What can we learn by remote sensing glyoxal (CHOCHO) from space?

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With contributions from:
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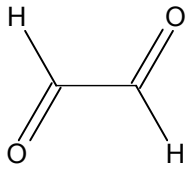
A. Richter, F. Wittrock – University of Bremen
T. Kurosu – Harvard Smithonian

- ☞ **What is glyoxal ? – sources and sinks**
- ☞ **Remote sensing glyoxal (ground and space)**
- ☞ **Relevance for urban air quality**

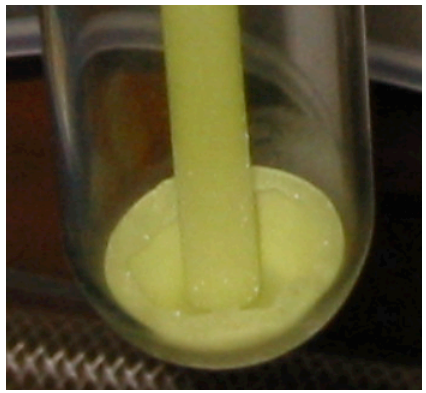
Integrated Program on Urban, Regional, and Global Air Pollution

Alexander von Humboldt Stiftung/Foundation

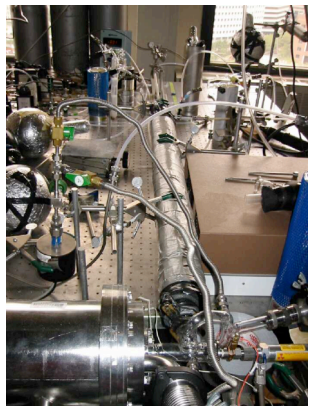
Introduction Glyoxal



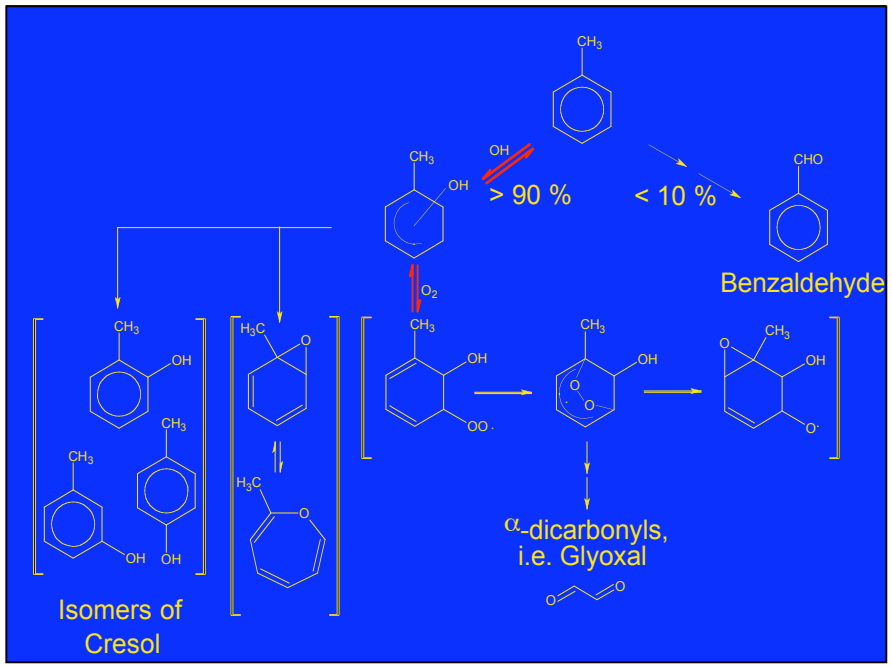
- $C_2H_2O_2$ or CHOCHO
- smallest α-dicarbonyl-type compound
- Natural sources: fermentation (beer, wine, yogurt products), biomass burning, BVOC oxidation, (oceans ?)
- Anthropogenic sources: emissions from mobile sources, AVOC oxidation, (energy sector, industrial processes ?)
- In urban air: Airborne AVOC oxidation source >> direct emissions from mobile sources (ca. 70% aromatics, 20% alkenes, 10% acetylene, virtually no glyoxal from alkanes)
- Residence time in the atmosphere: <1.2 hours
- Major gas-phase loss process is photolysis and OH-reaction (60% / 40%). Source for H_2, CO, HCHO and HO_2-radicals.
- Evidence for reactive uptake to aerosols, but significance is unclear in the atmosphere.



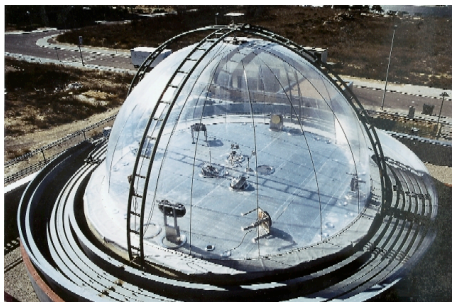
Mechanism development of VOC



Flow systems



Simulation chambers

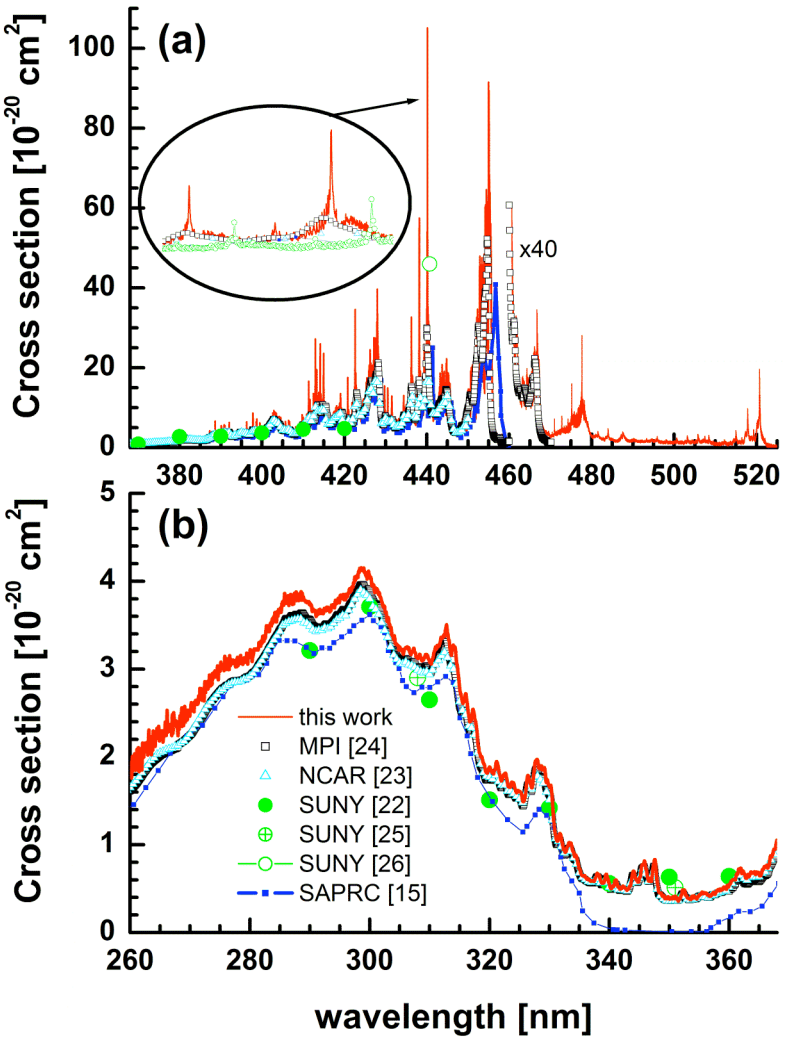


Glyoxal is exclusively formed a primary oxidation product from aromatic VOC

Secondary glyoxal is negligible !

Volkamer *et al.* (2001) *J. Phys. Chem.* 105, 7865

UV/vis and IR absorption cross section



Lifetime with respect to photolysis is shorter than previsouly believed !

Volkamer *et al*. (2005) *J. Photochem. Photobiol. A: Chemistry* 172, 35.

DOAS measurement of Glyoxal as an indicator for fast VOC chemistry in urban air

HIGHLIGHTS OF THE RECENT LITERATURE

EDITORS' CHOICE

edited by Gilbert Chin

CLIMATE SCIENCE

Urban Air Quality

The oxidation of volatile organic compounds (VOCs) is an important step in the formation of photochemical smog in urban areas, but the rate at which VOCs are oxidized has been difficult to quantify. A reliable way to measure this rate would lead to improved prediction of smoke/fog events.

Volkamer et al. used differential optical absorption spectroscopy (DOAS) to make direct measurements of atmospheric glyoxal concentrations over Mexico City in the spring of 2003. They show that VOC oxidation, of which glyoxal is a product, begins about an hour after sunrise and continues throughout the day. These observations allow a lower limit to be placed on the rate of VOC oxidation and reveal that VOC chemistry is active throughout sunlit hours. On the basis of these results, satellite measurements of glyoxal appear to be feasible, which would support the identification of photochemical hot spots in the atmosphere. — HJS

Smog above Mexico City.

Geophys. Res. Lett. 32, 10.1029/2005GL022616 (2005).

Volkamer *et al.* (2005) *Geophys.Res.Lett.*, 32, L08806.

