Urban and Rural Field Studies of HONO: A Review

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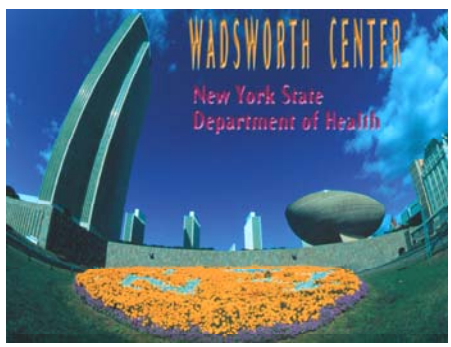

UNIVERSITY AT ALBANY
School of Public Health

HONO Workshop/Wuppertal, Germany/March 2008

About the talk

- Brief History of HONO field studies
- HONO Field Observations in Urban and Rural Environments:
  - Concentration distributions/variations
  - Sources/sinks/formation mechanisms
  - HO_x source
- HONO Flux/Exchange Between Atmosphere and Ground Surface

history

- The first unambiguous identification of HONO in the troposphere was made by Perner and Platt (*Pener and Platt*, GRL, 6:917-920, 1979)

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Date	day-time	HNO_2 ppb	NO_2 ppb	O_3 ppb	SO_2 ppb	remarks
Febr. 28	6:30	0.7±0.2	26			-2°C, 4100 ppm water, cloudy, little haze, sun during the day
	7:10	0.8±0.2	35			
	7:20	0.8±0.2	37			
	7:30	0.8±0.2	33	2-5		
	8:10	0.5±0.2	35		11	
	17:10	<0.1	31			
	17:40	<0.06	58			
Mar.1	15:40	<0.1	26			cloudy, rain
Mar.7	16:50	<0.07	15	12		clear, little sun
Mar.8	14:40	0.1±0.1	9	20		sunny, little haze
	15:40	<0.05	17			8°C, 5300 ppm water
Mar.9	5:53	0.13±0.07	4.7			cloudy, 6°C, 6000 ppm water
	6:30	0.06±0.03	6.5	32		
	7:30	0.12±0.06	9.3		59	

history

- The first unambiguous identification of HONO in the troposphere was made by Perner and Platt (Pener and Platt, *Geophys. Res. Let.*, 6:917-920, 1979)

- In the following ~10 years: ambient HONO measurement mostly made in urban/nighttime using DOAS

history

- The first unambiguous identification of HONO in the troposphere was made by Perner and Platt (Pener and Platt, *Geophys. Res. Let.*, 6:917-920, 1979)

- In the following ~10 years:
  DOAS/urban/nighttime

- Method developments since early 1990s:
  - Anular denuder, continuous wet scrubbing, with chemical detection/IC,
  - TDLAS, FTIR, CRDS, CIMS, TDC, and PF-LIF.

history

- The first unambiguous identification of HONO in the troposphere was made by Perner and Platt (Pener and Platt, *Geophys. Res. Let.*, 6:917-920, 1979)

- In the following ~10 years: DOAS/urban/nighttime

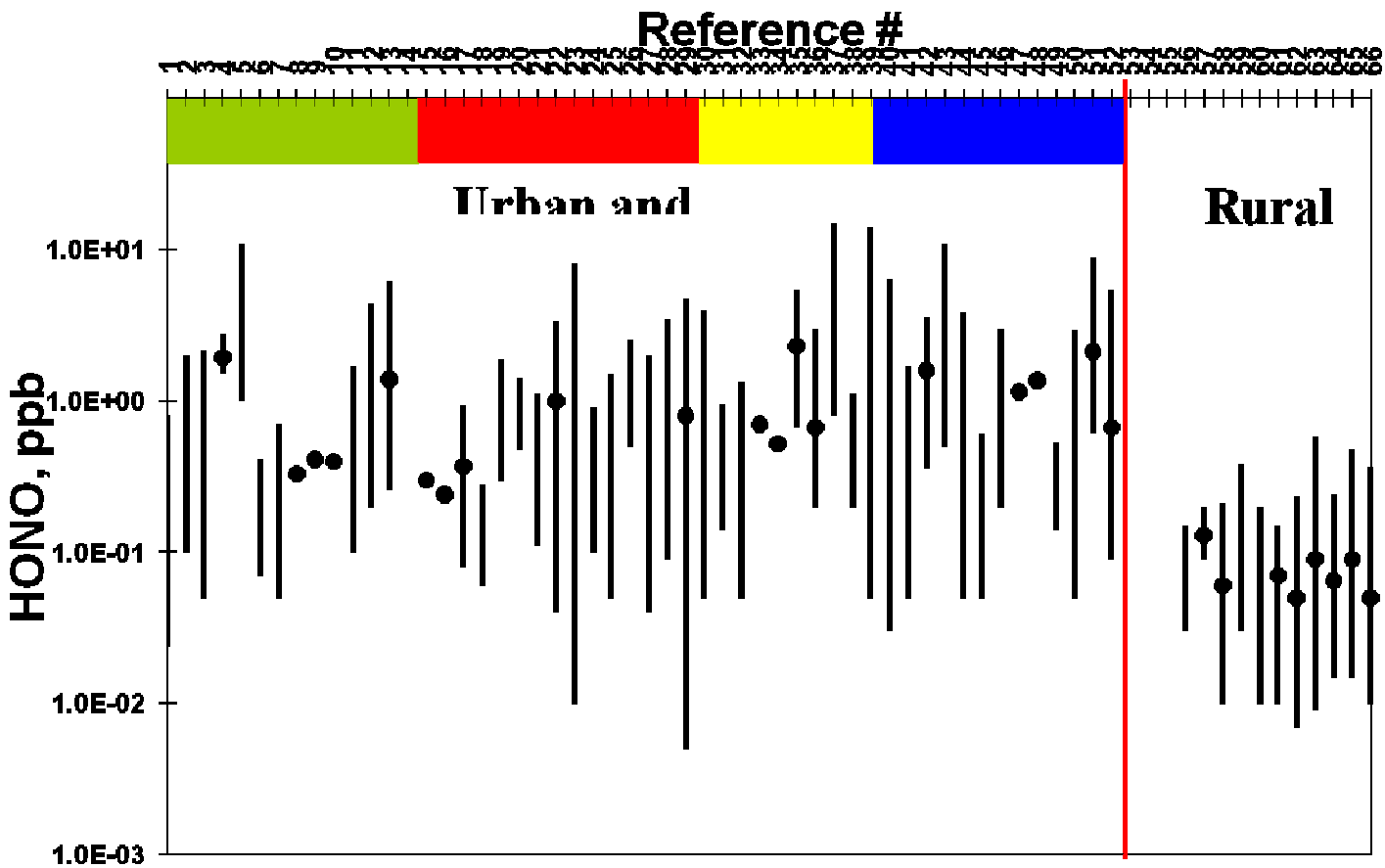
- Other techniques were developed since 1990s:

- Urban daytime studies/rural studies from mid 1990s:

  - Significant daytime HONO

  - Strong daytime HONO source

HONO distribution



#	Reference	Year of Study	Location	Season	Method
	Urban and Semi-Urban				
1	Perner & Platt, 1979	1979	Julich, Germany	Spring	DOAS
2	Vecera et al., 1991	1990	Lubbock, Texas	Spring	DS/IC
3	Notholt et al., 1992	1990	Ispra, Italy	Spring	DOAS
4	Harrison et al., 1994	1990	Colchester, UK	Spring	AD/IC
5	Febo et al, 1996	1994	Milan, Italy	Spring	DOAS
6	Harrison et al., 1996	1994	Wast Hills, UK	Spring	AD/IC
7	Harrison et al., 1996	1994	Edgbaston, UK	Spring	AD/IC
8	Zimmerling et al., 1996	1991	Rotenkamp, Germany	Spring	KAPS/AA
9	Zimmerling et al., 1996	1991	Rotenkamp, Germany	Spring	KAPS/AA
10	Zimmerling et al., 1996	1993	Rotenkamp, Germany	Spring	KAPS/AA
11	Huang et al., 2002	1999	Albany, New York	Spring	AS/HPLC
12	Alicke et al., 2002	1998	Milan, Italy	Spring	DOAS
13	Bari et al., 2003	2000	New York City	Spring	AD/IC
14	Harris et al., 1981	1980	Los Angeles	Spring	DOAS
15	Zimmerling et al., 1996	1991	Rotenkamp, Germany	Summer	KAPS/AA
16	Zimmerling et al., 1996	1992	Rotenkamp, Germany	Summer	KAPS/AA
17	Harrison et al., 1996	1994	Nottingham, UK	Summer	AD/IC
18	Harrison et al., 1996	1993	Wast Hills, UK	Summer	AD/IC
19	Schiller et al.., 2001	1998	Toronto, Canada	Summer	TDLAS
20	Perrino et al., 2001	1998-9	Gallese, Italy	Summer	DL/IC
21	Alicke et al., 2003	1998	Pabstthum, Germany	Summer	DOAS
22	Bari, A, 2003	1999	New York City	Summer	AD/IC
23	Genfa et al., 2003	1999	Atlanta, Georgia	Summer	WEDD/IC
24	Stutz et al., 2004	1999	Nashville, TN	Summer	DOAS
25	Stutz et al., 2004	2000	Houston, TX	Summer	DOAS
26	Stutz et al., 2004	2001	Phoenex, Arizona	Summer	DOAS
27	Kleffmann & Gavriloaiei, 2005	2003	Julich, Germany	Summer	AS/LPAP
28	Kleffmann, J., 2006	2001	Milan, Italy	Summer	AS/LPAP
29	He, 2006	2001	New York City	Summer	AS/LPAP
30	Amoroso et al., 2008	2005	Ashdod, Israel	Summer	AS/HPLC

