Vertical column observations of HONO, NO_2, HCHO and Glyoxal: linking ground-, aircraft- and satellite observations

Rainer Volkamer, Roman Sinreich, André Merten, Ulrich Platt, Steffen Beirle, Thomas Wagner, Philip Sheehy, Luisa T. Molina, Jim Barnard, David McCabe, Paul Wennberg

U.C. San Diego, IUP (Heidelberg), MPI (Mainz), MIT, MCE2, PNNL, Caltech

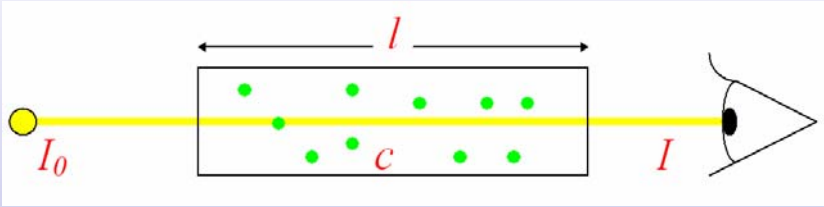
Outline

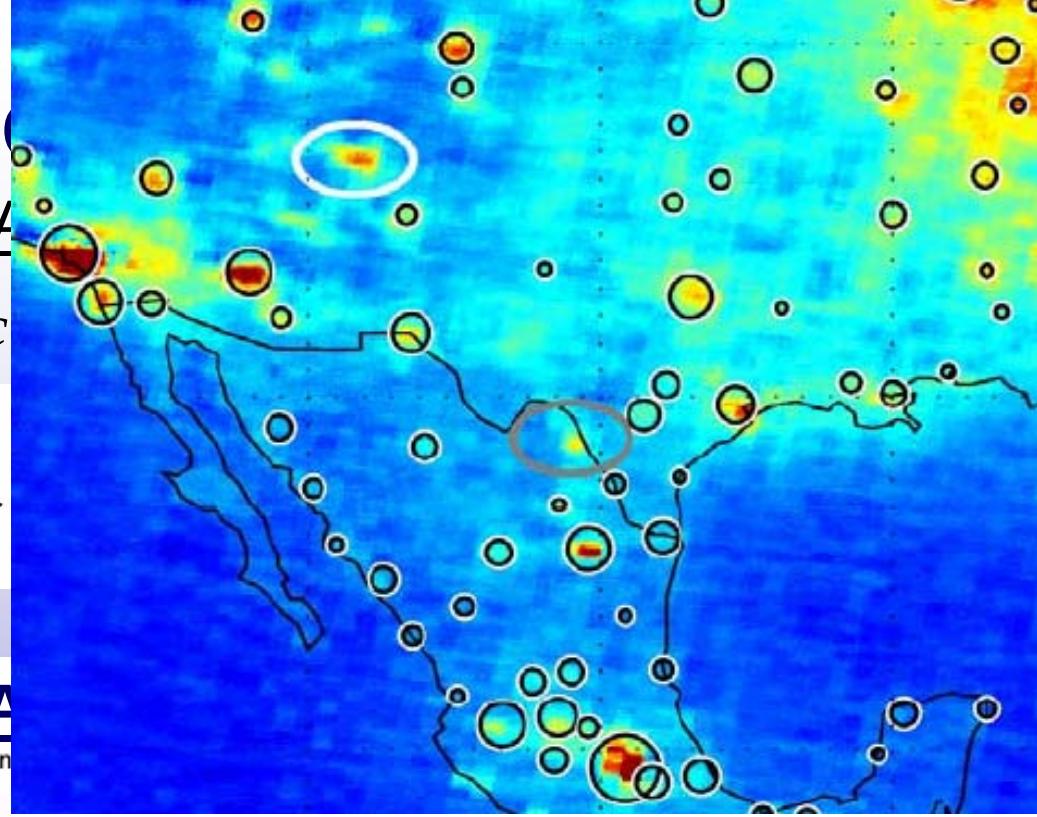
DOAS and MAX-DOAS technique
Vertical gradients of Nitrous Acid (HONO)
C-130 intercepts of HONO VCDs over T0
Satellite comparison of NO_2
SSA in the near UV and UV