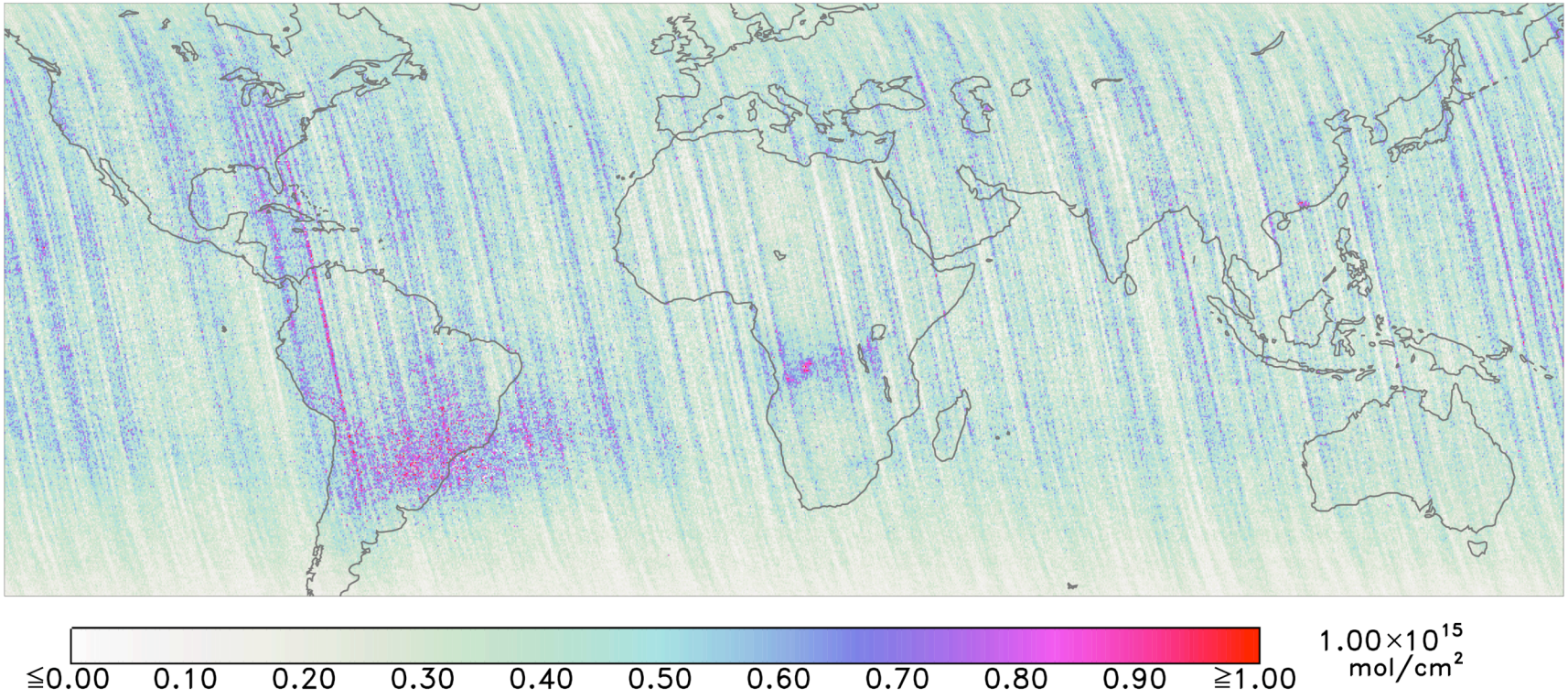
http://dx.doi.org/10.1029/2005GL022616

SCIENCE, June 3 2005, VOL 308, 1379

http://www.sciencemag.org/

Detection of CHOCHO from space (OMI)

Following the suggestion of our GRL article



T. Kurosu, K. Chance, and R. Volkamer (2005) Global Measurements of BrO, HCHO, and CHOCHO from the Ozone Monitoring Instrument on EOS Aura, *Eos Trans. AGU, 86*(52), Fall Meet. Suppl., Abstract A54B-01

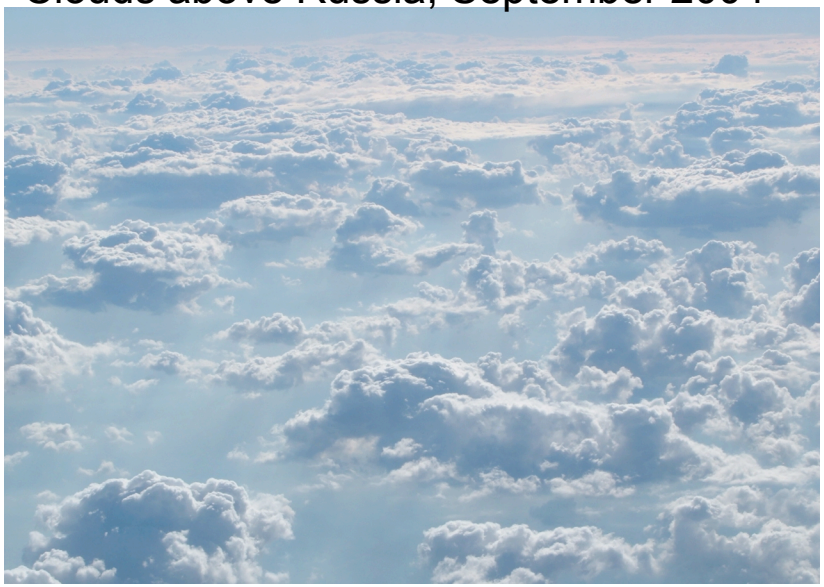
Ambient glyoxal measurements

Reference	Location	Airmass	Mixing ratio [ppb]
(Volkamer et al. 2005)	Mexico City, Mexico	polluted urban	< 0.15 – 1.82
(Ho and Yu 2002)	Hong Kong, China	polluted urban	0.5 – 4.1
(Kawamura et al. 2000)	Los Angeles, USA	polluted urban	0.04 – 0.95
(Grosjean et al. 1996b)	Los Angeles mean Long beach Central LA Azusa Claremont	polluted urban	0.78 ± 0.85 <0.12 – 0.8 <0.12 – 2.2 <0.12 – 3.0 0.4 – 3.8
(Jing et al. 2001)	Las Vegas, USA Summer Winter	urban	0.12 – 0.42 0.09 – 0.21
(Grosjean et al. 1999)	Porto Allegre, Brazil	urban	0.3
(Borrego et al. 2000)	Giesta, Portugal	semi-urban	0.52 – 2.42
(Moortgat et al. 2002)	Pabsthum, Germany	Semi-rural	0.01 – 0.12
(Lee et al. 1995)	Georgia, USA	rural	0.02 – 0.19

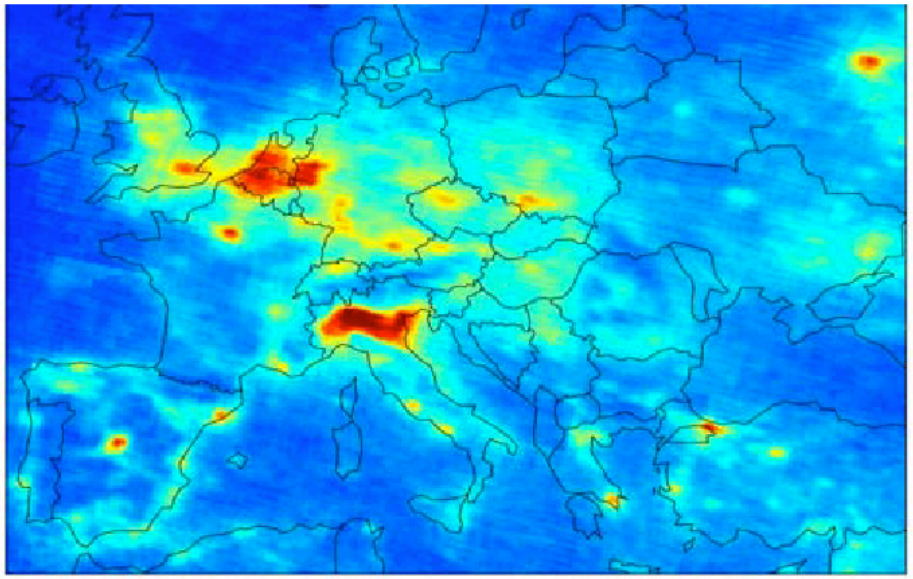
Highest concentrations are indeed observed in Hong Kong !

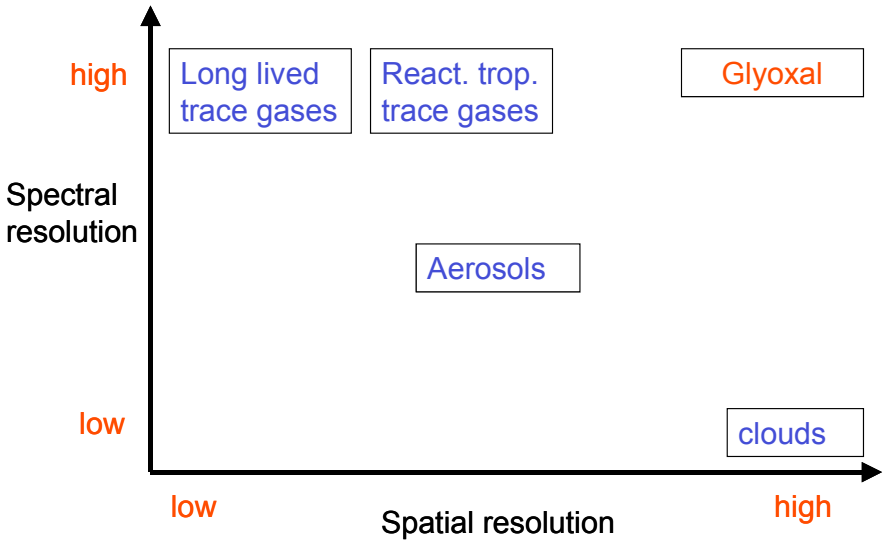
Which spatial resolution is actually needed?