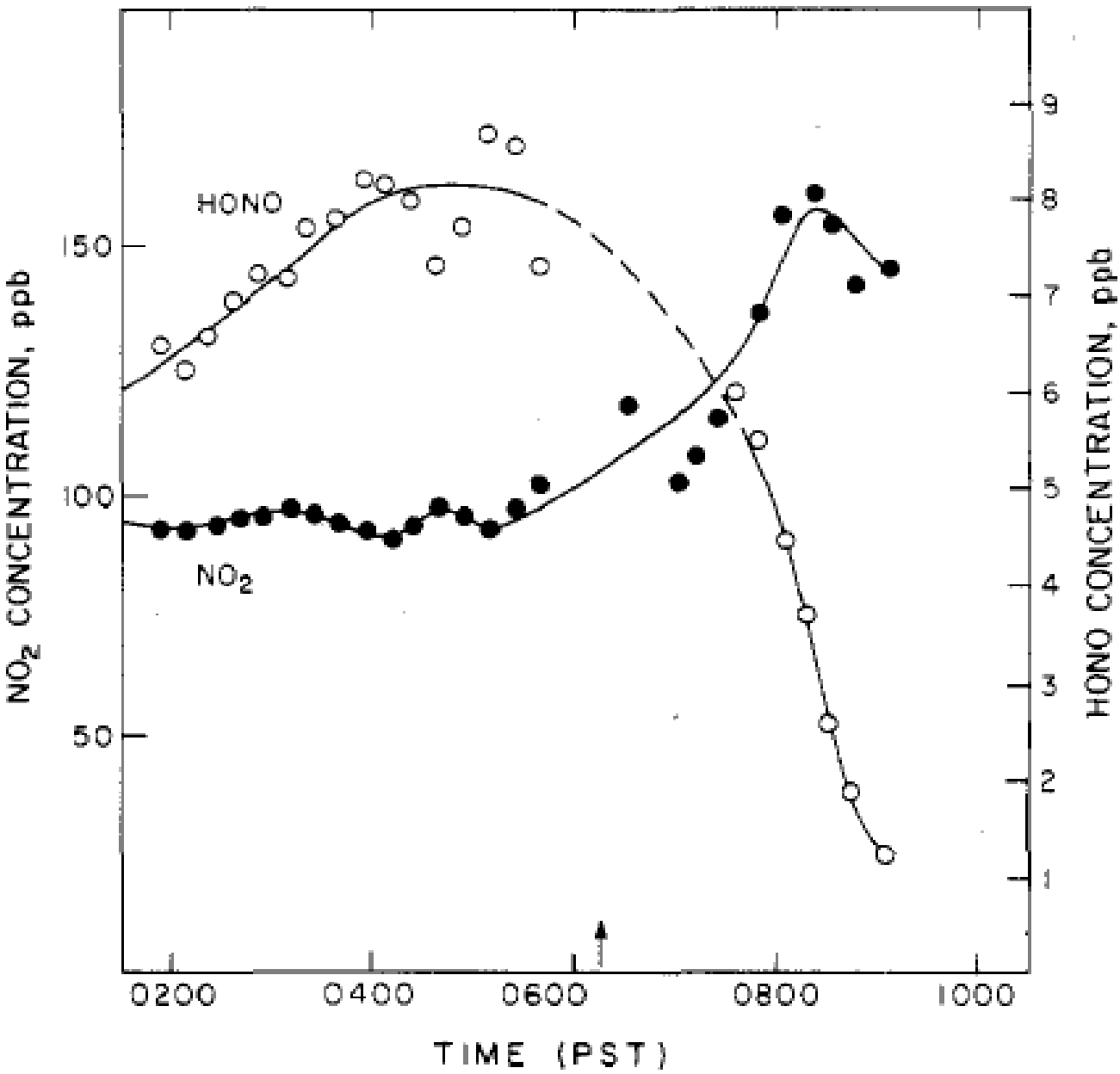
31	Harrison et al., 1994	1989	Halvergate, UK	Autumn	AD/IC
32	Andres-Hernandez et al., 1996	1989	Ticino Valley, Switzerland	Autumn	DOAS
33	Zimmerling et al., 1996	1991	Rotenkamp, Germany	Autumn	KAPS/AA
34	Zimmerling et al., 1996	1992	Rotenkamp, Germany	Autumn	KAPS/AA
35	Bari et al., 2003	1999	New York City	Autumn	AD/IC
36	Parket al., 2004	2001	Kwangju, South Korea	Autumn	AS/IC
37	Wineret al., 1994	1987	Long Beach, California	Autumn	DOAS
38	Kleffmannet al., 2003	2001	Forschungszentrum Karlsruhe, Germany	Autumn	AS/LPAP
39	Amoroso et al., 2008	2004	Ashdod, Israel	Autumn	AS/HPLC
40	Rogers, 1989	1986	Atlanta, Georgia	Winter	PF/LIF
41	Notholt et al., 1992	1990	Ispra, Italy	Winter	DOAS
42	Harrison et al., 1994	1990	Colchester, UK	Winter	AD/IC
43	Evangelisti et al., 1995	1993	Milan, Italy	Winter	DOAS
44	Andres-Hernandez et al., 1996	1991	Milan, Italy	Winter	DOAS
45	Andres-Hernandez et al., 1996	1990	Ispra, Italy	Winter	DOAS
46	Harrison et al., 1996	1994	Edgbaston, UK	Winter	AD/IC
47	Zimmerling et al., 1996	1991	Rotenkamp, Germany	Winter	KAPS/AA
48	Zimmerling, R., 1996	1992	Rotenkamp, Germany	Winter	KAPS/AA
49	Zimmerling et al., 1996	1995	Petten, Netherlands	Winter	WRAD/IC
50	Reisinger, 2000	1997	Christchurch, New Zealand	Winter	DOAS
51	Bari et al., 2003	1999	New York City	Winter	AD/IC
52	He, 2006	2004	New York City	Winter	AS/LPAP

	Rural				
53	Platt & Berner, 1981	1979	Deuselbach, Germany		DOAS
54	Platt & Berner, 1981	1979	Loophead, Ireland,		DOAS
55	Acker, K., 2001	1999	Mt. Broken, Germany		WEDD/IC
56	Thornberry et al., 2001	1998	Pellston, MI		AD/IC
57	Zhou et al., 2002	1998	Pinacle State Park, NY		AS/HPLC
58	Acker et al., 2004	2000	Melpitz, Germany		WEDD/IC
59	Acker et al., 2006	2004	Hohenpeissenberg.		WEDD/IC
60	He, 2006	2003	Pellston, MI		AS/HPLC
61	He, 2006	2000	Pellston, MI		AS/HPLC
62	He, 2006	2002	Whiteface Mt., NY		AS/LPAP
63	He, 2006	2003	Pellston, MI		AS/LPAP
64	He, 2006	2003	Pellston, MI		AS/LPAP
65	Zhou et al., 2007	1999	Whiteface Mt., NY		AS/HPLC

In Urban Atmosphere

- Under direct influence of anthropogenic emissions
- High NOx (up to hundreds of ppbv)
- High HONO

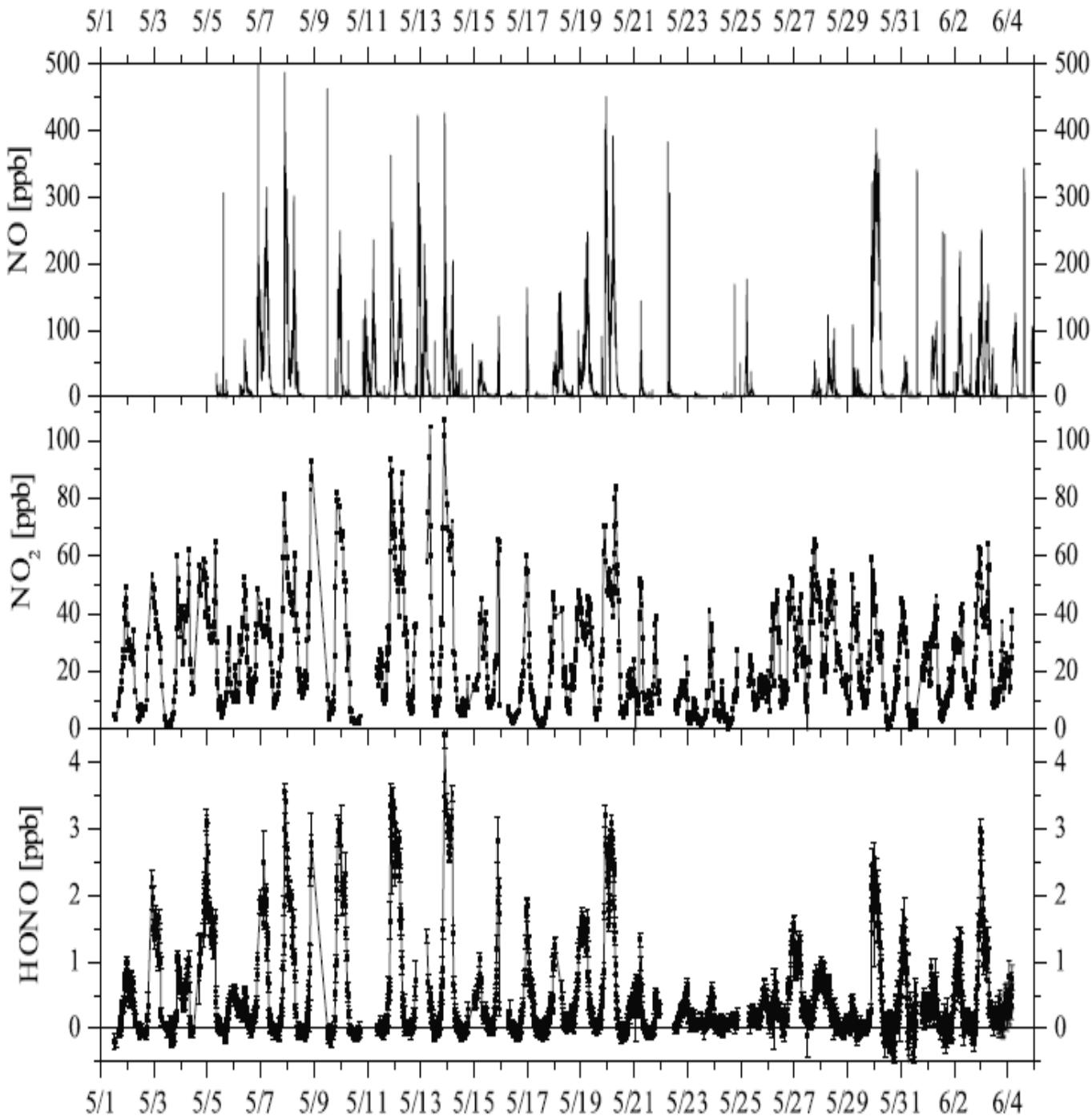
HONO in urban atmosphere



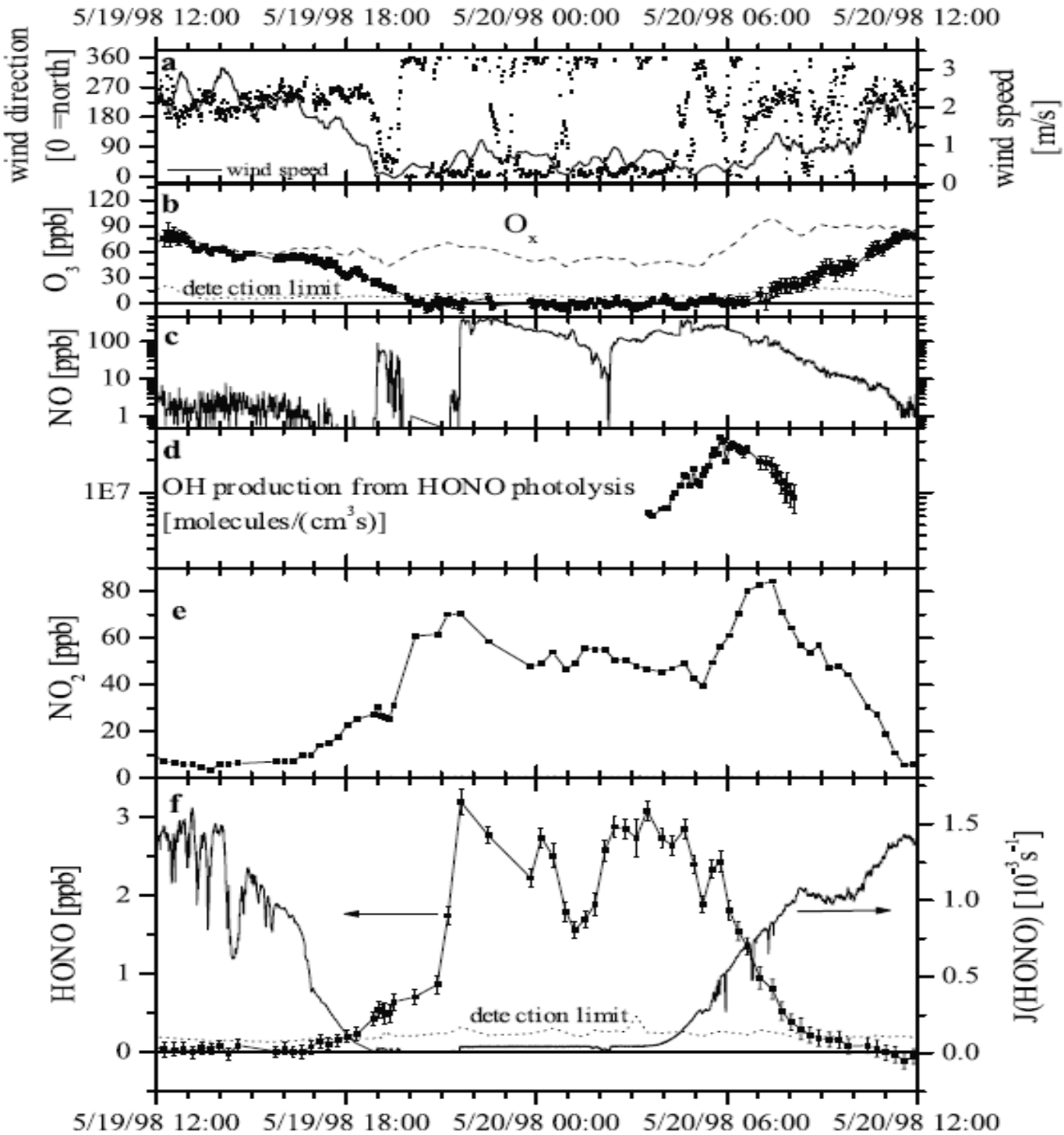
Time-concentration profiles for NO_2 and HONO in Los Angeles, August 8, 1980; arrow marks time of sunrise. (*Harris et al.*, EST, 1982).