1) DOAS and MAX-D

Differential Optical A

Lambert-Beers Law: $I = I_0 \cdot \exp(-\sigma \cdot c$

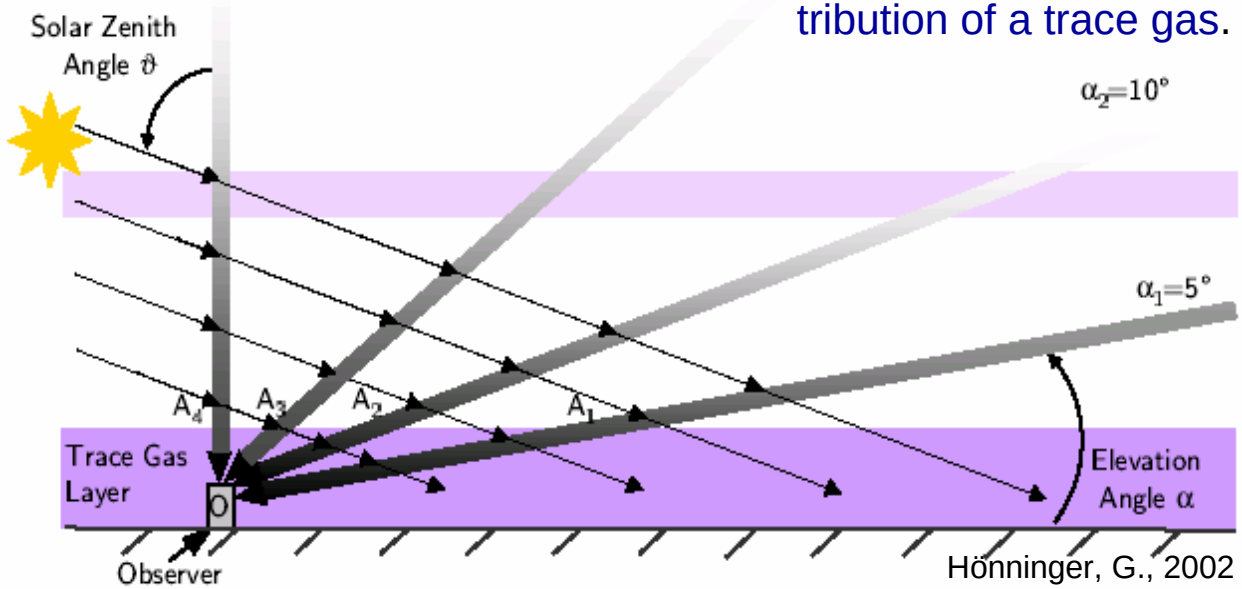




tribution of a trace gas.

Multi-A

Zen



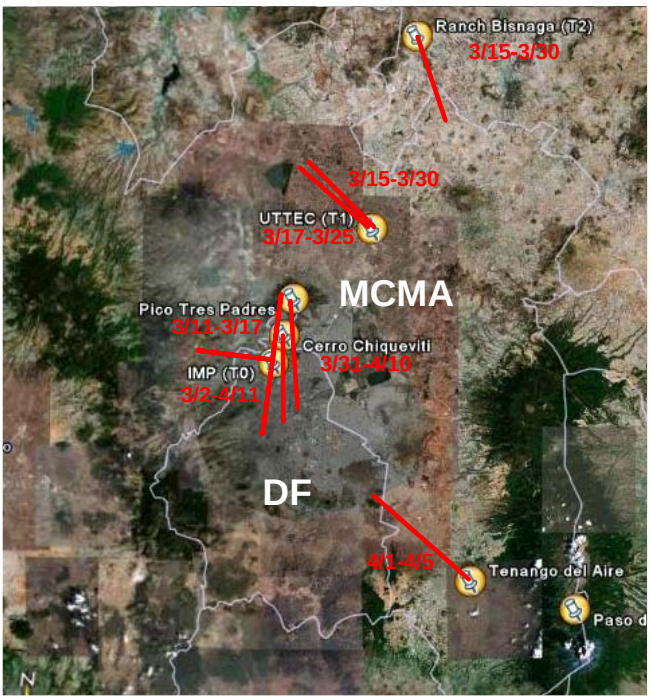
Hönninger, G., 2002

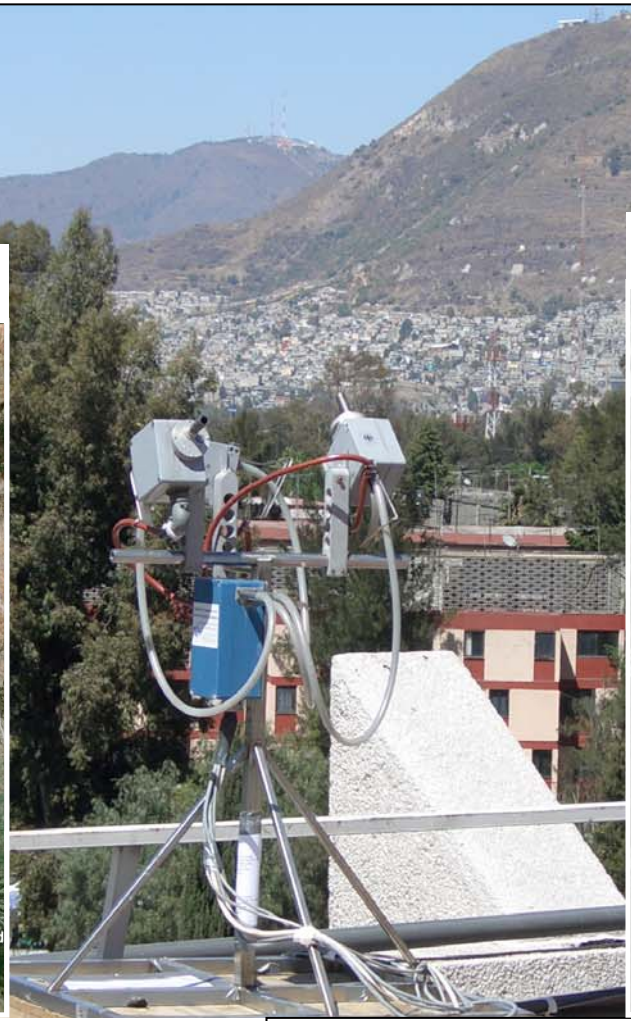
Advantages of DOAS:

- I_0 can remain undetermined
- High sensitivity (down to optical densities ≤ 0.001)
- Simultaneous measurement of several absorbers

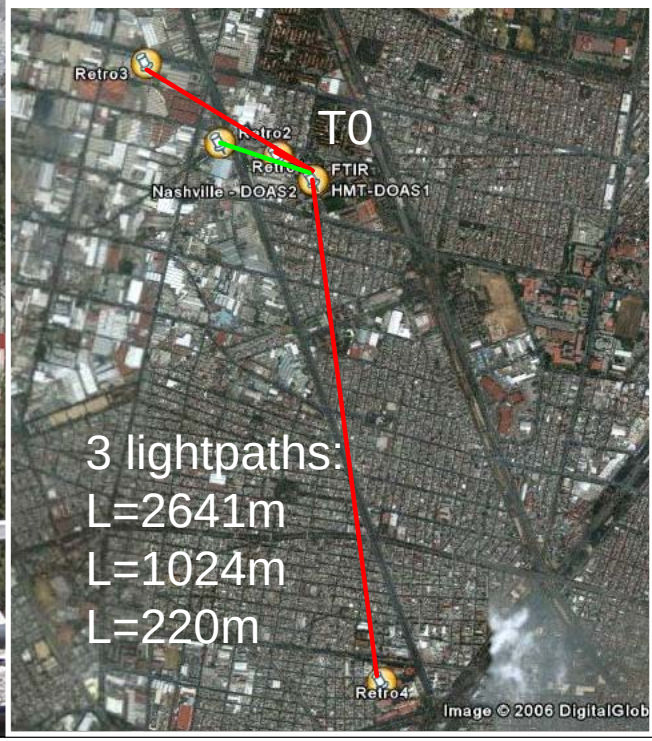
Field projects Mexico City (2003, 2006)

Multi-Axes DOAS Network





Open-Path DOAS at T0



- Quasi-Lagrangian Pollution Transport
- **Vertical, and horizontal gradients**
- Planetary Boundary Layer height
- **Satellite validation**

- Fast-photochemistry (HOx res, SOA prec)
- Glyoxal and Polycyclic Aromatic VOCs
- MAX-DOAS Validation
- Horizontal gradients

2) Nitrous Acid (HONO)

Sources:

- Direct emission from combustion sources
- Homogenous gas phase reactions:
  $OH + NO$, $NO_x + H_2O$, $NO_x + HO_2$
- Heterogenous reactions on/in aerosols
- Heterogenous reactions on surfaces (urban, forest, etc.)
- Photo enhanced in soil (Stemmler et al., 2006)

} **lead to a vertical gradient in the atmosphere**

Sinks:

- $HONO + h\nu \rightarrow OH + NO$ (faster than expected, Wall et al., 2006)
- ($HONO + OH \rightarrow NO_2 + H_2O$)

During MCMA-2003, HONO contributed 50% to HOx sources at 7am, and <3% at 12pm (Volkamer et al., 2007, ACPD 7, 5365).

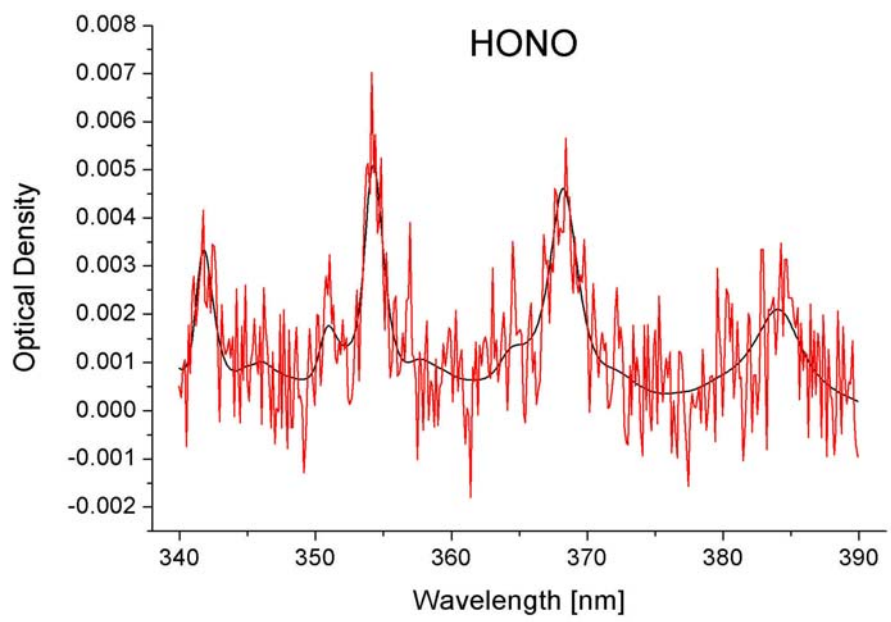
→ Refined knowledge about source apportionment of HONO requires better detection sensitivity during the day.

→ Oxidant fields control secondary pollutant formation (O_3, SOA)

Example Retrieval

NEW !!

