 August 2008 for SO₂ VCD greater than 1 DU, using $z_{ap}=10$ km and $\epsilon_{zap}=2$ km.





Review of the questions

What enables us to make measurements to $2-5 \times 10^{-4}$?

- Careful algorithm physics, spectroscopy, calibration

What is the state of the art (SOTA)?

- SNR of 3000-5000 @ 0.2-0.4 nm FWHM resolution
- Next UV gas (on Earth)? Maybe nitrous acid (HONO)

What does the SOTA imply for near-term monitoring from space?

- Enough for UV/visible geostationary monitoring. Like TEMPO.

Where are the limitations?

- In the PBL, ~40% artifacts from instrumentation, radiative transfer (not SNR)
- 20-40% AMF effects, requires improved distributions from CTMs, validation
- *N.B.* O_3 can be better than H_2CO or NO_2 because no assumptions on height distribution are necessary
- Overcome differences among instruments and algorithms by looking in detail at spectra to rationalize them (e.g., SCIAMACHY versus OMI $C_2H_2O_2$)

How might the SOTA be improved?

- Bigger light bucket (photon noise limited) followed by better radiance modeling (e.g., detector nonlinearity)
- Add visible O_3 intentionally. Like TEMPO.



Smithsonian Astrophysical Observatory



The End!