➔Nighttime accumulation
➔Morning hour OH source

HONO in urban atmosphere



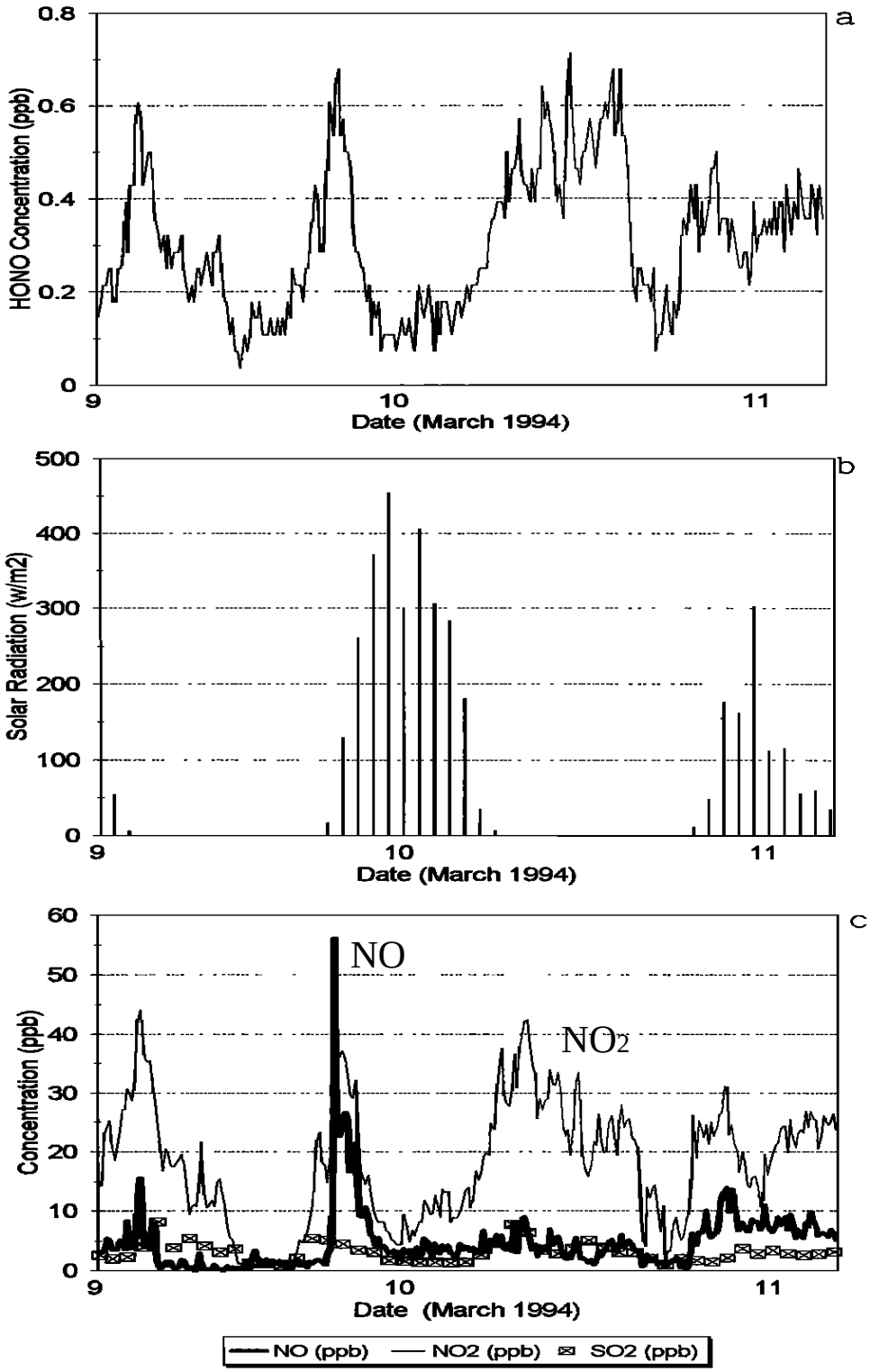
Time series of HONO, NO_2, and NO mixing ratios in Milan during LOOP/PIPAPO study in May–June 1998. (*Alicke et al.*, JGR, 2002)



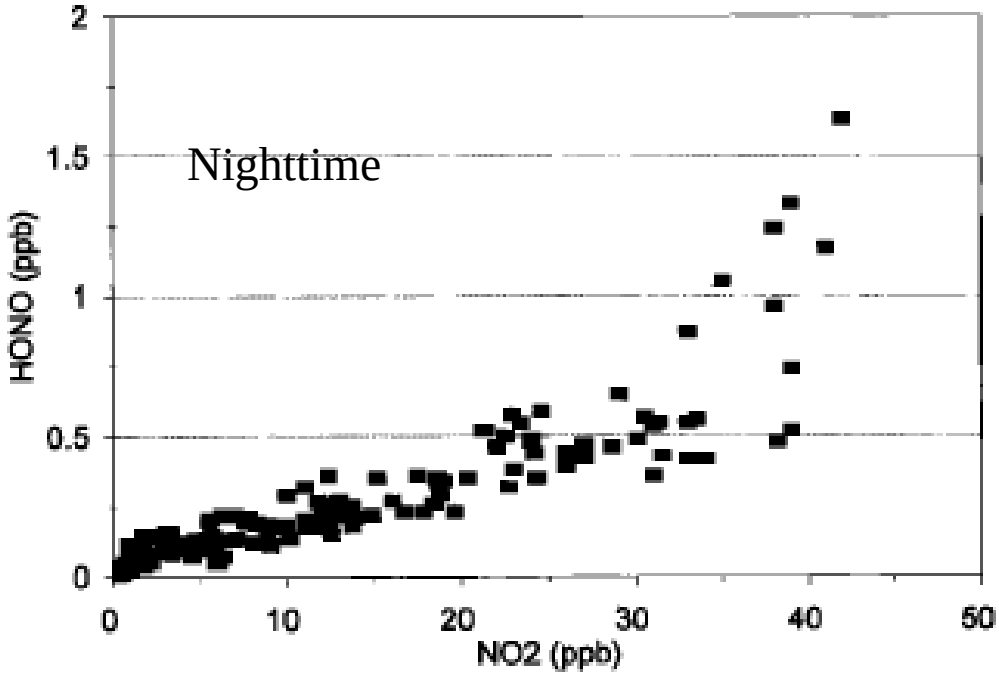
Data during 19–20 May 1998: (a) the wind direction and the wind speed, (b) O3 and Ox (= NO_2 + O_3); (c) NO; (d) OH production from HONO photolysis; (e) NO_2; and (f) HONO mixing ratios and J(HONO). (*Alicke et al.*, JGR, 2002).

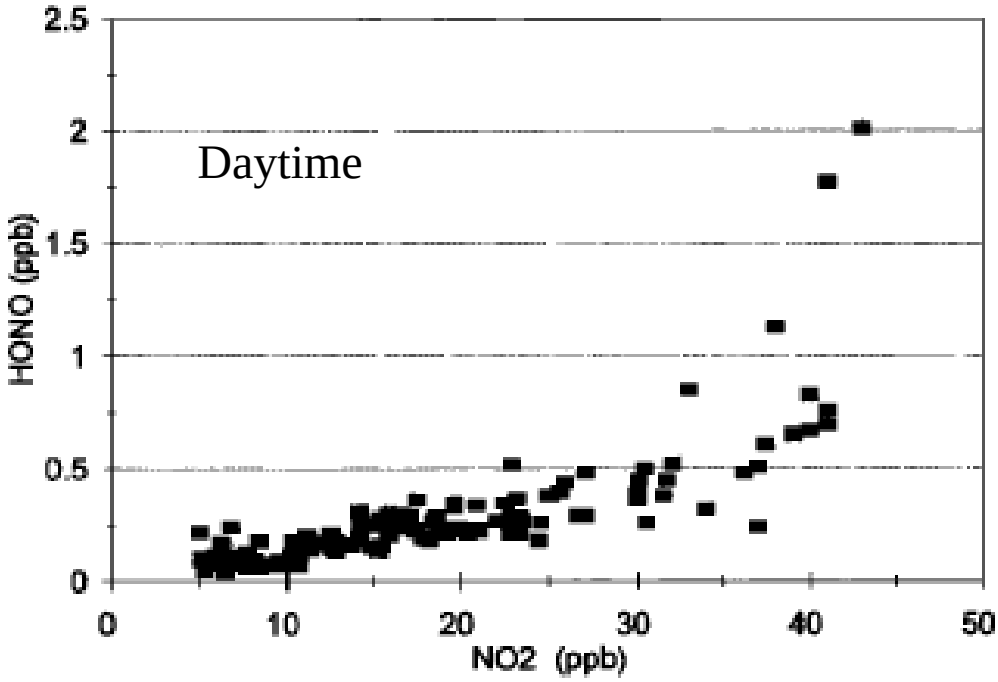
➔Morning OH source

HONO in urban atmosphere

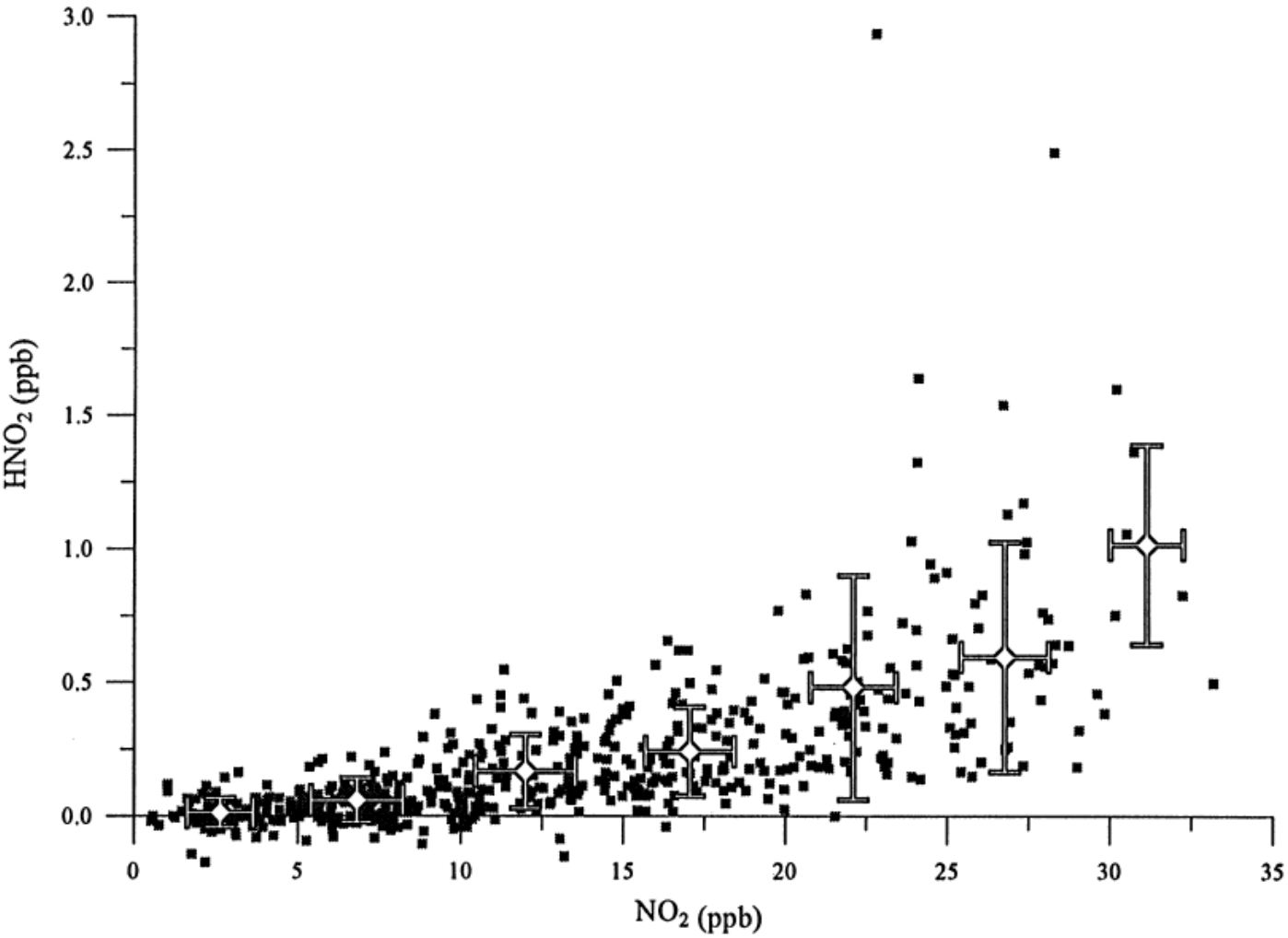


Measurements of (a) HONO (b) solarr adiation; and (c) NO, NO_2 and SO_2 at the University of Birmingham site. (*Harrison et al.*, JGR, 1996)