March 14, 7:25 am, 1° elevation angle

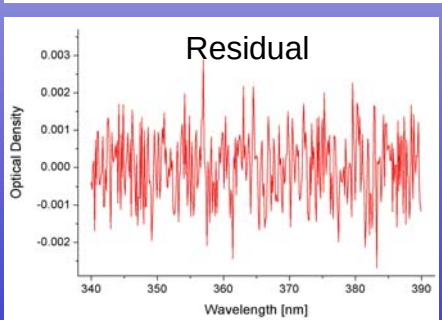


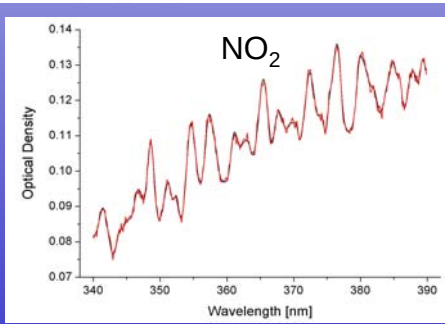
dSCD: 1.07e+16 molecules/cm^2

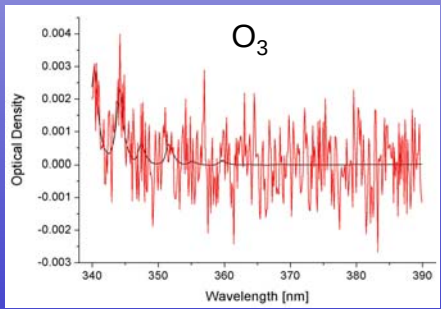
Wavelength range: 340 - 390 nm

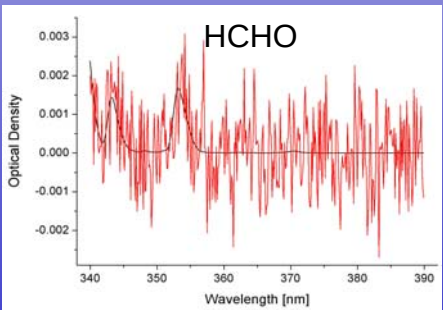
Included trace gases:
HONO, NO_2, O_3, HCHO, BrO and O_4

Further:
Ring spectrum
Quadratic prelogarithmic offset
Polynomial of 5th order



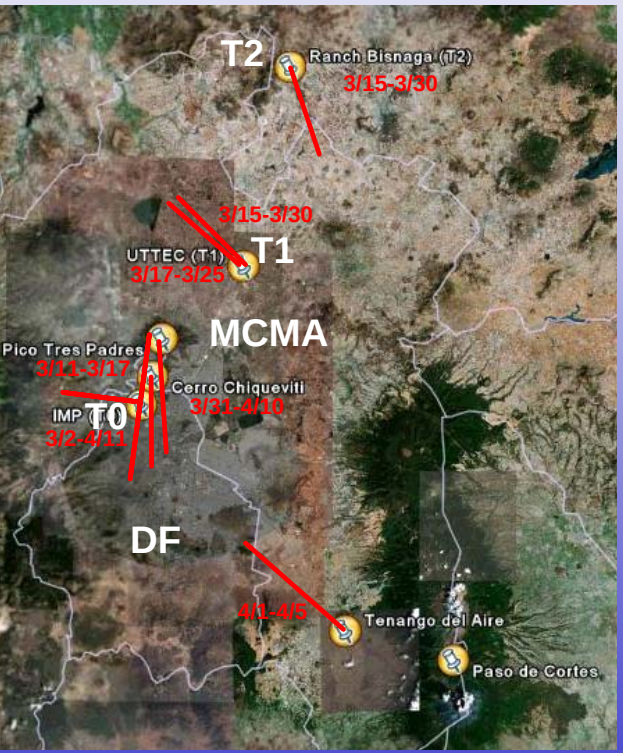






Measurement Results

„Alignment event“ on March 19 (wind came from the south):



Values at 7am:

	HONO VCD [cm^{-2}]	NO_2 VCD [cm^{-2}]	HONO-to-NO_2 ratio [%]	Distance from T0 [km]
T0	$1.8 \cdot 10^{15}$ ($\pm 1.6 \cdot 10^{14}$)	$3.5 \cdot 10^{16}$ ($\pm 6.1 \cdot 10^{14}$)	5.2 (± 0.5)	0
T1	$5.3 \cdot 10^{14}$ ($\pm 9.4 \cdot 10^{13}$)	$2.8 \cdot 10^{15}$ ($\pm 3.7 \cdot 10^{14}$)	19 (± 4)	30
T2	$5.1 \cdot 10^{14}$ ($\pm 1.63 \cdot 10^{14}$)	$2.05 \cdot 10^{15}$ ($\pm 4 \cdot 10^{14}$)	25 (± 10)	63

~ x3 **~ x15**

→ HONO production on surfaces

→ Relatively more HONO outside the city, why ?