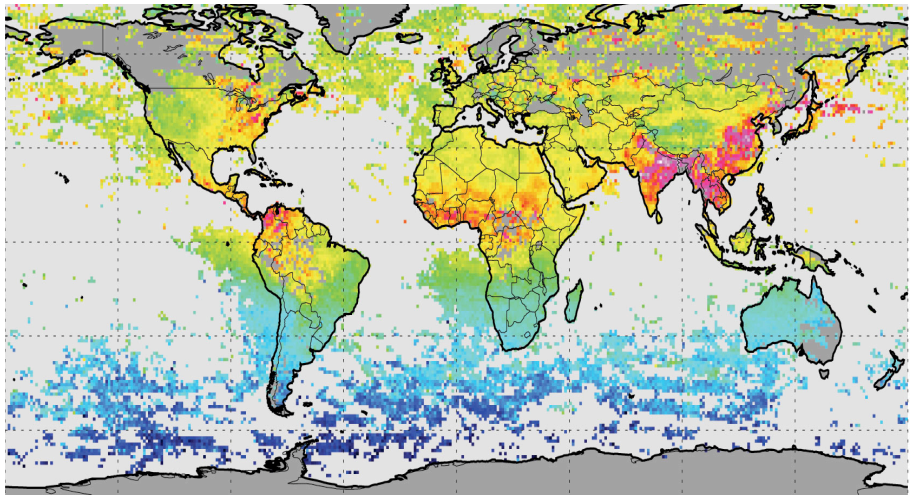
Clouds above Russia, September 2004



Trop NO2 SCIA VCD, January 2003 – June 2004, Steffen Beirle, IUP Heidelberg





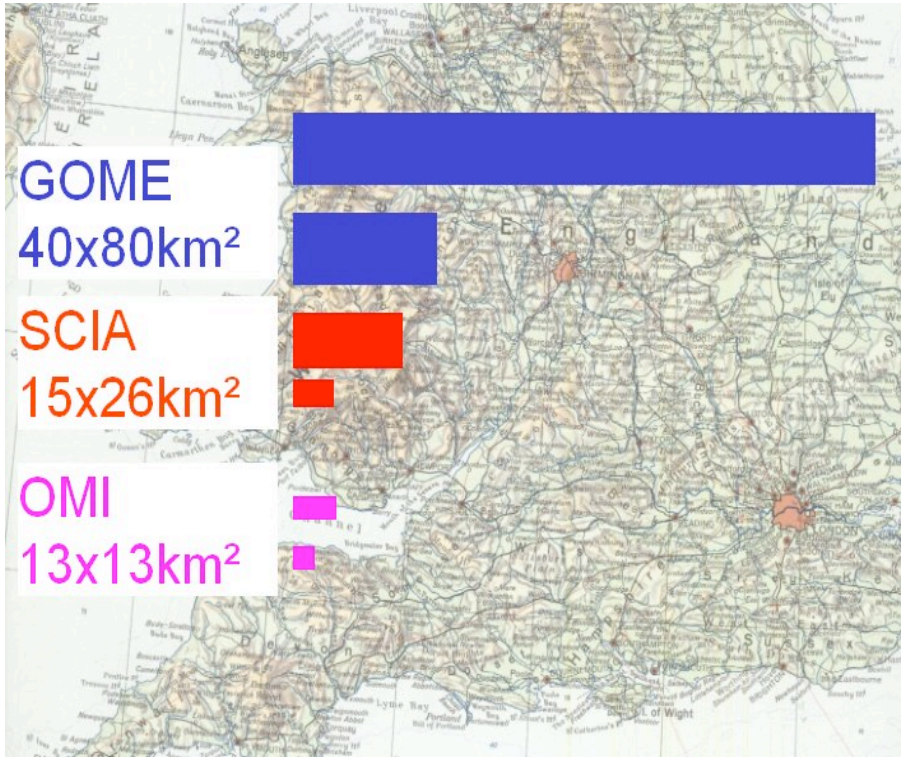


CH_4 SCIA VCD, Aug.-Nov. 2003, C. Frankenberg, IUP Heidelberg

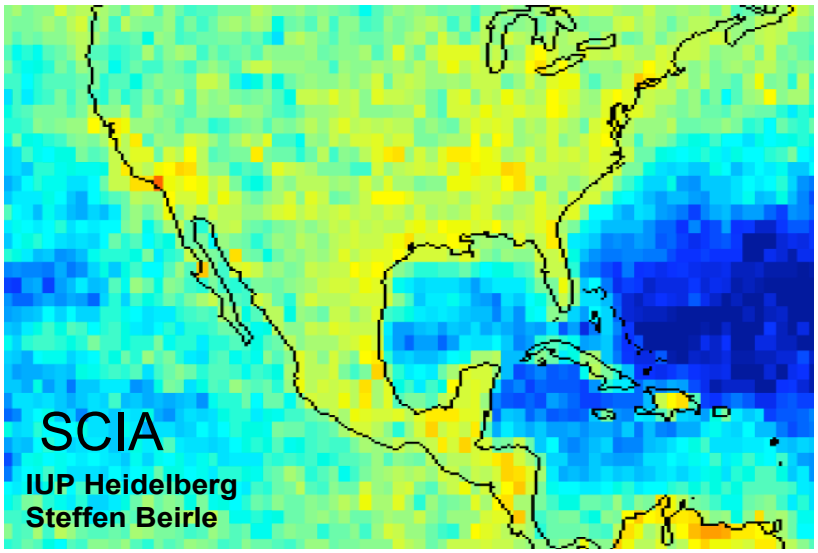
Glyoxal lifetime 1h: 5-20 km spatial scale !

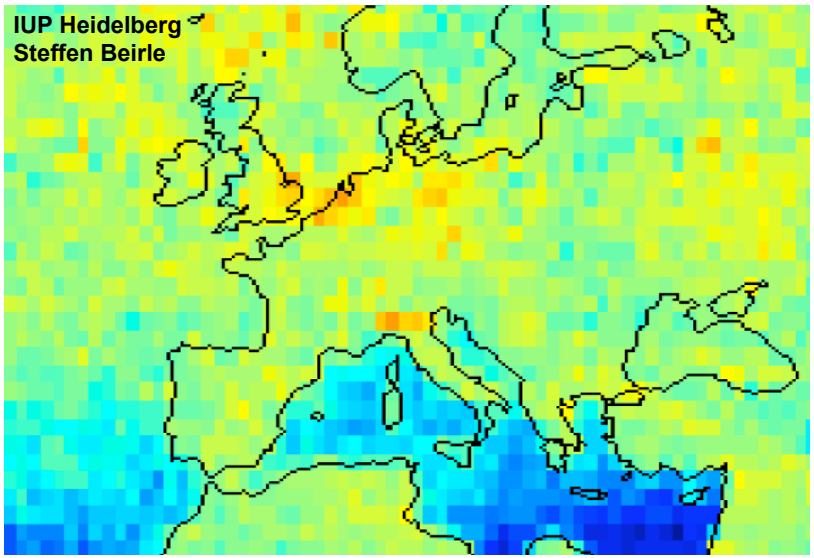
Achievable spatial resolution

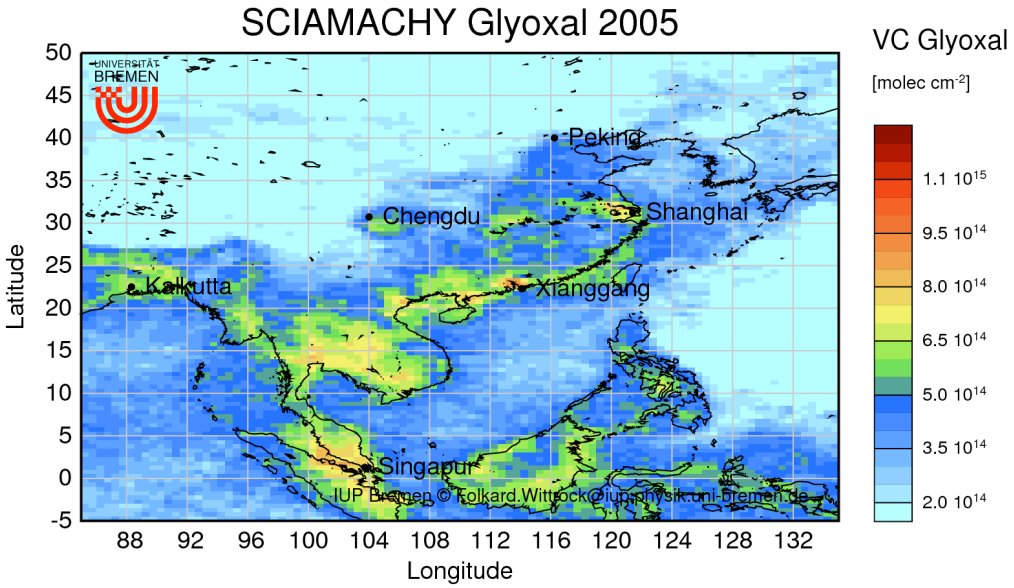
Spatial Resolution of instruments with ‚high' spectral resolution