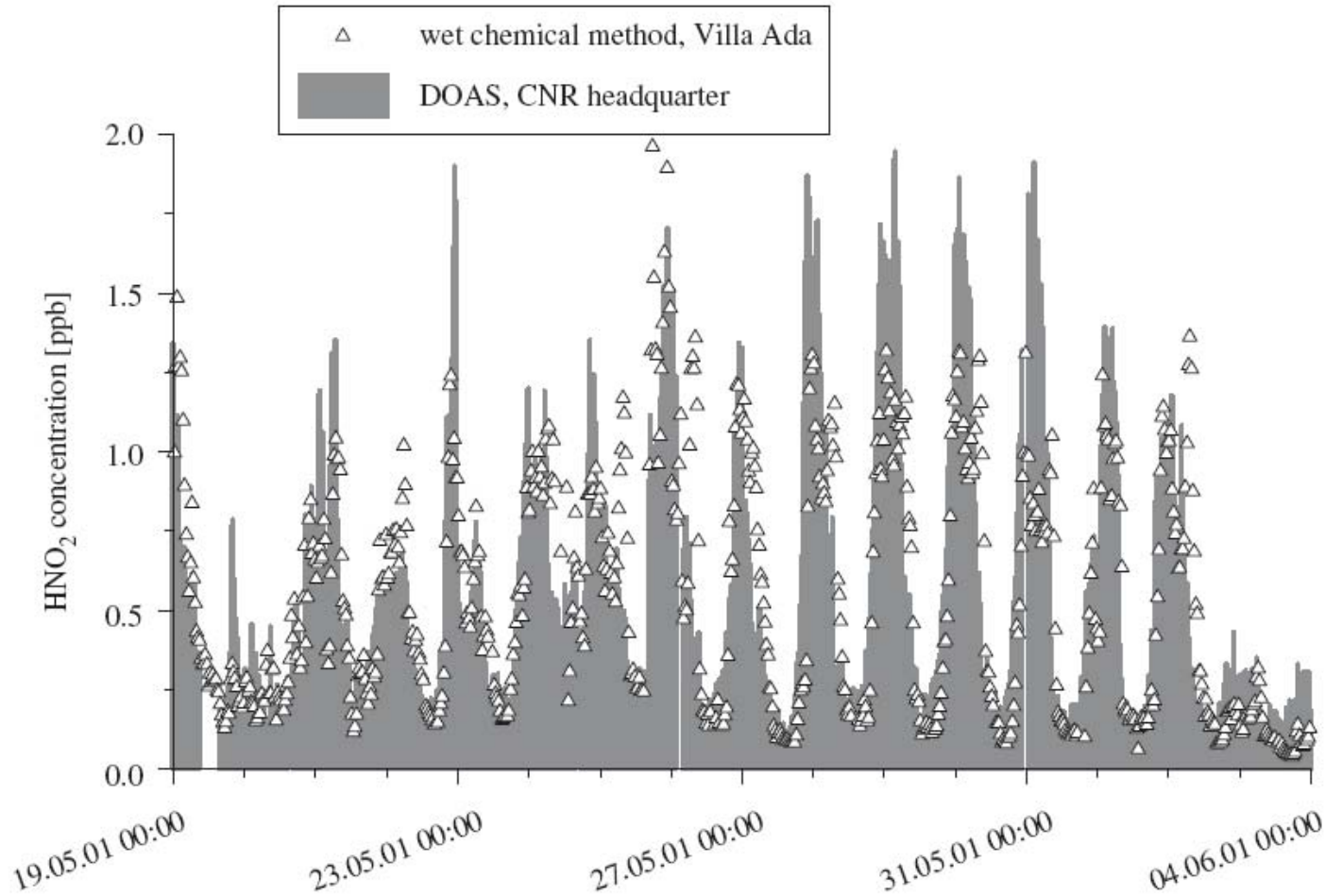
Relationship between HONO and NO_2 at the University of Birmingham site. (*Harrison et al.*, JGR, 1996).



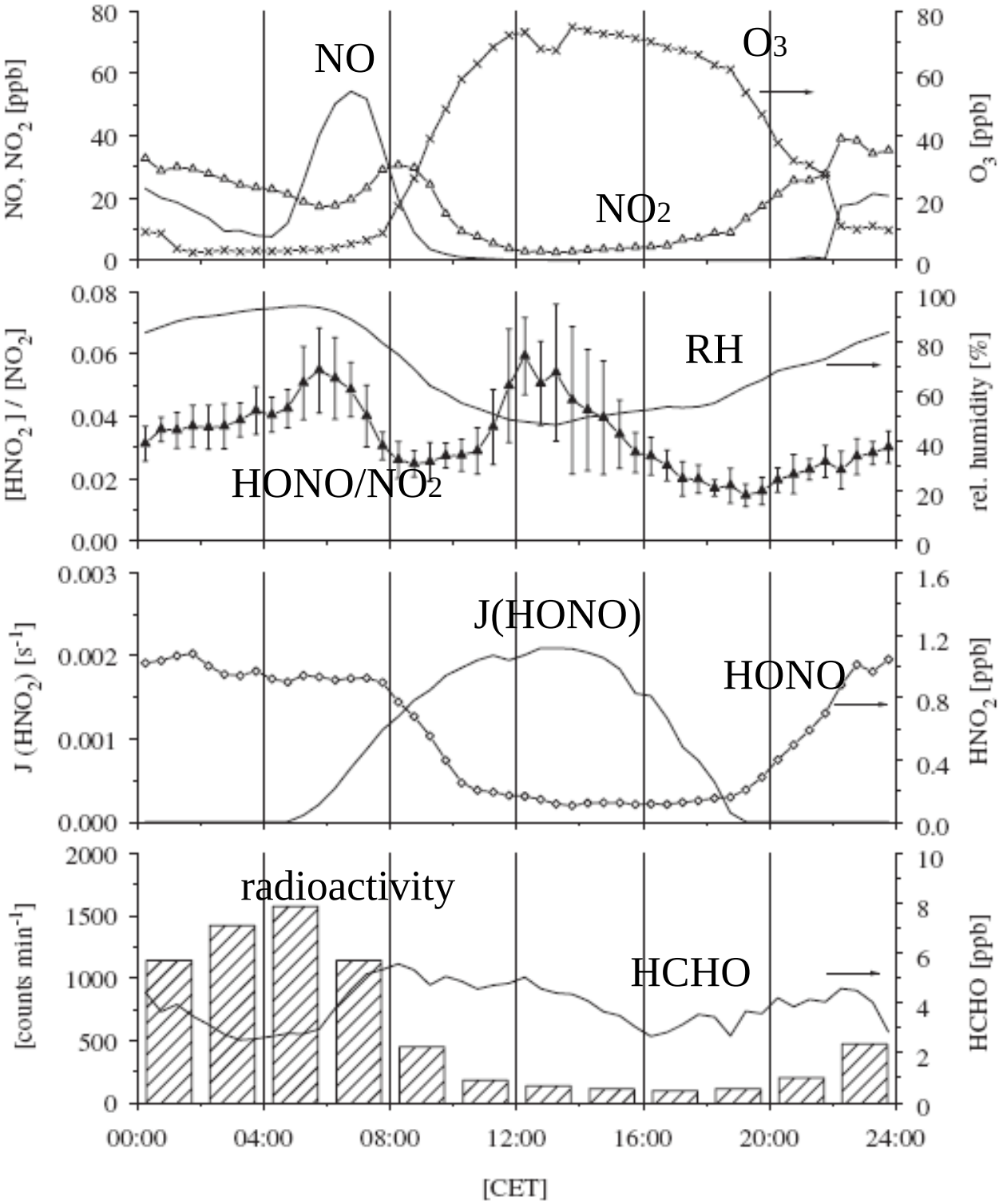
Correlation between HONO and NO_2. Squares are individual measurements, diamonds are averages in steps of 5 ppb NO_2. Error bars represent one standard deviation of the averages. (*Reisinger*, Atmos. Environ., 2000*)*.

$$2NO_2 + H_2O + S \rightarrow HONO + HNO_3 + S$$

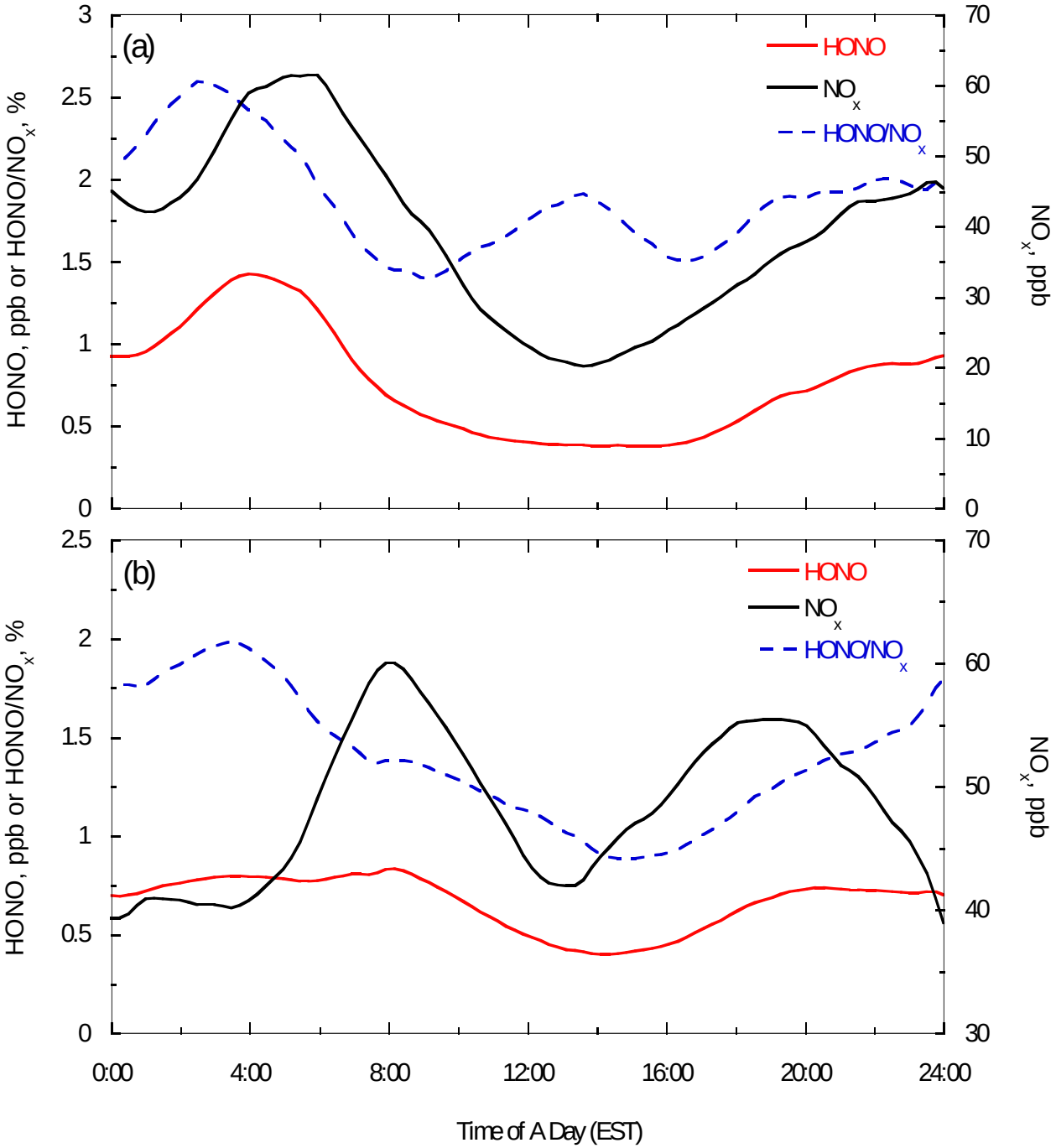
$$NO + NO_2 + H_2O + S \rightarrow 2HONO + S$$