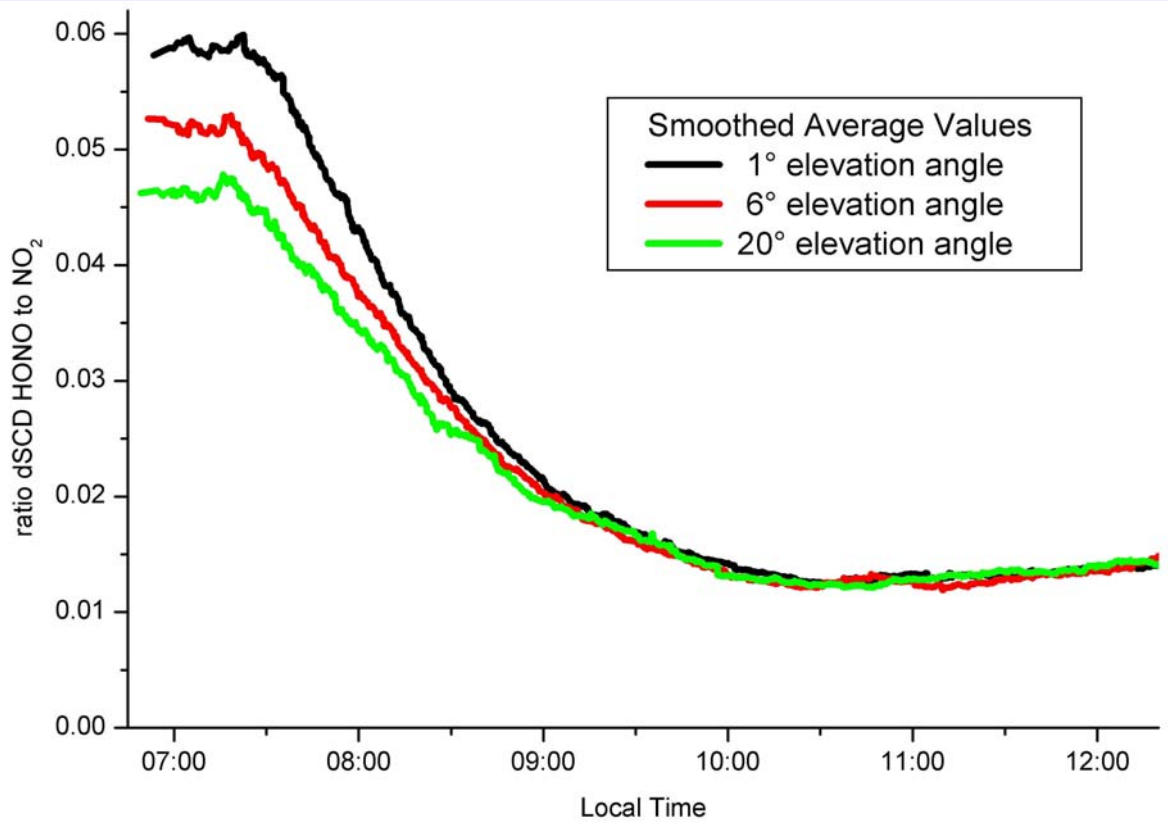
→ Differences in PBL height can NOT explain this

Measurement Results

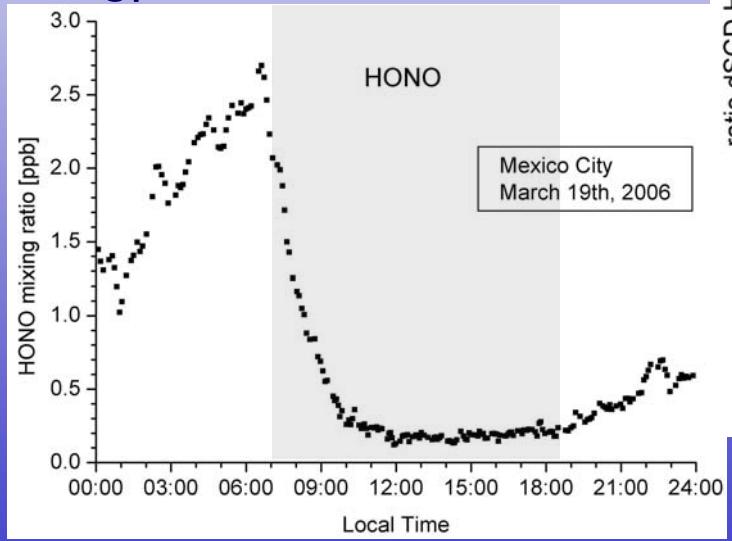
Typical diurnal cycle throughout the measurement campaign:

HONO degradation in the morning and a slight accumulation in the evening.

MAX-DOAS:



Longpath-DOAS:

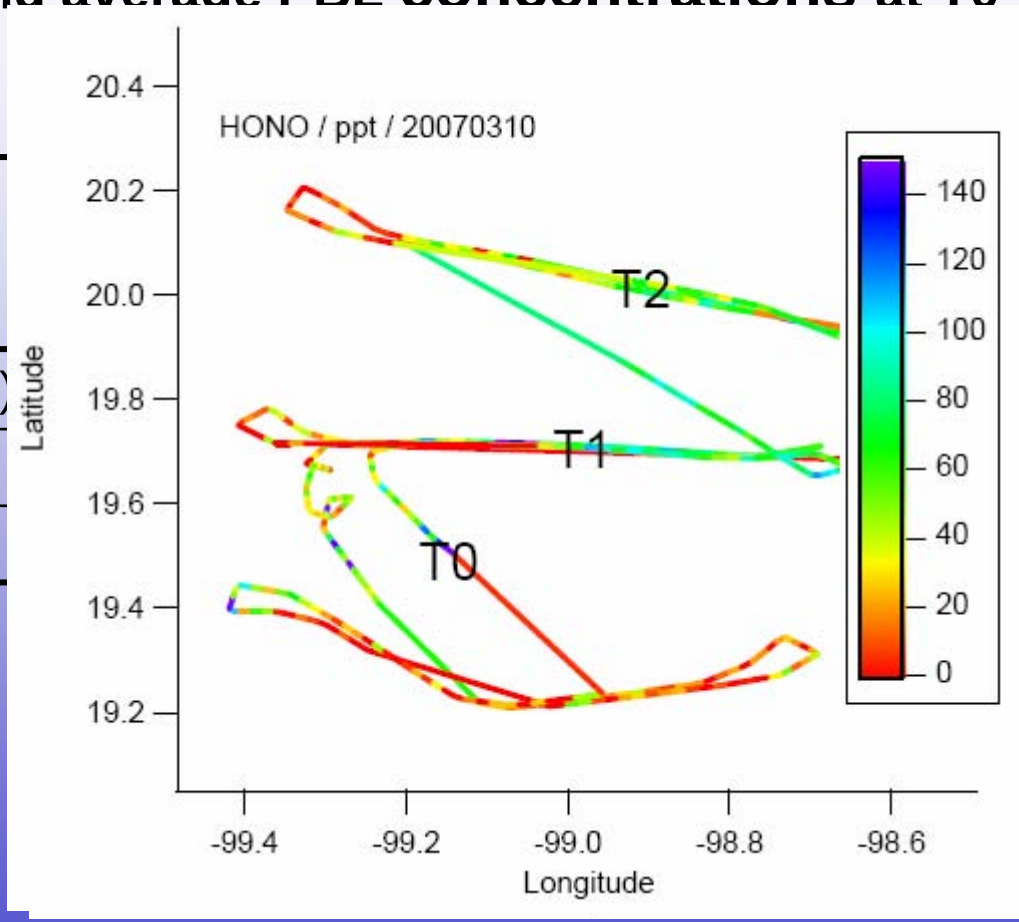


Direct evidence for ground-level HONO sources !

Measurement Results

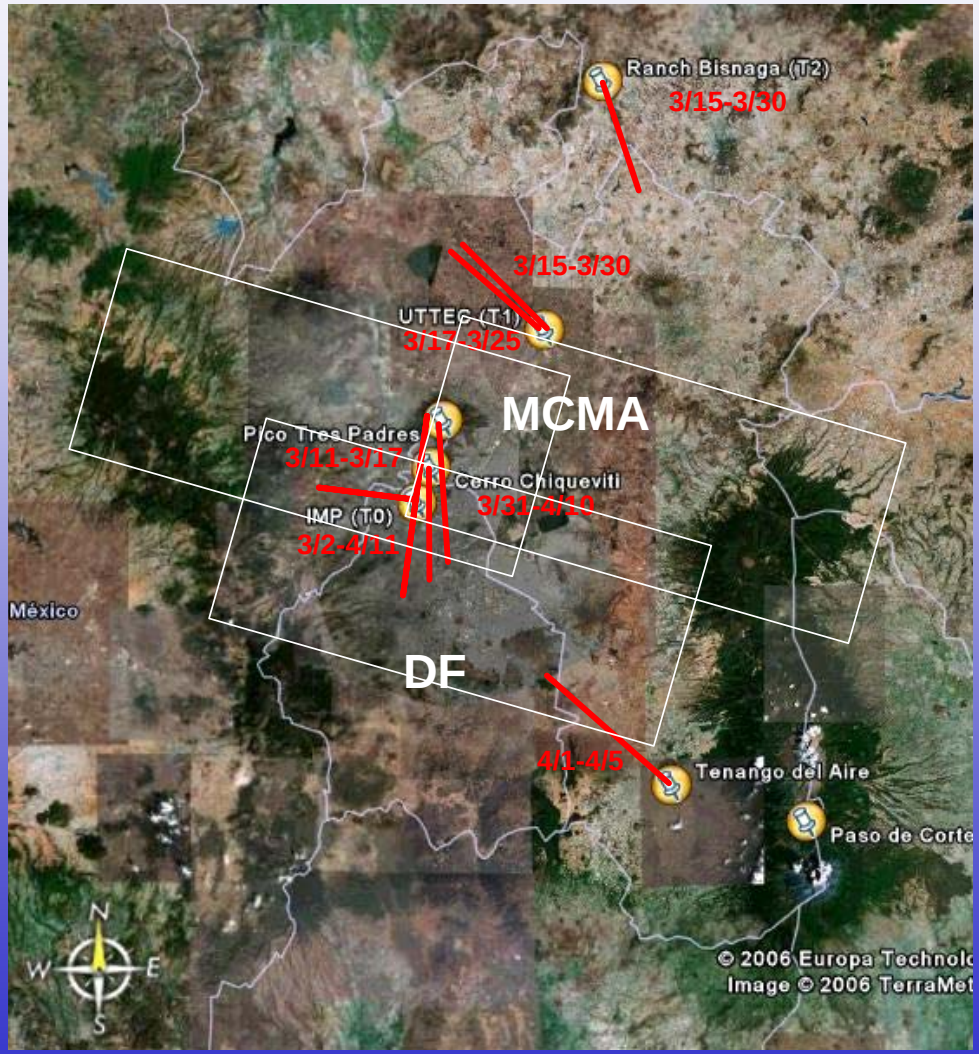
Comparison of ground-level and average PBL concentrations at T0 (campaign average):