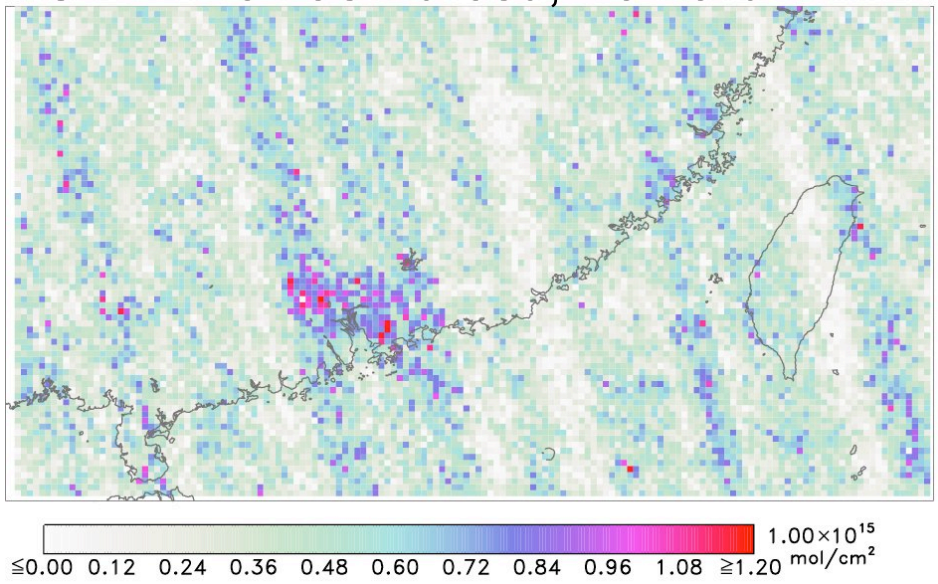
Anthropogenic pollution



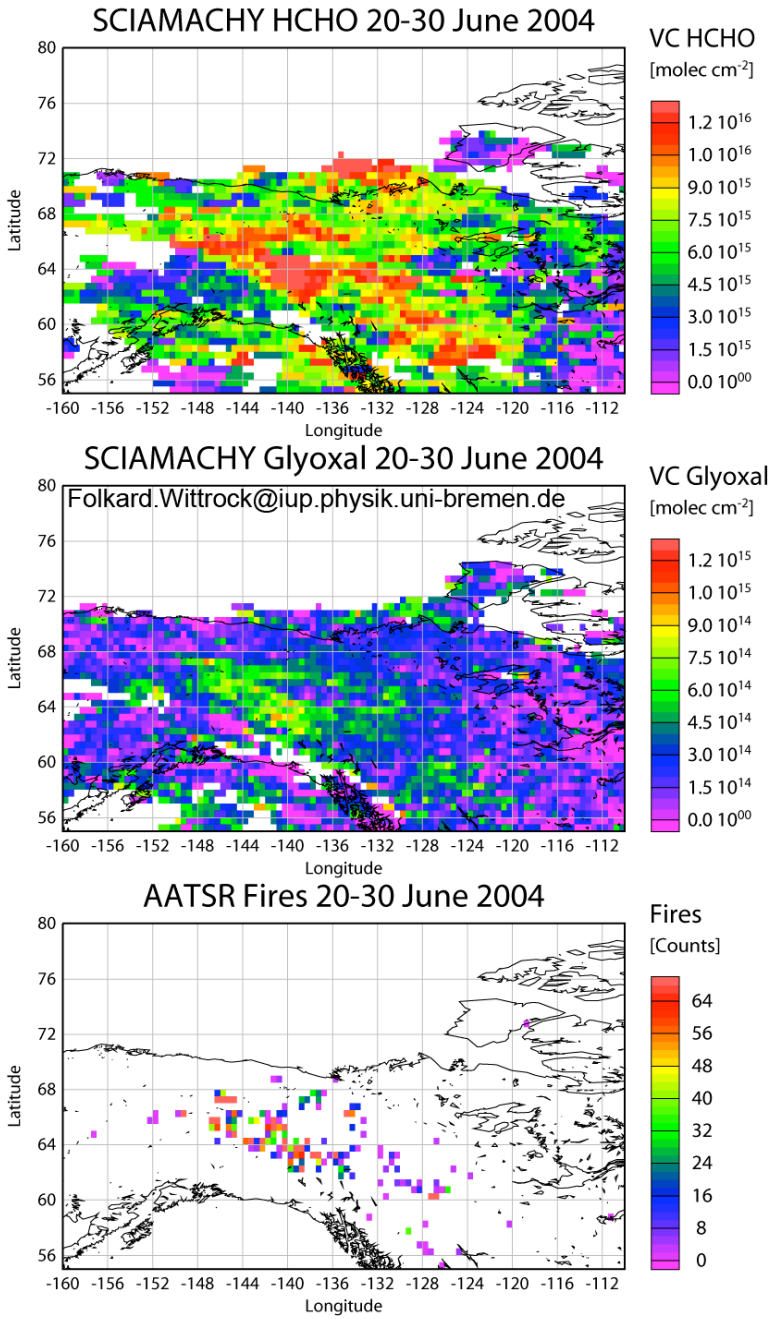




OMI: Thomas Kurosu, Harvard



Biomass burning pollution



Source: IUP Bremen

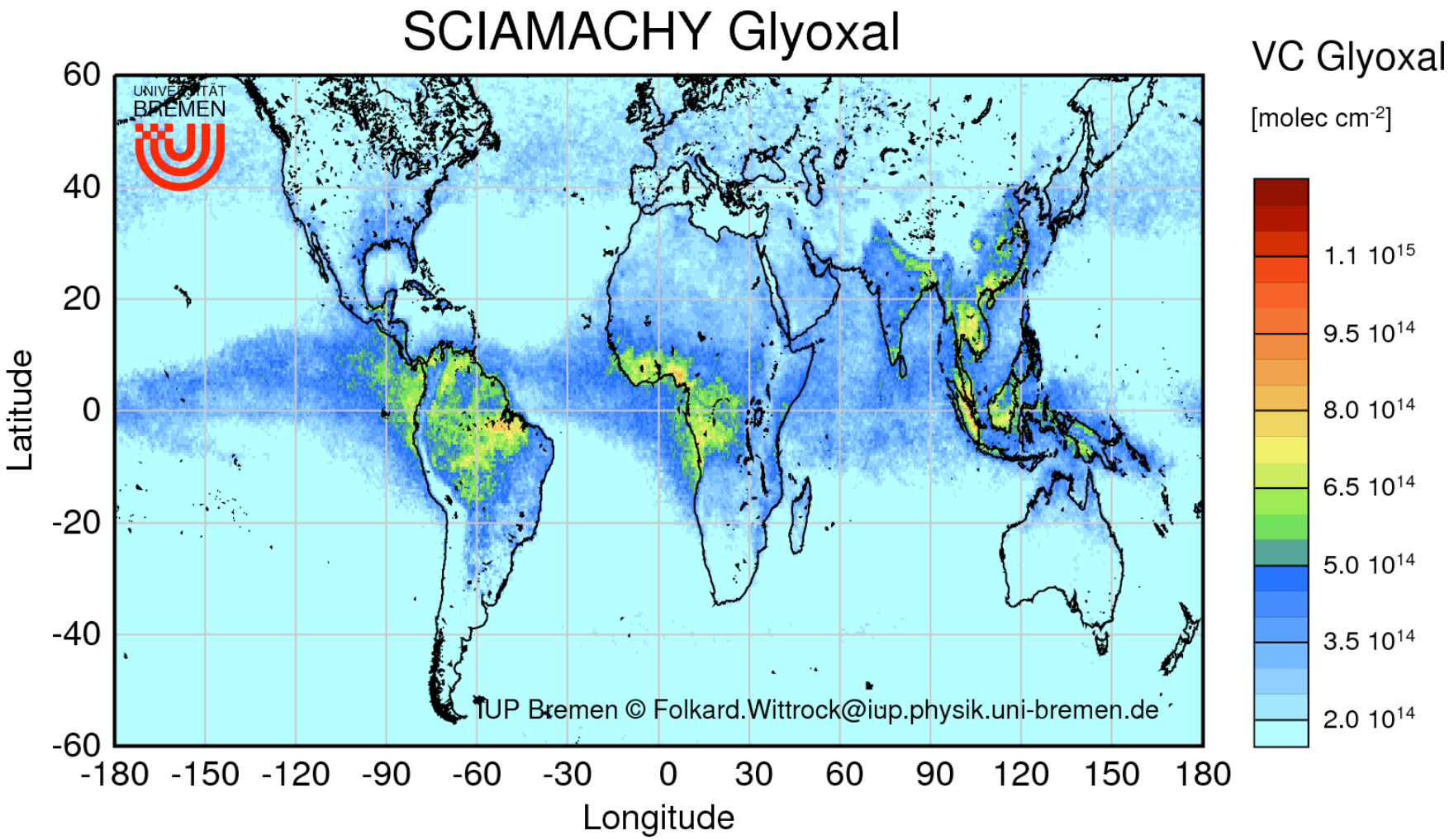
- CHOCHO concentrations in the range of 0.1-1ppb, corresponding to these VCDs, can easily be rationalized on the basis of existing emission factors and fuel consumption data.

- In fact glyoxal concentrations seem low (factor 10-100).

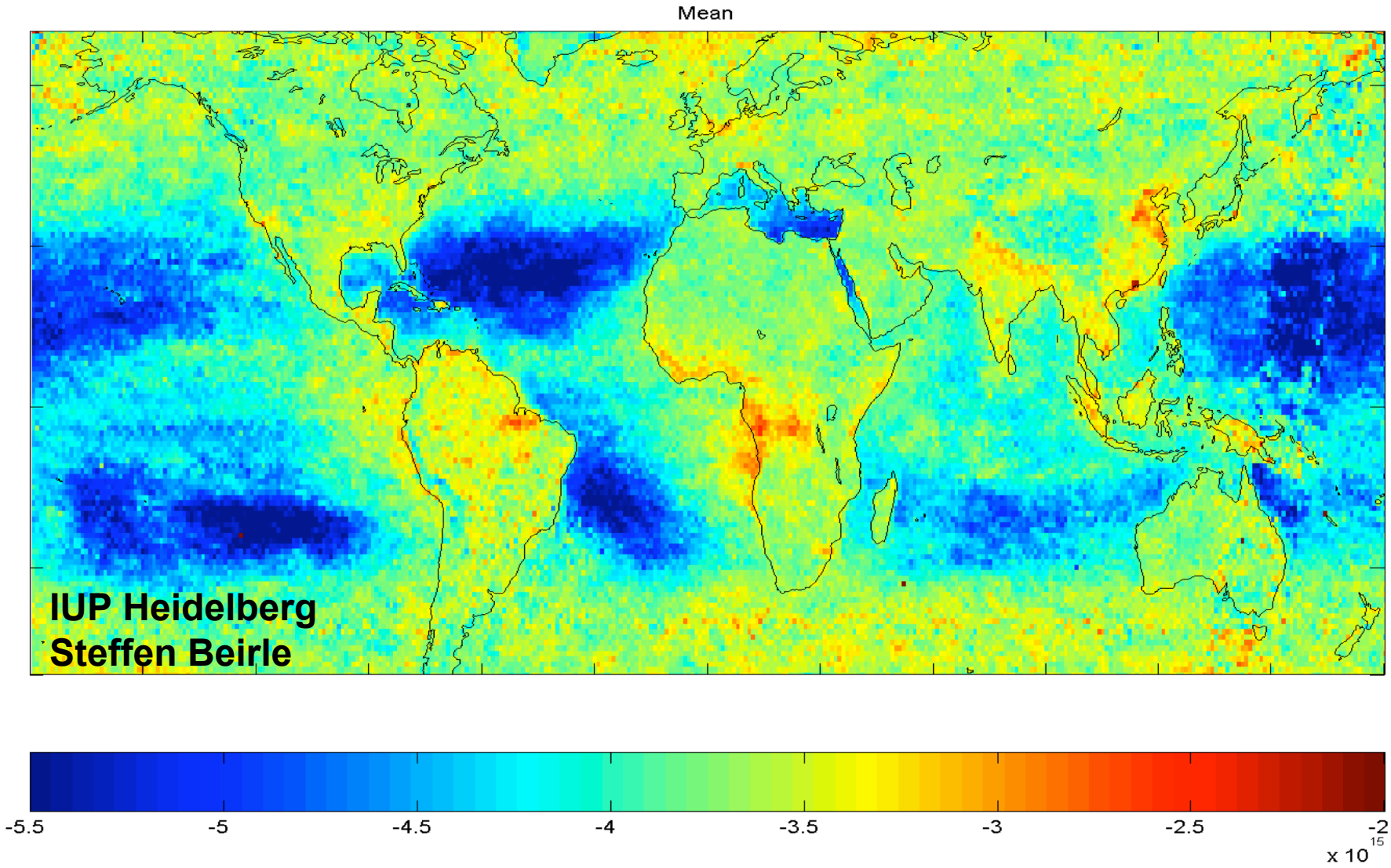
- Recent results from the urban atmosphere (MCMA-2003 field campaign) suggest a strong effect of aerosols on the atmospheric lifetime of glyoxal (see later).