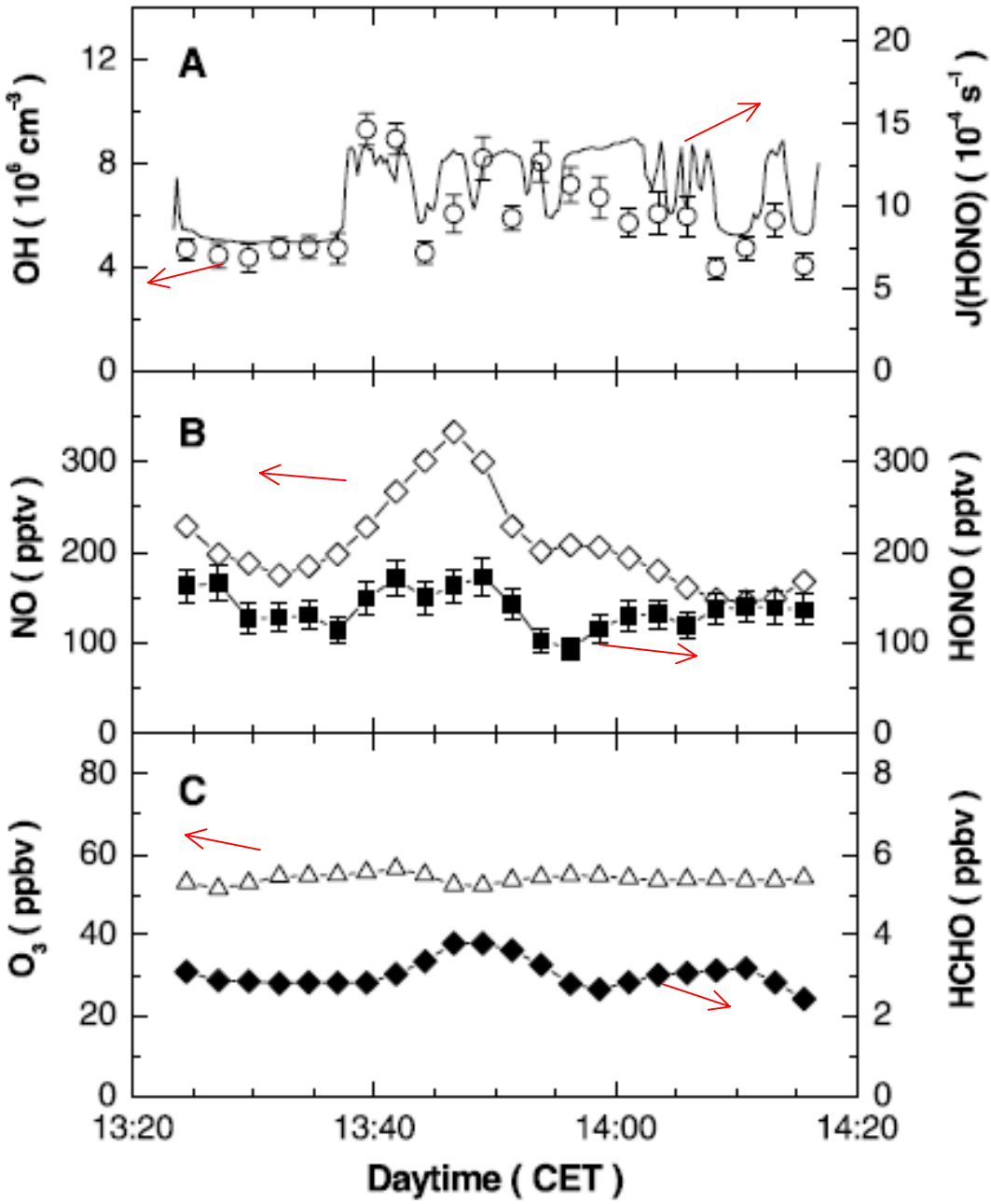
Nitrous acid in the centre of Rome measured by LP-DOAS (grey area) and wet chemical methods (open triangles) from 19 May to 03 June 2001. (*Acker et al.*, Atmos. Environ., 2006)



Diurnal variation of different parameters in Rome (averaged over the high pressure period 27 May—01 June 2001). (*Acker et al.*, Atmos. Environ., 2006)



Diurnal variations of composite HONO, NO_x, and $HONO/NO_x$ ratios in New York City, during the EPA Suppersite Study in (a) 2001 summer and (b) 2004 winter. (*He*, 2005)



Measurements of trace gases and J(HONO) above a forest canopy at 38 m height, close to the research centre Jülich, Germany, on 29 July 2003 (*Kleffmann et al.*, GRL, 2005).

➔ HONO photolysis accounts for ~33% of overall HOx production.

Summary of Findings from Recent Urban HONO Studies

- Significant levels of HONO exist during the day;

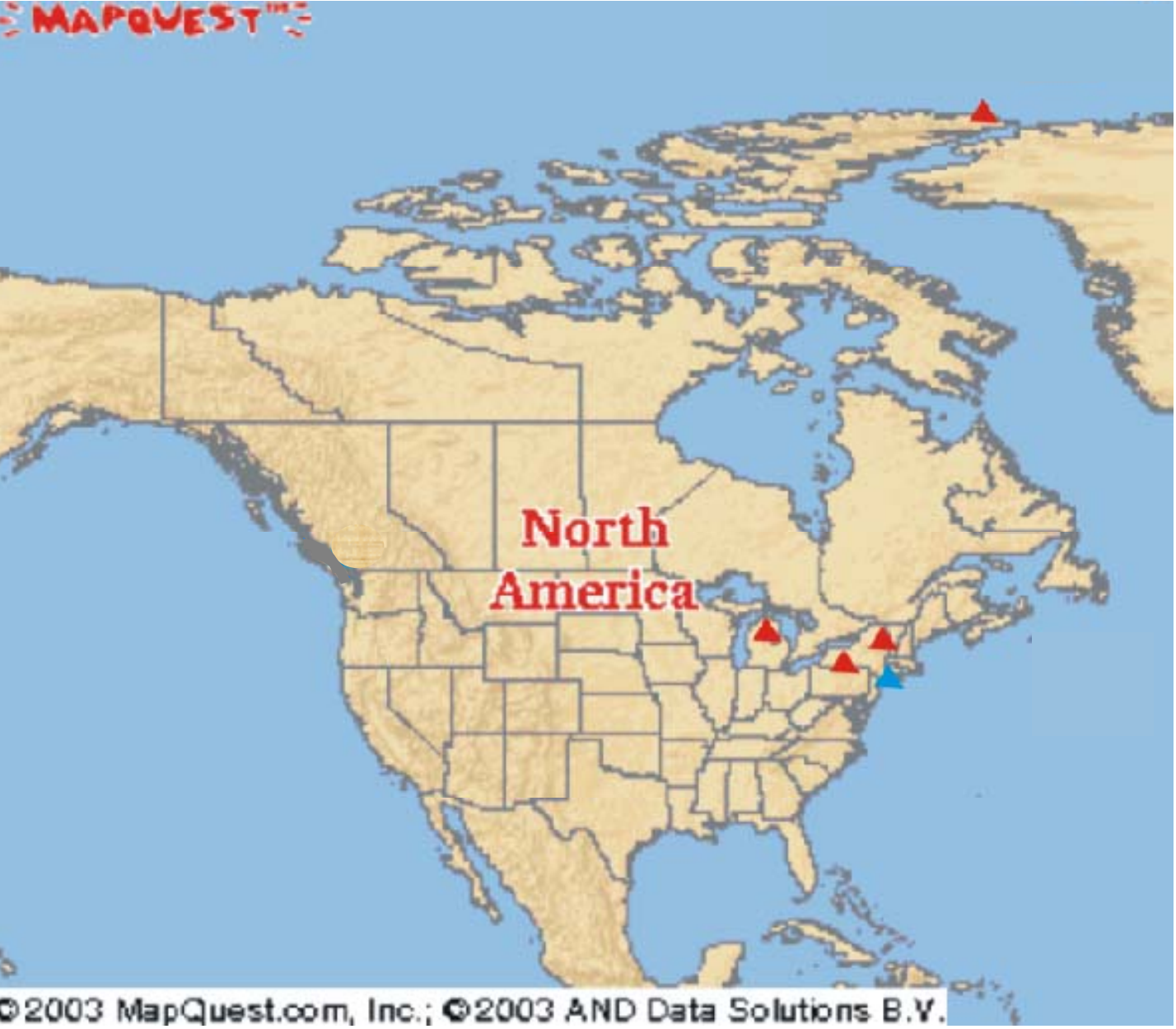
- A large daytime source is needed to sustain the observed HONO concentrations against its photolytic loss;

- Daytime HONO formation may involve photo-enhanced NO_x reaction with organic matter on surfaces.

- HONO photolysis is an important HO_x source, not only during the morning hours but also throughout the day;

In Rural Atmosphere

- Not under direct influence of anthropogenic emissions
- Low NO_x (lower to sub ppbv)
- Low HONO

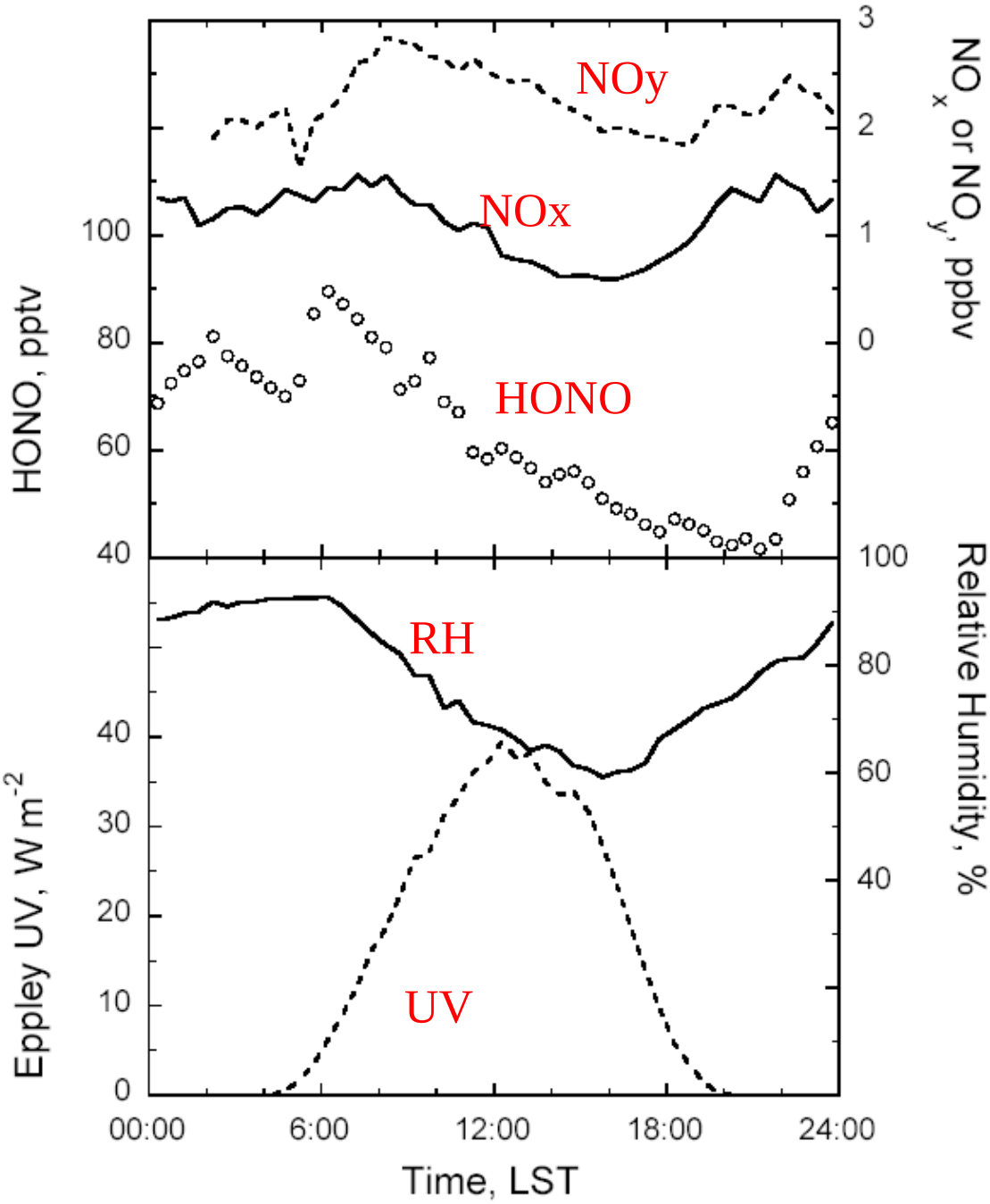


Urban:
•New York City (2001 summer and 2004 winter)