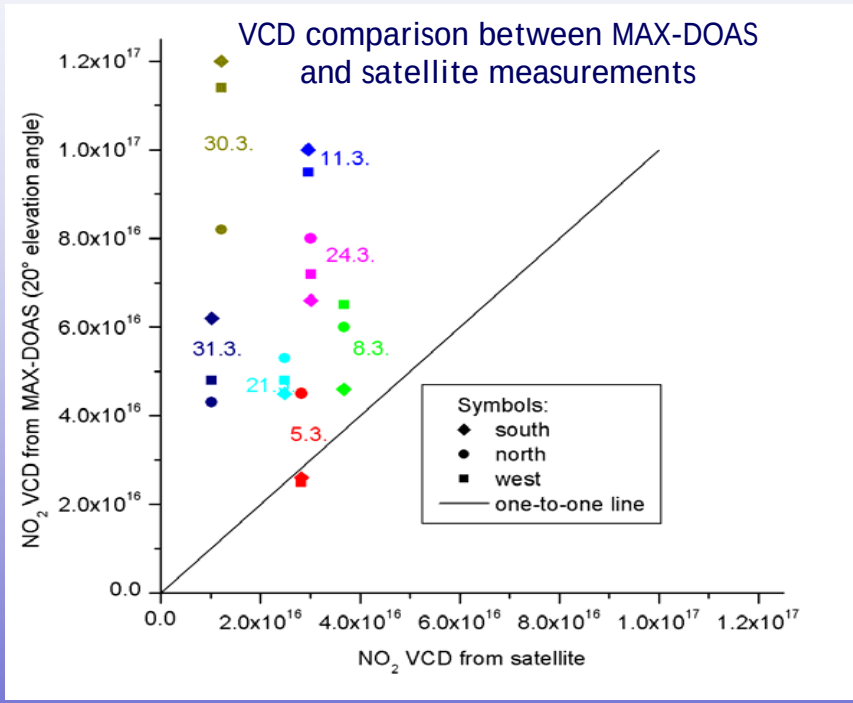
HONO	LP-DOAS [ppt]	MAX-DOAS [ppt]
9am	900 (±400)	340 (±110)
10am	600 (±200)	190 (±80)
12pm	300 (±200)	90 (±40)



C-130 comparison with HONO-CIMS

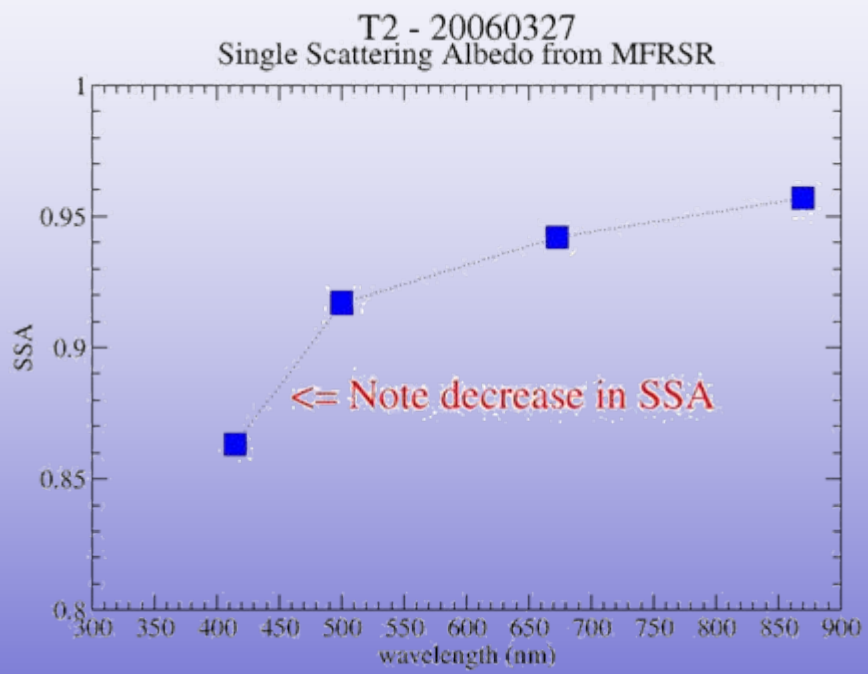
NO_2 comparison of VCDs measured by MAX-DOAS and SCIAMACHY