- The influence of aerosols during biomass burning events is presently unclear.

SCIAMACHY CHOCHO VCD



SCIAMACHY CHOCHO (prel)

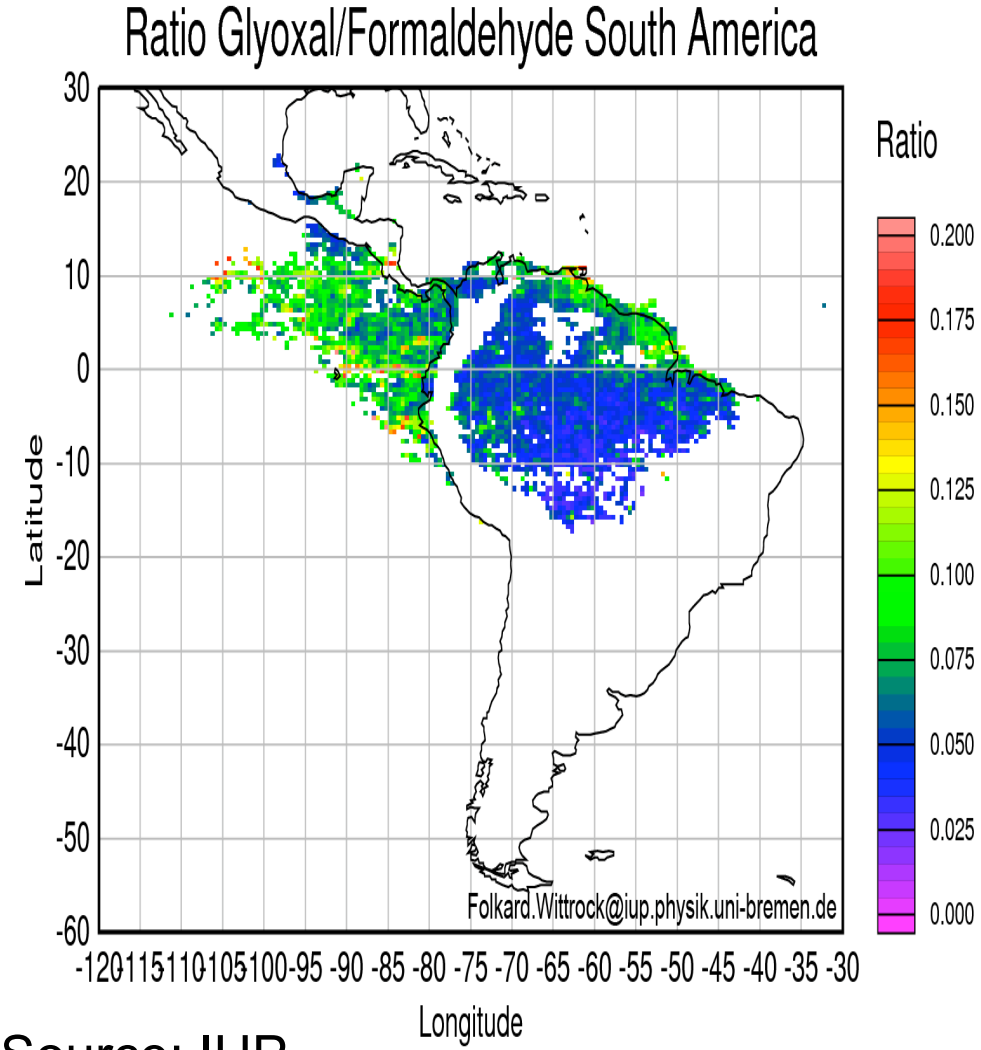


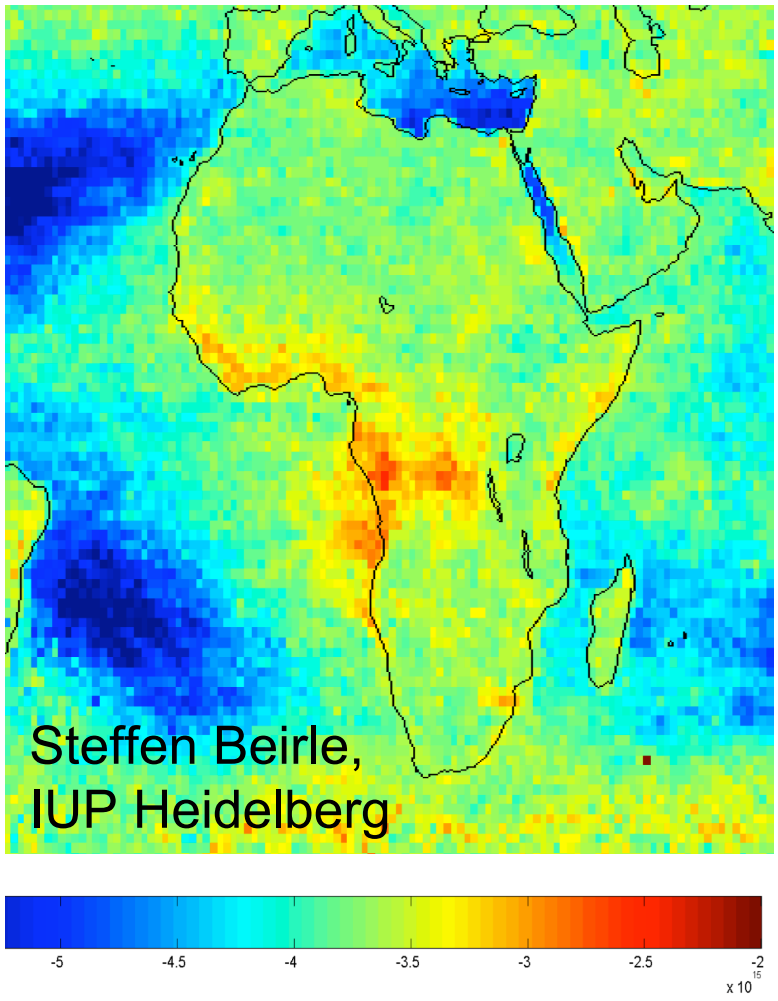
Mean of months 6,7,9,10,11 of 2003

(other months: no global coverage or some strong outliers)

CHOCHO sources over oceans

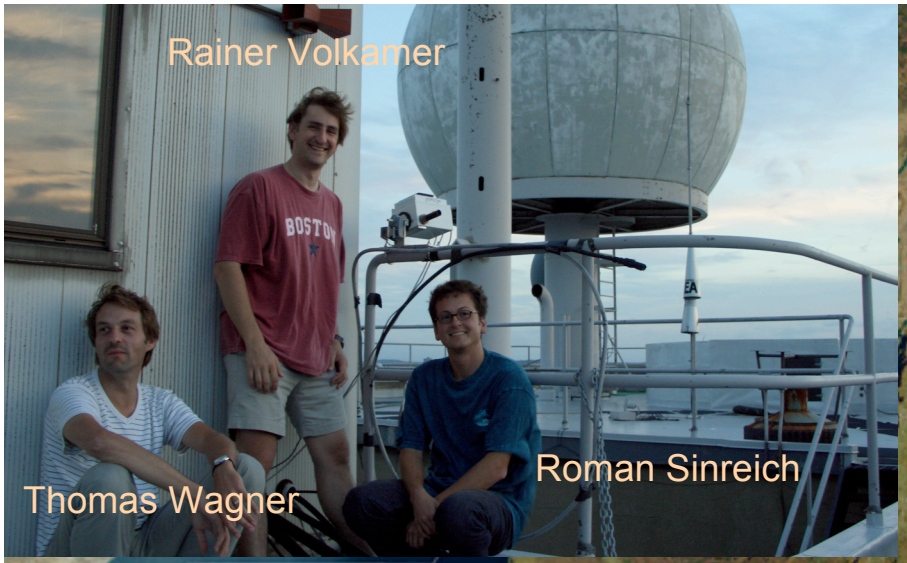
Elevated HCHO and CHOCHO are observed over oceans...
Spectral interference with liquid water, chlorophyll increasingly unlikely...