Rural:
•Pinnacle State Park, NY (1998 summer)
•Whiteface Mountain, NY (1999 &2002 summers)
•UMBS at Pellston, MI (2000, 2003 & 2007 summers)

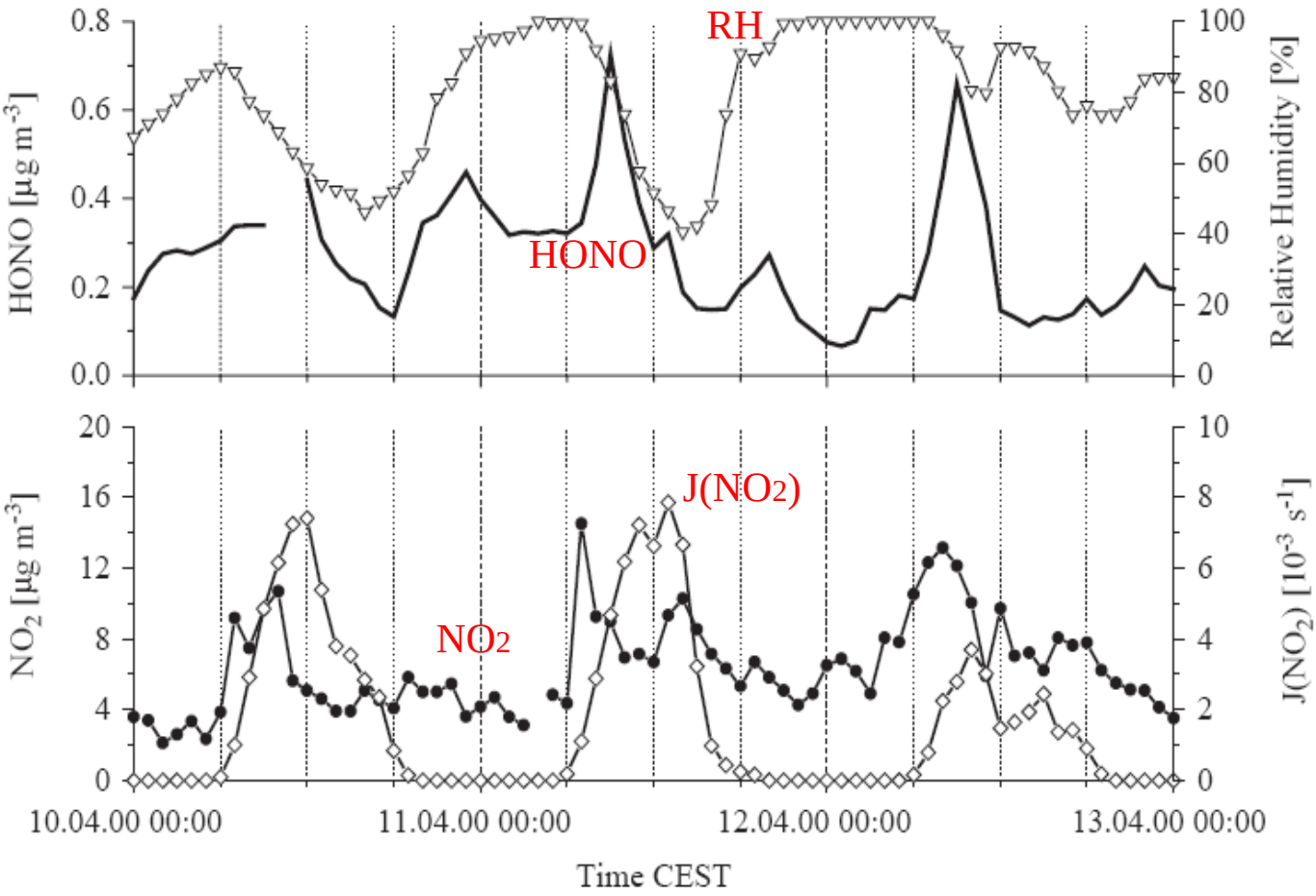
Remote
•Alert, Canada (2000 winter & spring)

HONO in rural atmosphere



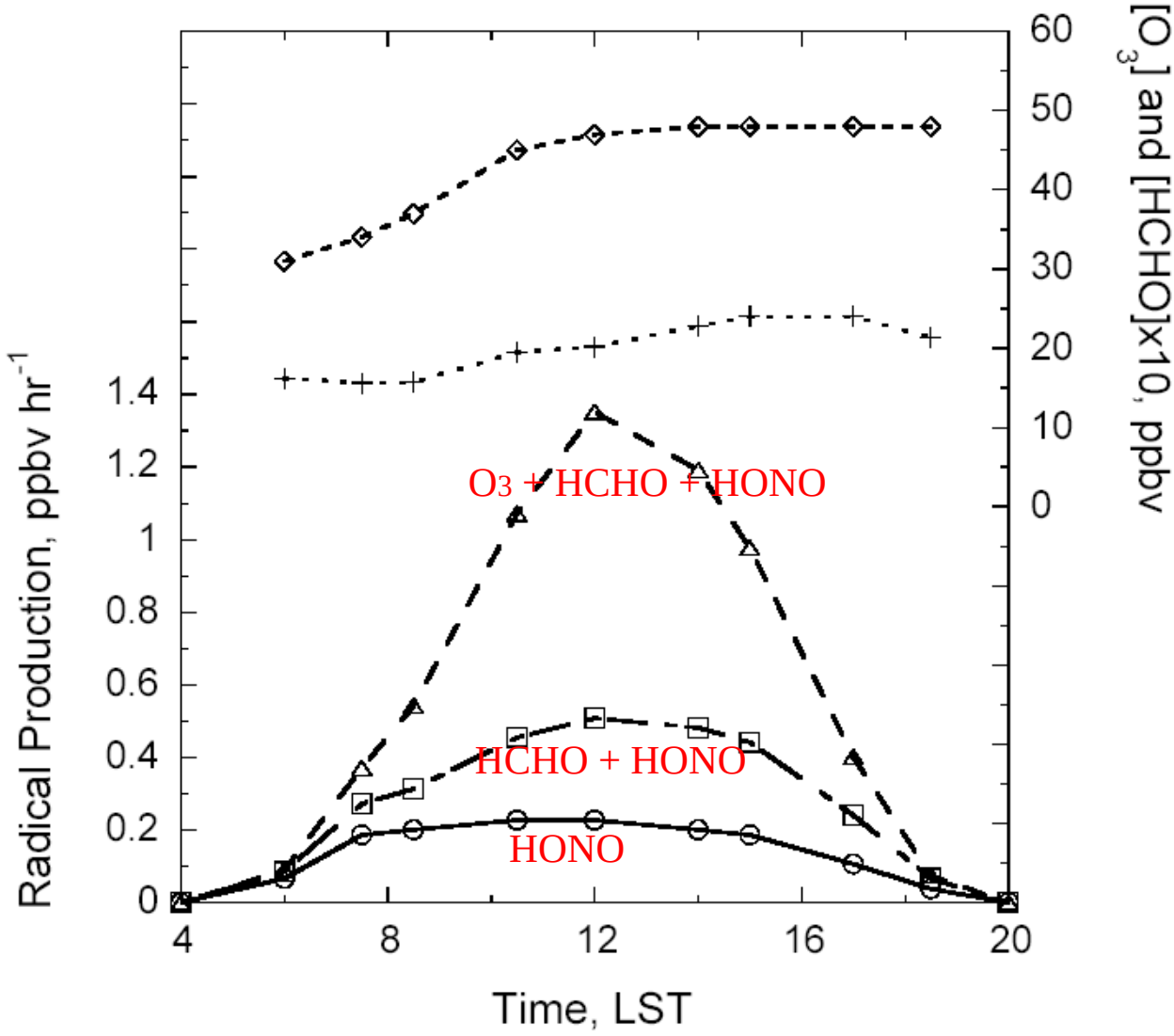
Composite diurnal plots for HONO and other parameters at the Pinnacle State Park site during 1998 summer campaign. (*Zhou et al.*, JGR, 2002)

HONO in rural atmosphere



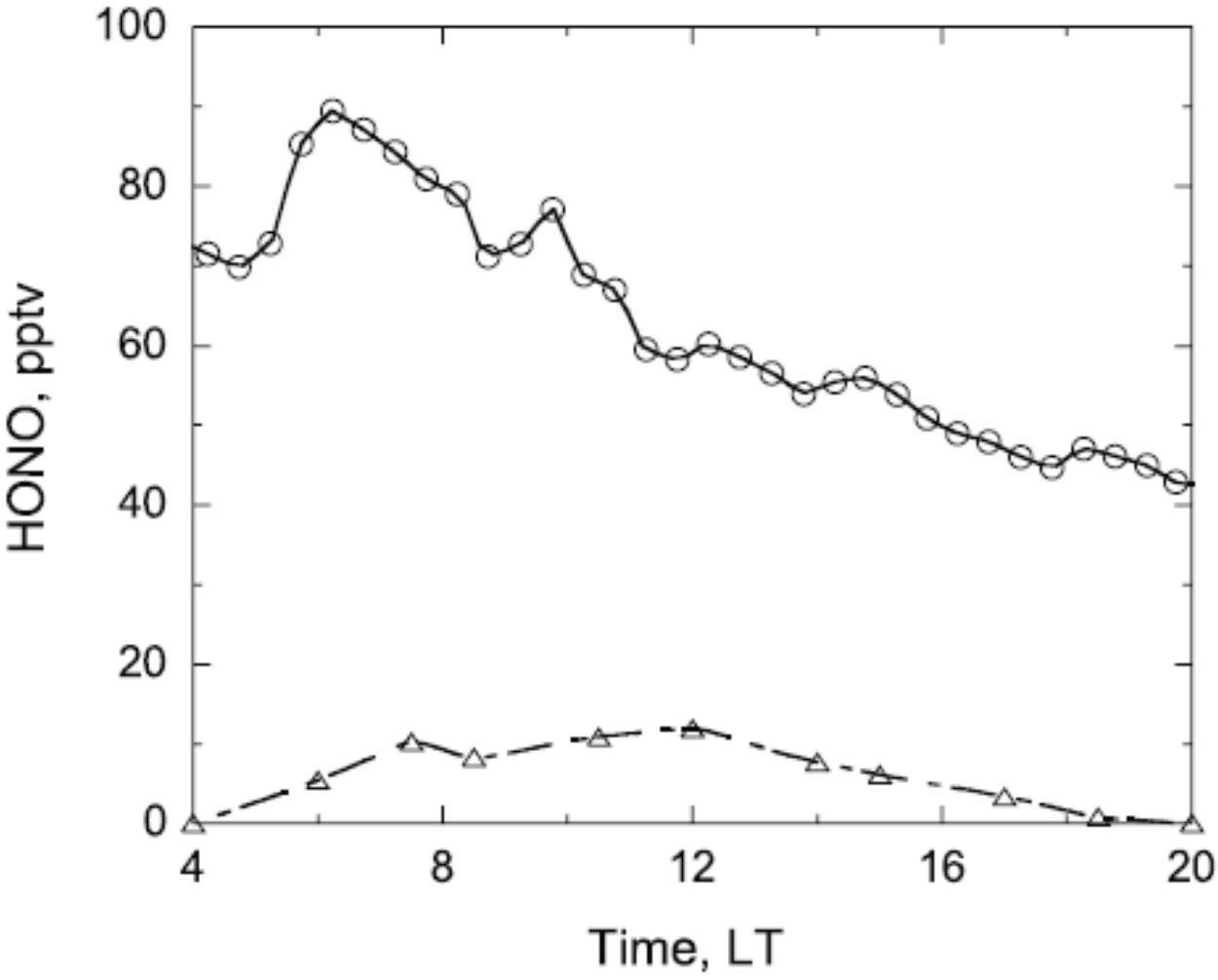
Diurnal variation of HONO, relative humidity, along with NO_2 and photolysis frequency of NO_2 at the field site Melpitz from 10 to 12 April , 2000. (*Acker et al.*, Atmos. Environ. 2004)