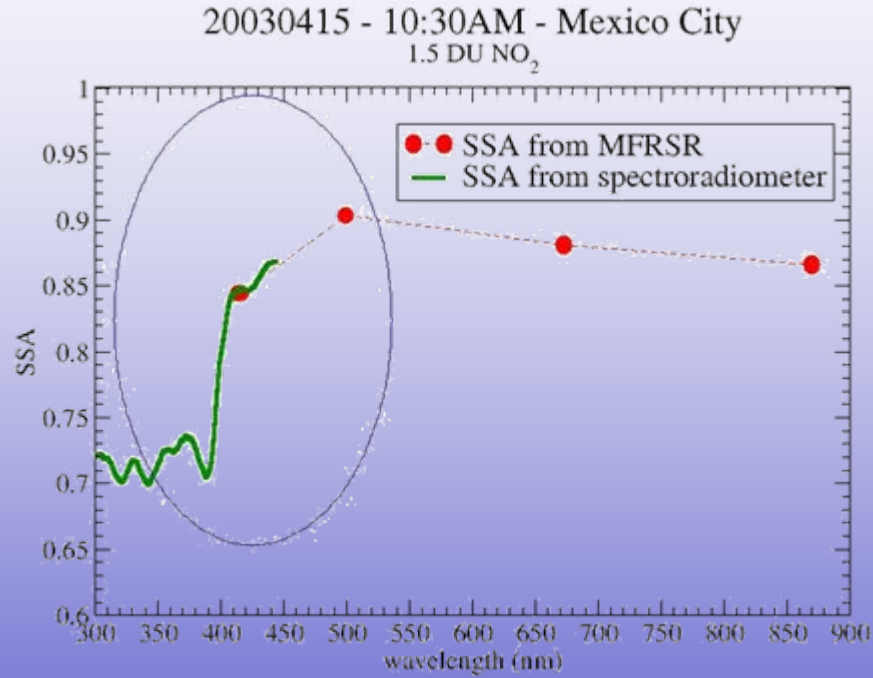




Factors to consider: Spatial (temporal) overlap, radiative transfer, clouds, aerosols, albedo…

Evidence of enhanced absorption in UV and near-UV from ϖ_0 measurements





- Several W m^{-2} “heating” from OA !
- Strong effect on radiative transfer !

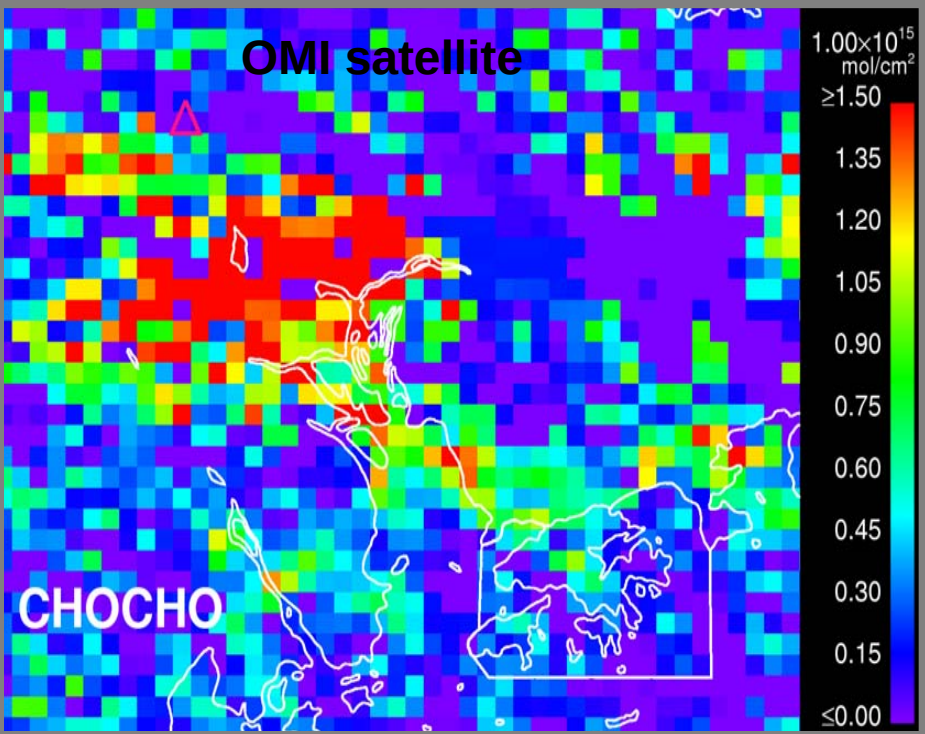
Conclusions

- **Vertical HONO gradients:**
  - exist DURING THE DAY
  - create a high bias in the relevance of HONO as a radical source as inferred from probing only the lower PBL.
  - direct confirmation from C-130 intercepts of the trace-gas column over T0
- **Horizontal HONO gradients**
  - show relatively enhanced VCDs outside the city.
- **MAX-DOAS:**
  - sensitively measures low HONO concentrations DURING THE DAY
  - offers a solution by integrating over the PBL.
- **Satellite comparison:**
  - SCIAMACHY is limited by the 40x80 km^2 ground-pixel size
  - Small ground pixel size is essentially useful to study urban environments (OMI data)
  - The strong wavelength dependence of Single Scattering Albedo (SSA) affect quantitative satellite retrievals ?

Case Study in the Pearl River Delta, China: Spatial Variability of Glyoxal, HCHO and NO_2 during PRD-2006

Alexander von Humboldt Stiftung/Foundation

Volkamer *et al.* 2006, *Eos Trans. AGU, 87*(52), Fall Meet. Suppl., Abstract A31B-0897



Thank you!

Mexico City