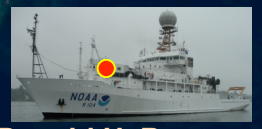




Source: IUP

MAX-DOAS Sites ICARTT 2004



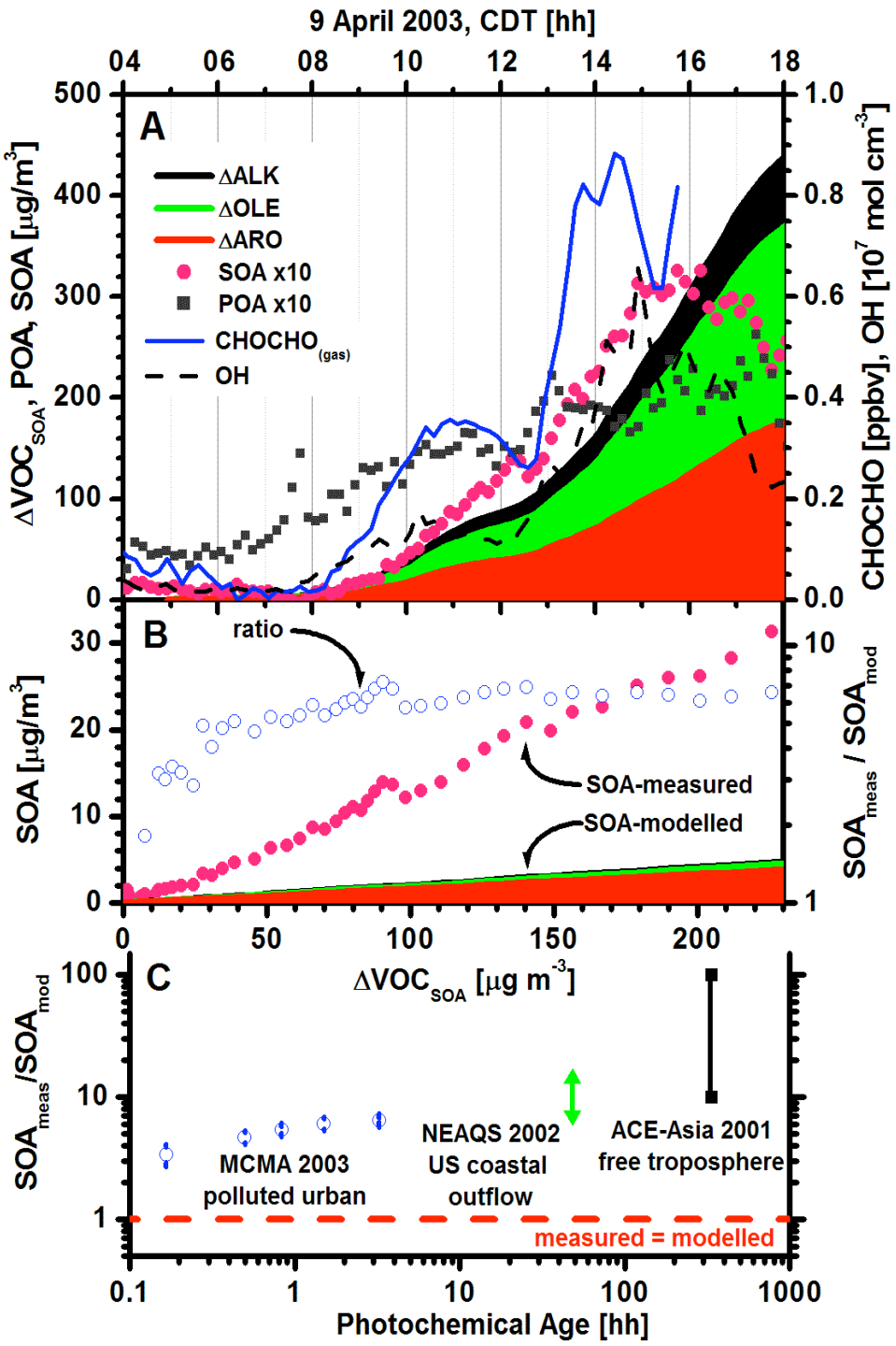


Ronald H. Brown

MIT Cambridge

Detection of elevated glyoxal over the Gulf of Maine!
Transport of VOC precursors or ocean sources ?


Relevance of CHOCHO

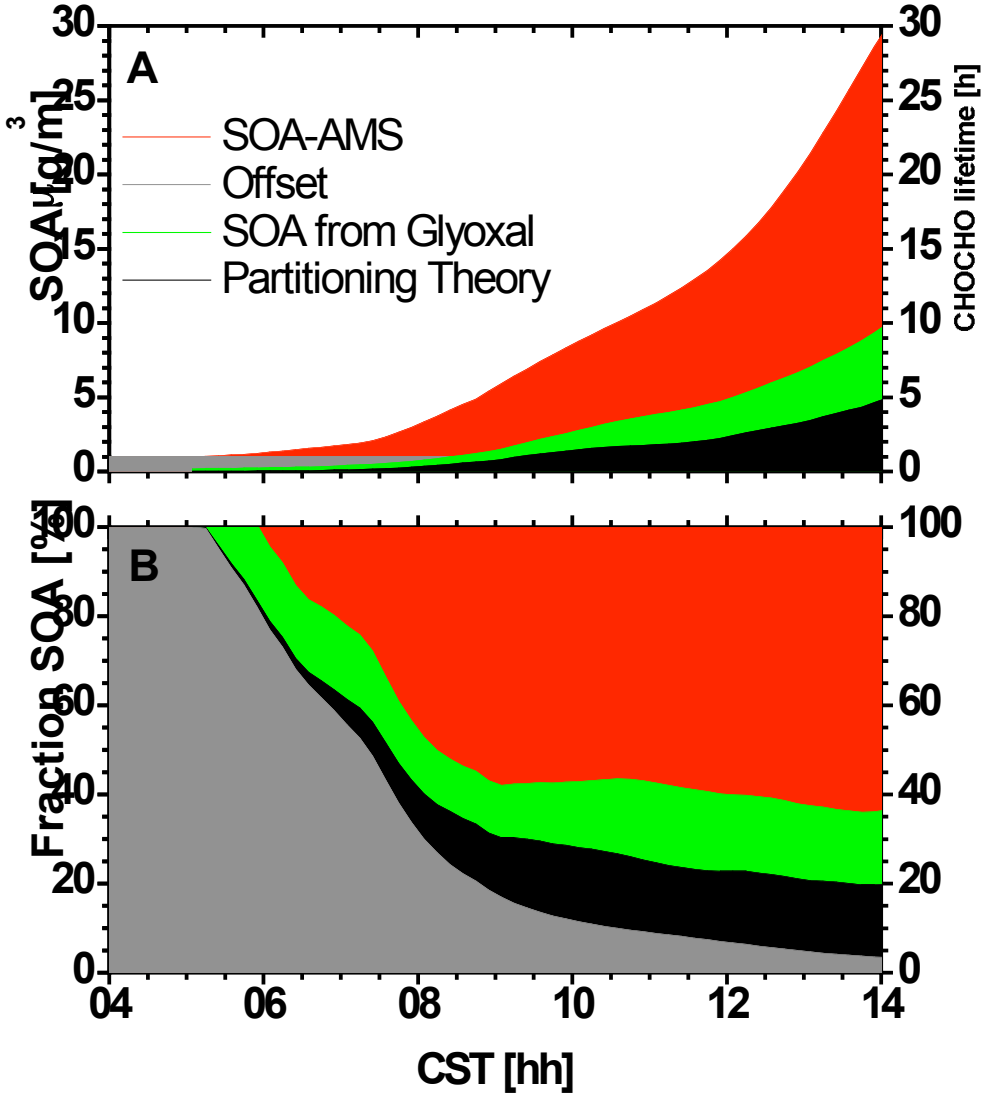


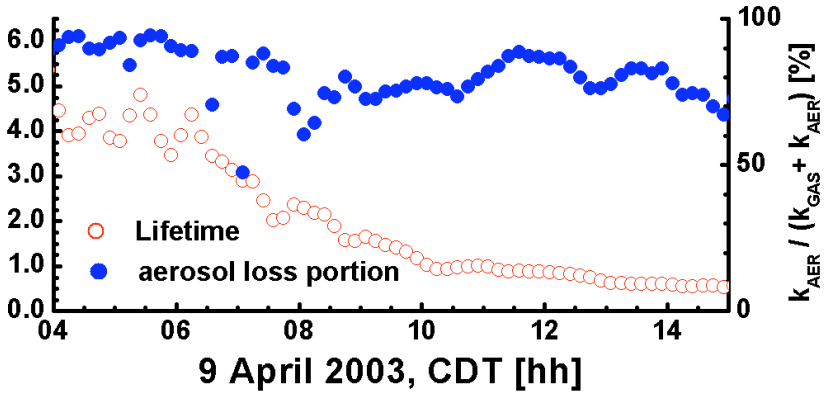
Missing SOA source in urban air

- SOA and glyoxal form simultaneously (A).
- A standard multicomponent partitioning model can not account for the observed SOA amount (B).
- Complementary results are found in very different and large compartments of the troposphere: NEAQS (De Gouw et al. 2005), ACE-Asia (Heald et al. 2005).
- **The missing SOA source is associated to primary AVOC oxidation products (A, B, C).**
- Higher generation products may contribute further SOA at longer time scales (C).

Volkamer et al. (2006) GRL, submitted.

Atmospheric lifetime of CHOCHO: Aerosol effect during MCMA-2003

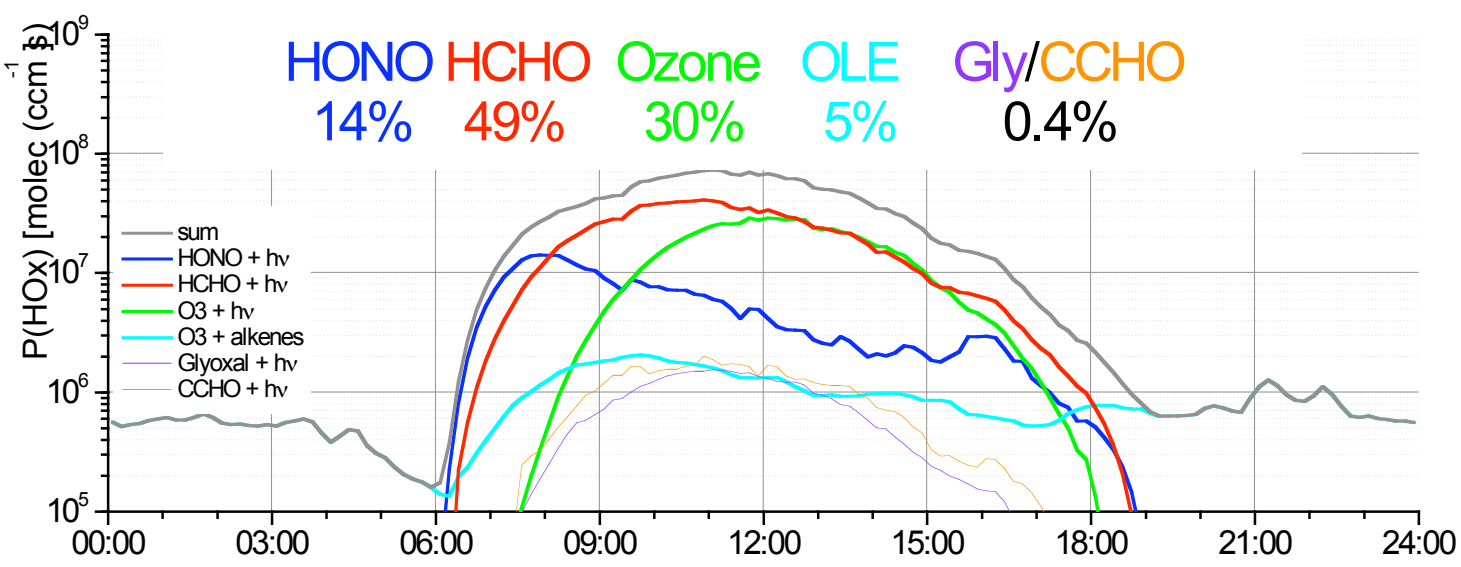


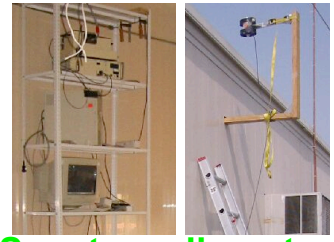


- Lifetime strongly affected by aerosol losses
- CHOCHOcan account for about 15% of the presently unaccounted SOA mass in MC.