HONO in rural atmosphere

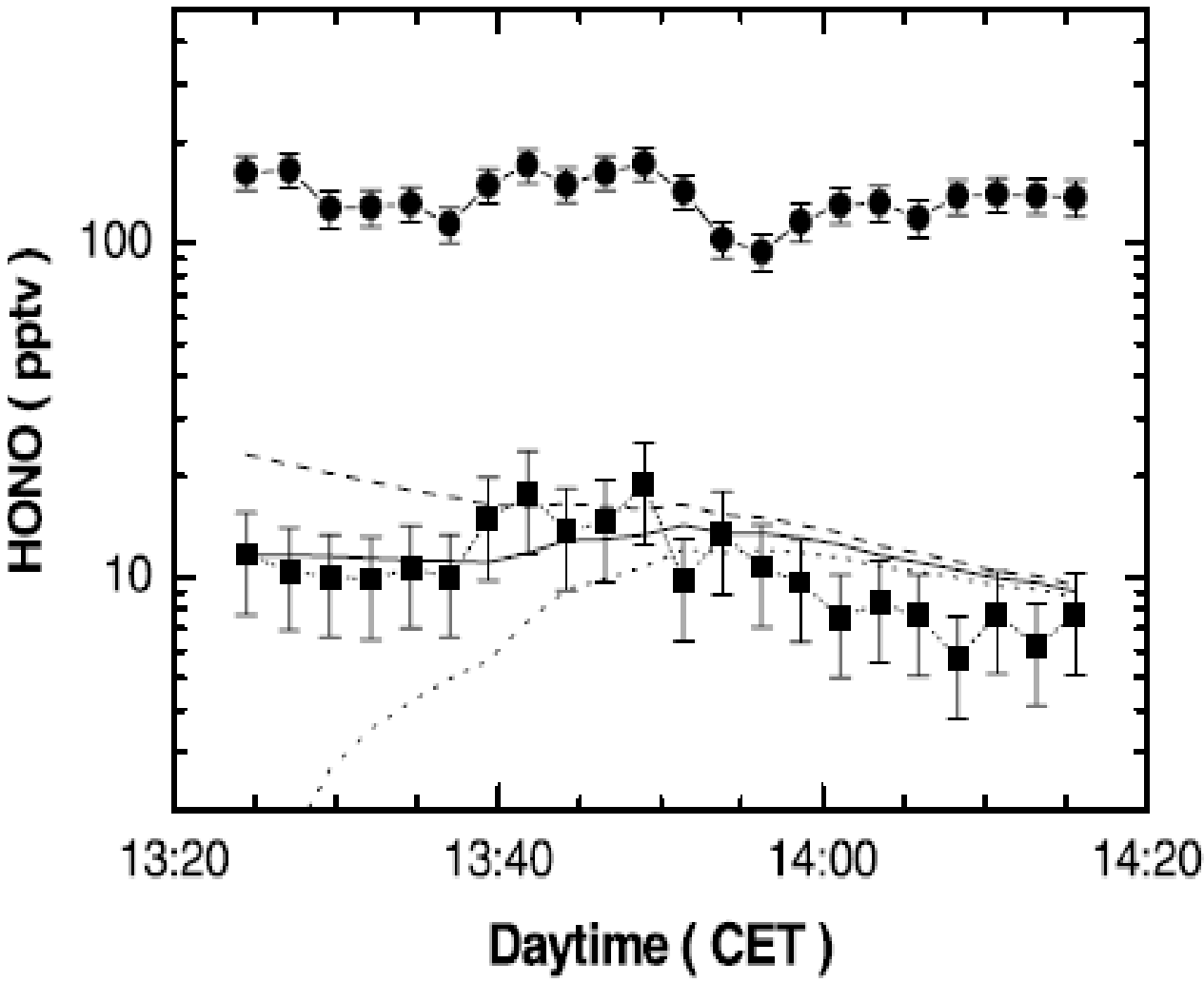


HOx production from photolysis of HONO, HCHO and O_3 (*Zhou et al.*, JGR, 2002)

HONO in rural atmosphere



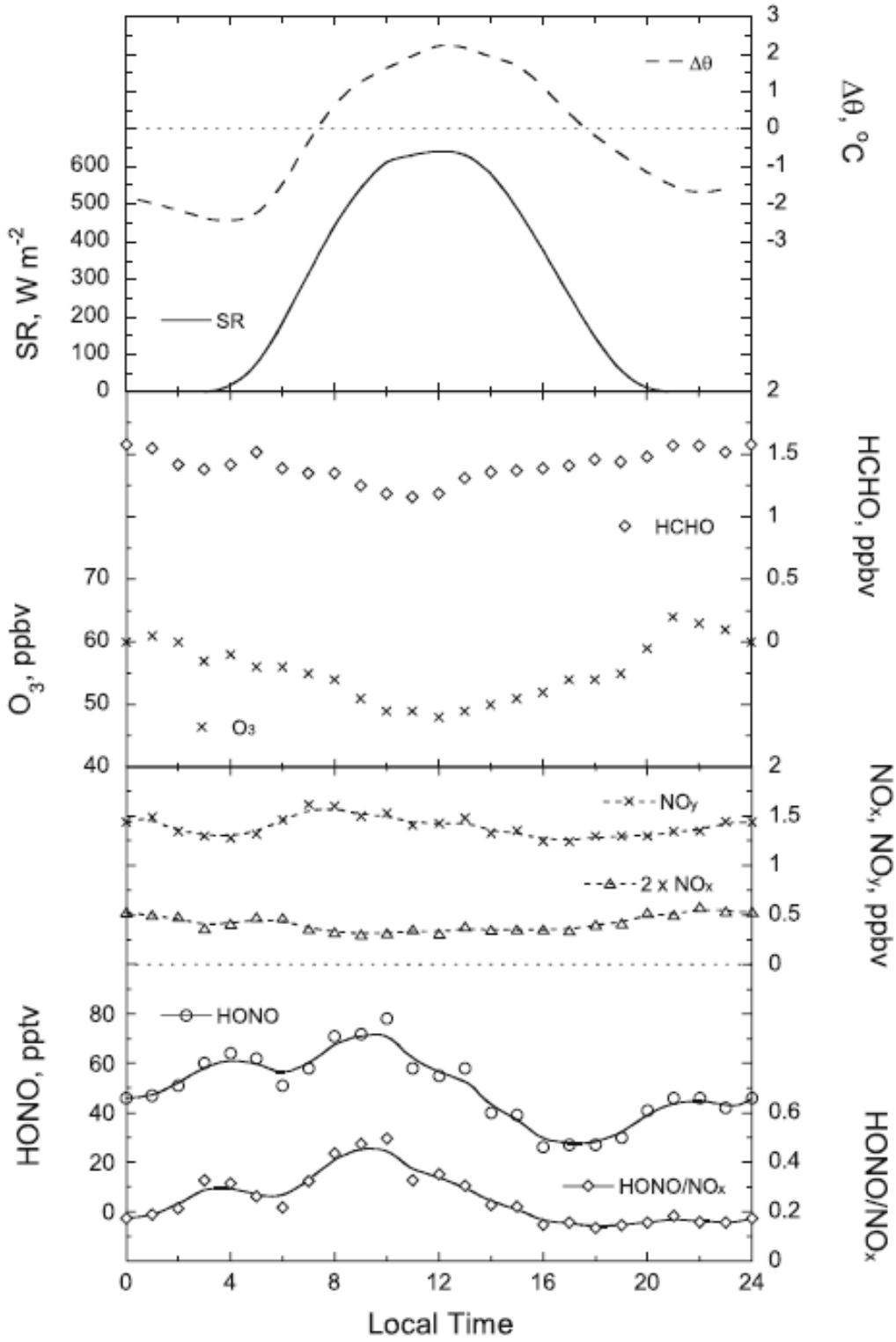
Observed (solid line with circles) and predicted photo-steady state (dashed line with triangles) HONO concentrations during the daytime. (*Zhou et al.*, JGR, 2002)



Comparison of measured HONO concentrations over a forest with model predictions for a pure gas phase mechanism: (*Kleffmann et al.*, GRL, 2005).

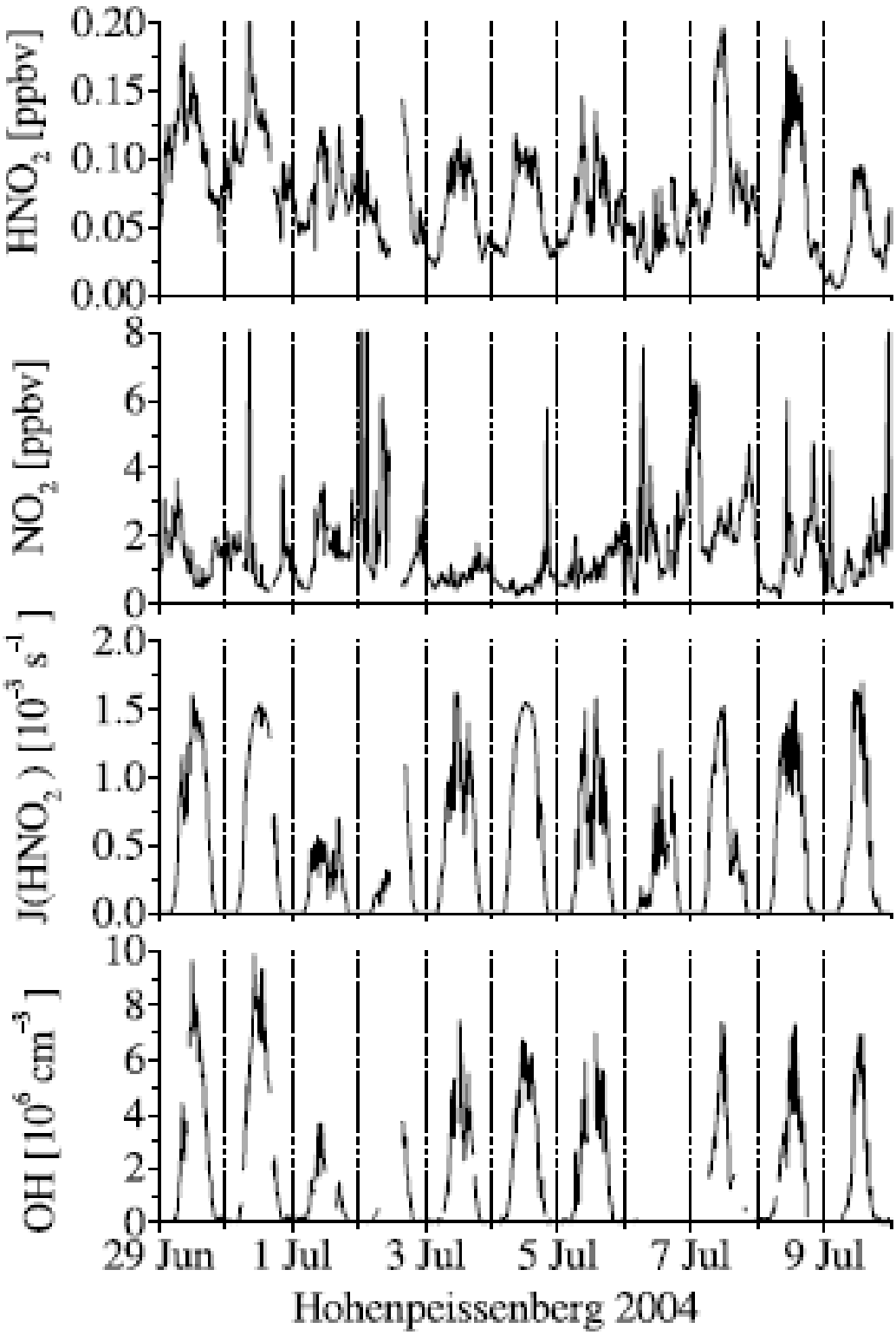
➔ Strong Daytime Source.