… stay tuned.

HOx production in Mexico City smog (MCMA-2003)





Spectroradiometry

HOx sources:

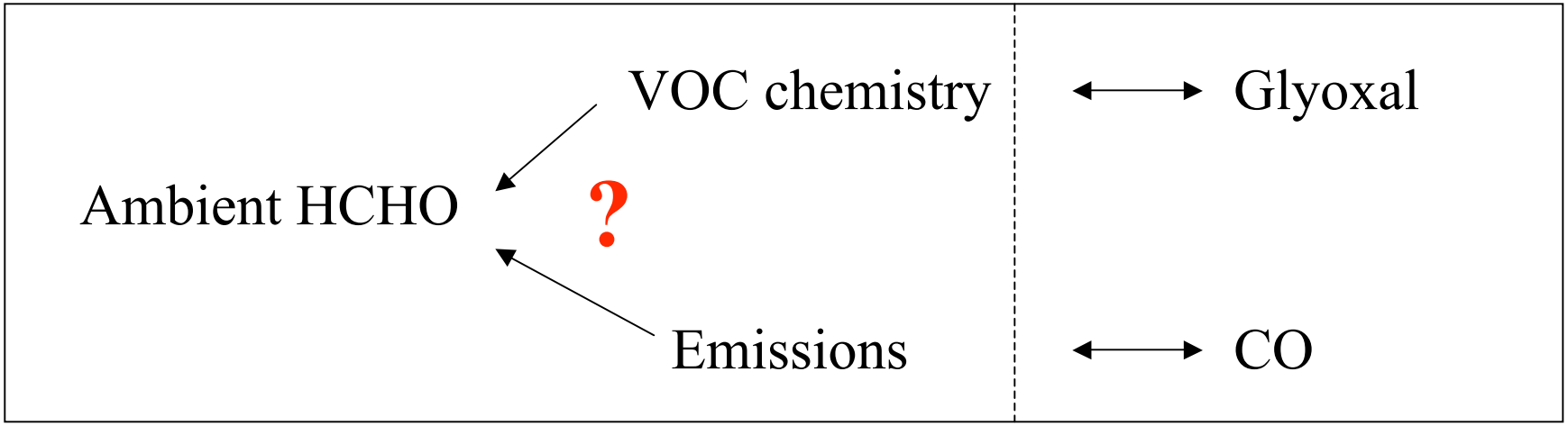
1. HONO + hν
2. O_3 + hν (+ H_2O)
3. HCHO + hν
4. Glyoxal + hν
5. CCHO + hν
6. O_3 + Alkenes

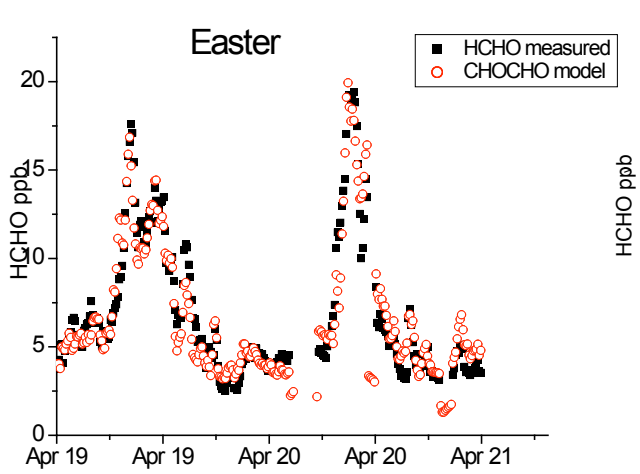
DOAS-2: L= 4420m, H= 70m
HONO, HCHO, O3, NO2,(NO3), SO2, Glyoxal

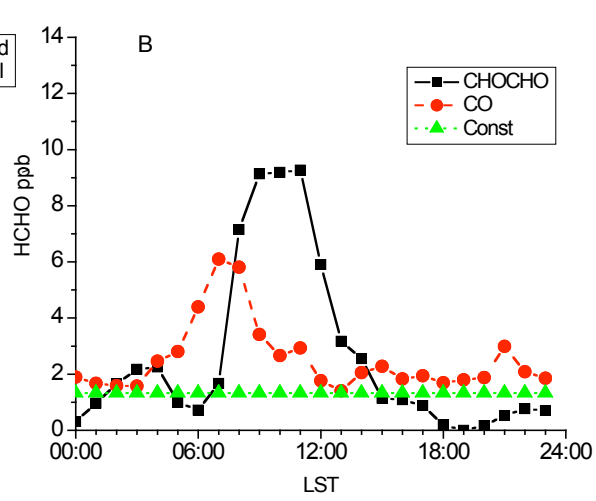
East South South-West

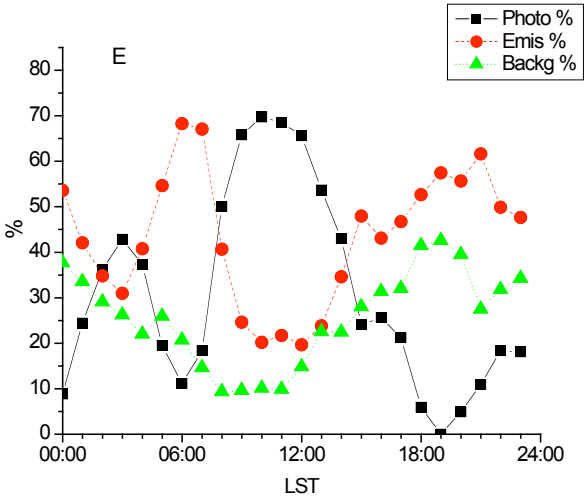
Volkamer et al. (2006) in preparation

Emitted and photochemical HCHO



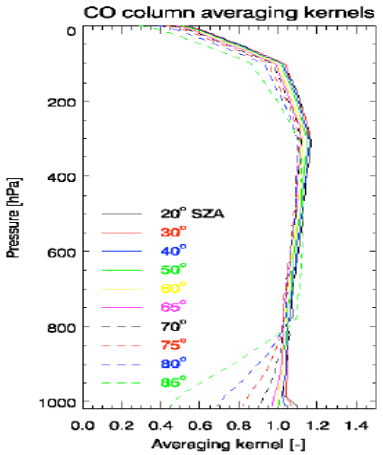






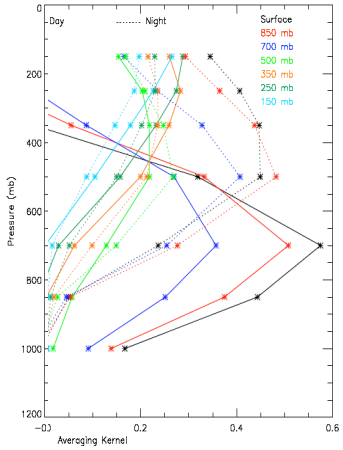
Garcia, Volkamer et al. (2005) ACPD, 5, 11583

CO: SCIAMACHY and MOPITT

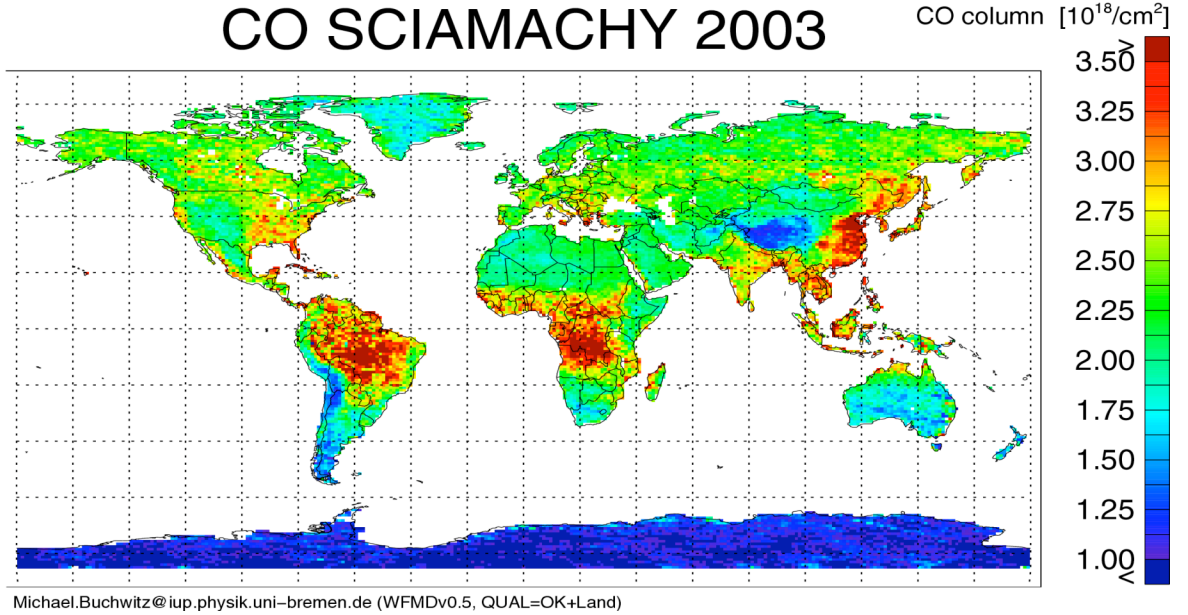


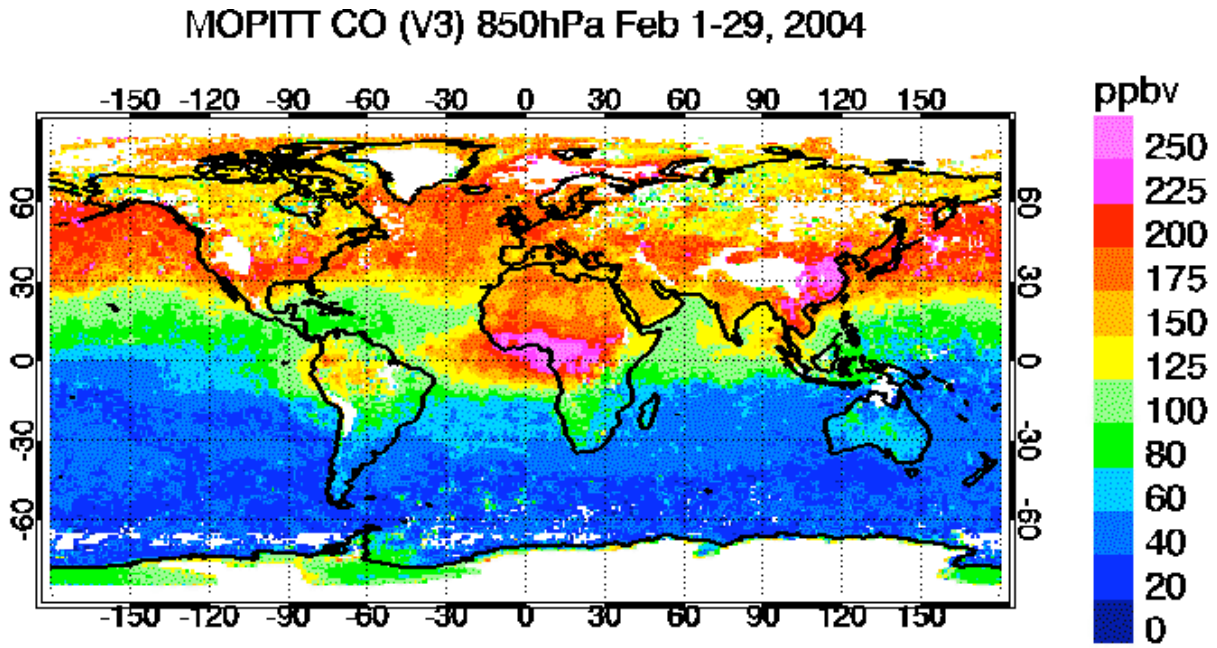
Buchwitz et al., 2004

Averaging kernels

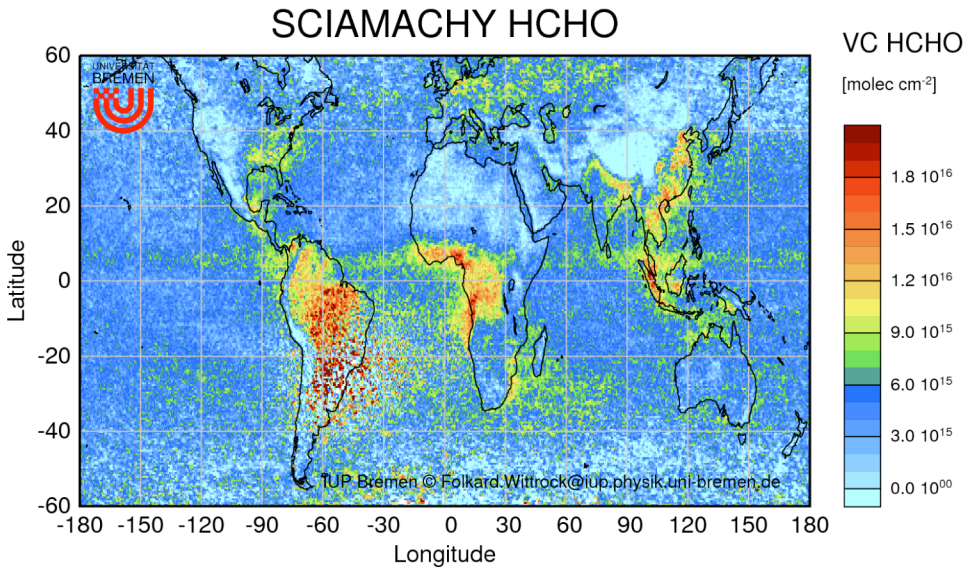


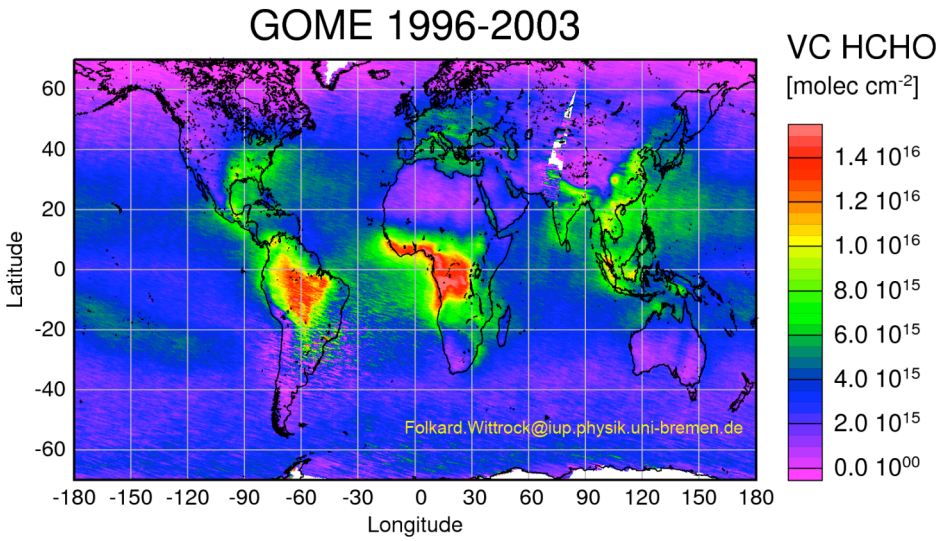
Remedios et al., 2005



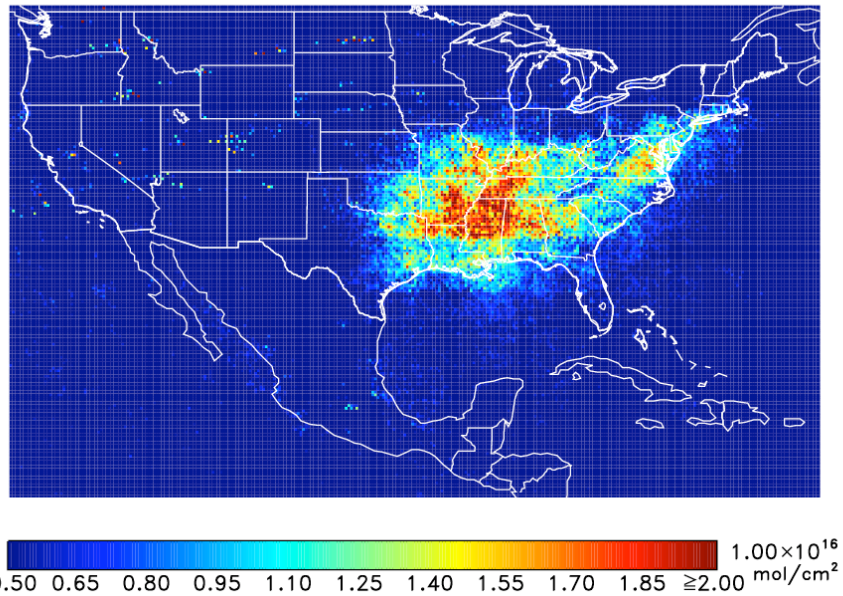


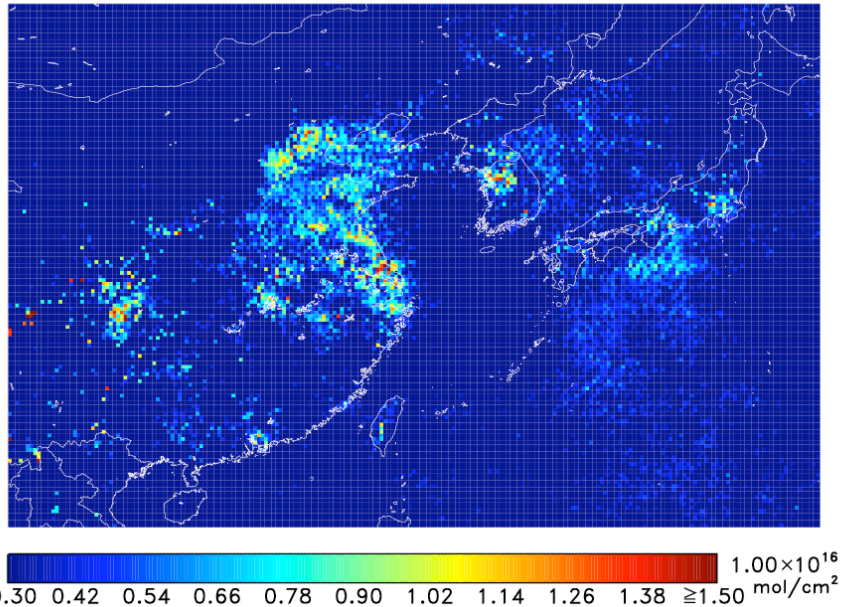
HCHO: OMI, SCIA, GOME





OMI, Source: T. Koruso, Harvard





Conclusions

- The full potential use of the CHOCHO indicator is only developed by time resolved observations (geostationary observation strategies)
- Glyoxal indicates anthropogenic photochemical hot-spots (gas-phase and SOA) and is observed over biomass burning regions and oceans.
- Model predictions of CHOCHO require updates in sources, and sinks before any meaningful comparison can be carried out.
- The necessary combination of high spectral and spatial resolution is actually achievable with geostationary satellites (Lagrange invariante).

Thank you!

See you in Mexico 2006 ?

Acknowledgements:

• NSF, DoE, CAM (Mexico)

• Consecutive Fellowships:
  - Marie Curie Doctoral (CEAM)
  - Dreyfus Postdoctoral (MIT)
  - Feodor-Lynen Postdoctoral (UCSD)