HONO in rural atmosphere



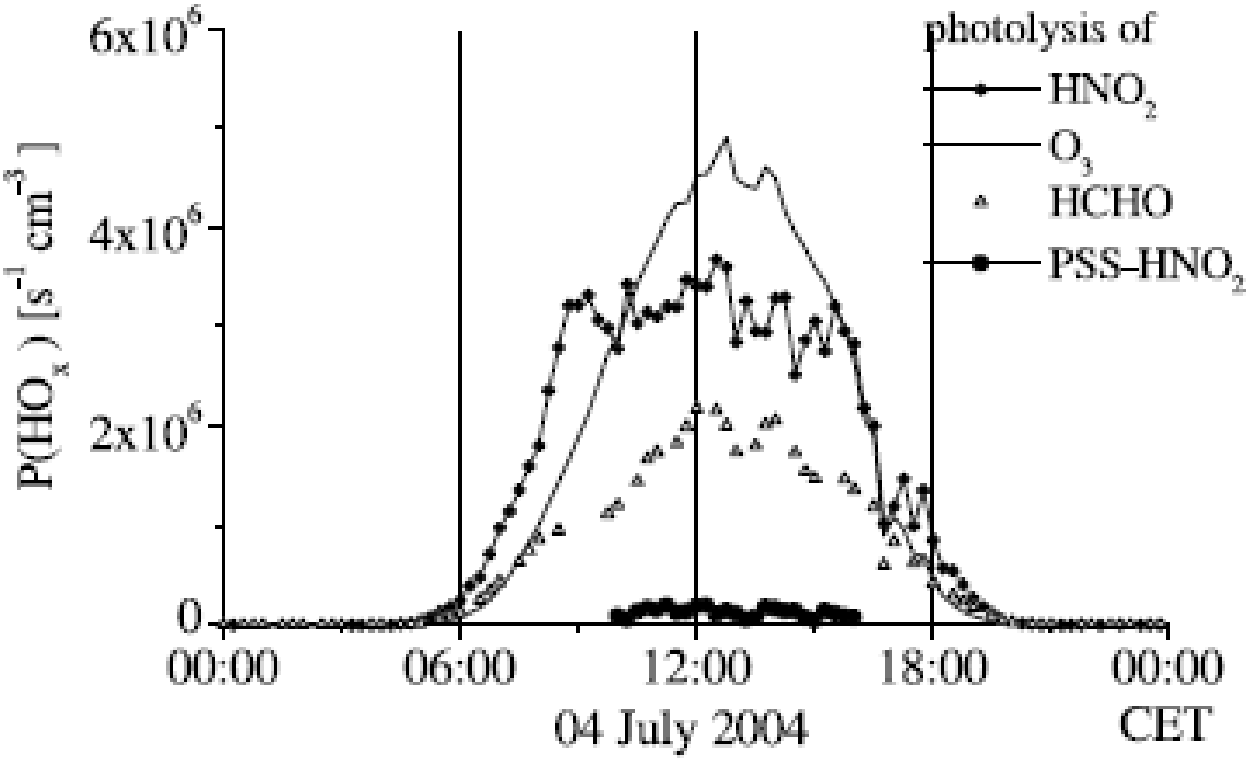
Measurements of HONO and other parameters at the summit of Whiteface Mountain during 1999 summer campaign (*Zhou et al.*, JGR, 2007)

HONO in rural atmosphere



Time series of HNO2, NO2, photolysis frequency J(HNO2), and OH measured between 29 July and 09 July 2004 at Hohenpeissenberg. (*Acker et al*., GRL, 2006)

HONO in rural atmosphere

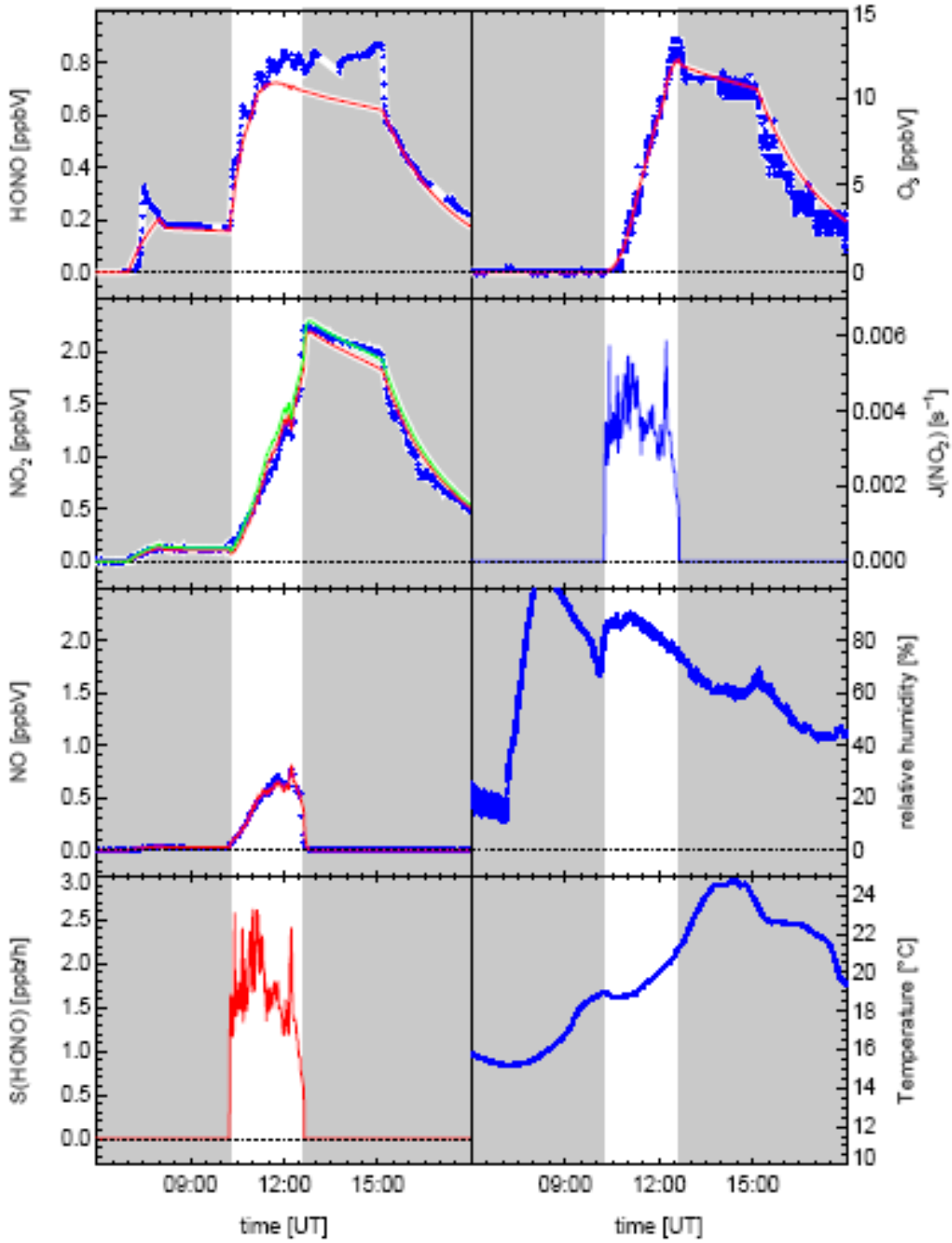


HOx radical production rates at Hohenpeissenberg for July 4, 2004 from the photolysis of HONO, HCHO, O_3, and HONO calculated from PSS neglecting the unknown daytime source. (*Acker et al.*, GRL, 2006)

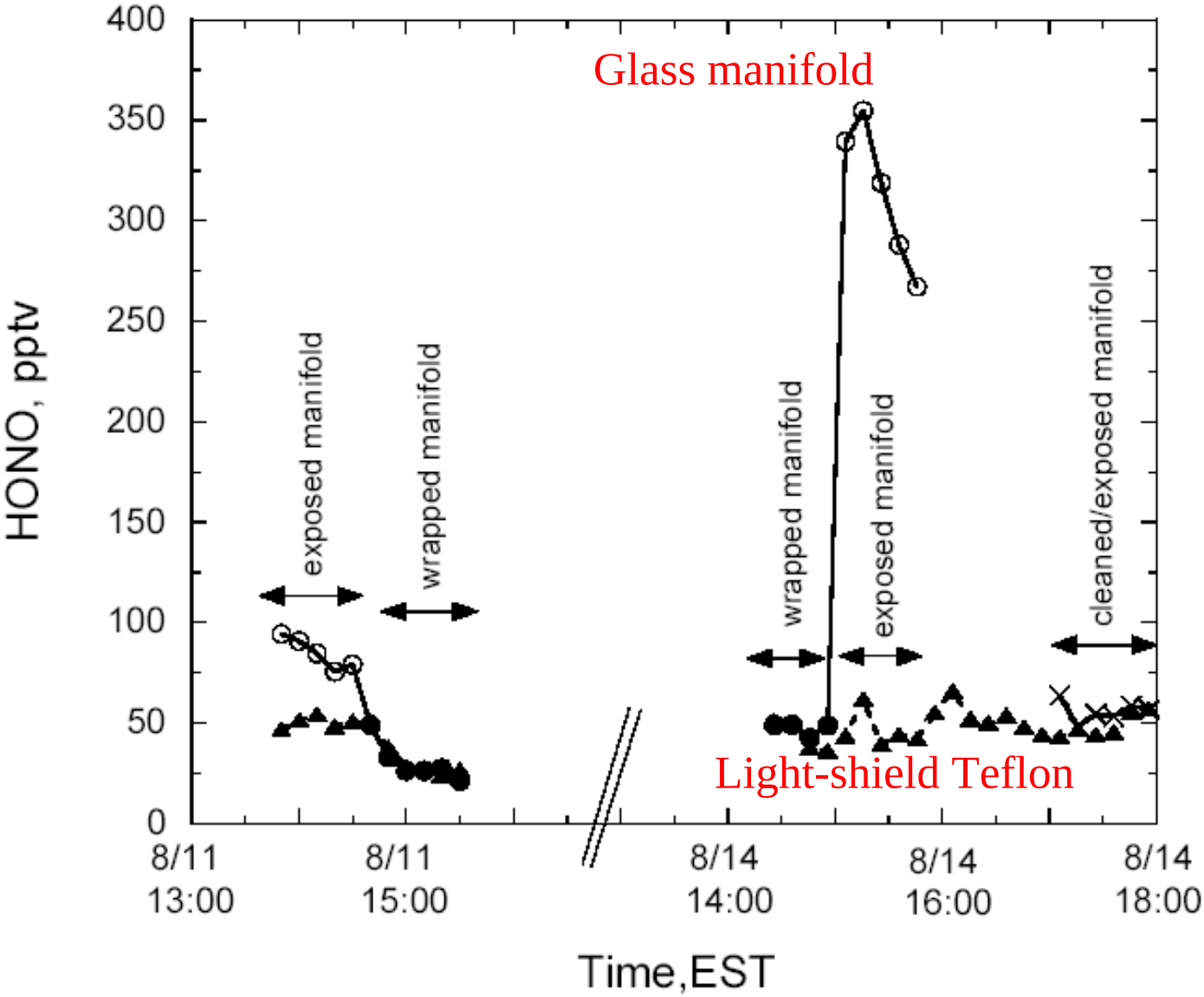
➔ HONO photolysis contributed ~42% of HOx production

➔ Strong daytime HONO source

Chamber experiment



HONO, NOx, and ozone formation in SAPHIR illuminated with sunlight on August 08, 2001. Blue symbols mark observations, red and green lines show the result of model calculations. The shaded areas mark the dark periods. (*Rohrer et al.*, Atmos. Chem. Phys., 2005).



HONO production from Pyrex sample inlet manifold when exposed to sunlight. (*Zhou et al.*, GRL, 2002).

$HNO_{3(ads)} + h\nu \rightarrow \rightarrow HONO + NO_x$

Summary of Findings from Recent Rural HONO Studies

- different diurnal variation pattern;
- Significant levels of HONO exist during the day;
- A large daytime source is needed to sustain the observed HONO concentrations against its photolytic loss;
- NO_X is only a minor HONO precursor;
- Some other photochemical processes are responsible for daytime HONO formation .
- HONO photolysis is an important OH radical source.

Quantification of air/surface exchange of HONO

- Gradient/vertical profile measurements
- direct flux measurement

Several measurements published, including:

Harrison & Kitto, Atmos. Environ., 1994

Neftel et al., Atmos. Environ., 1996

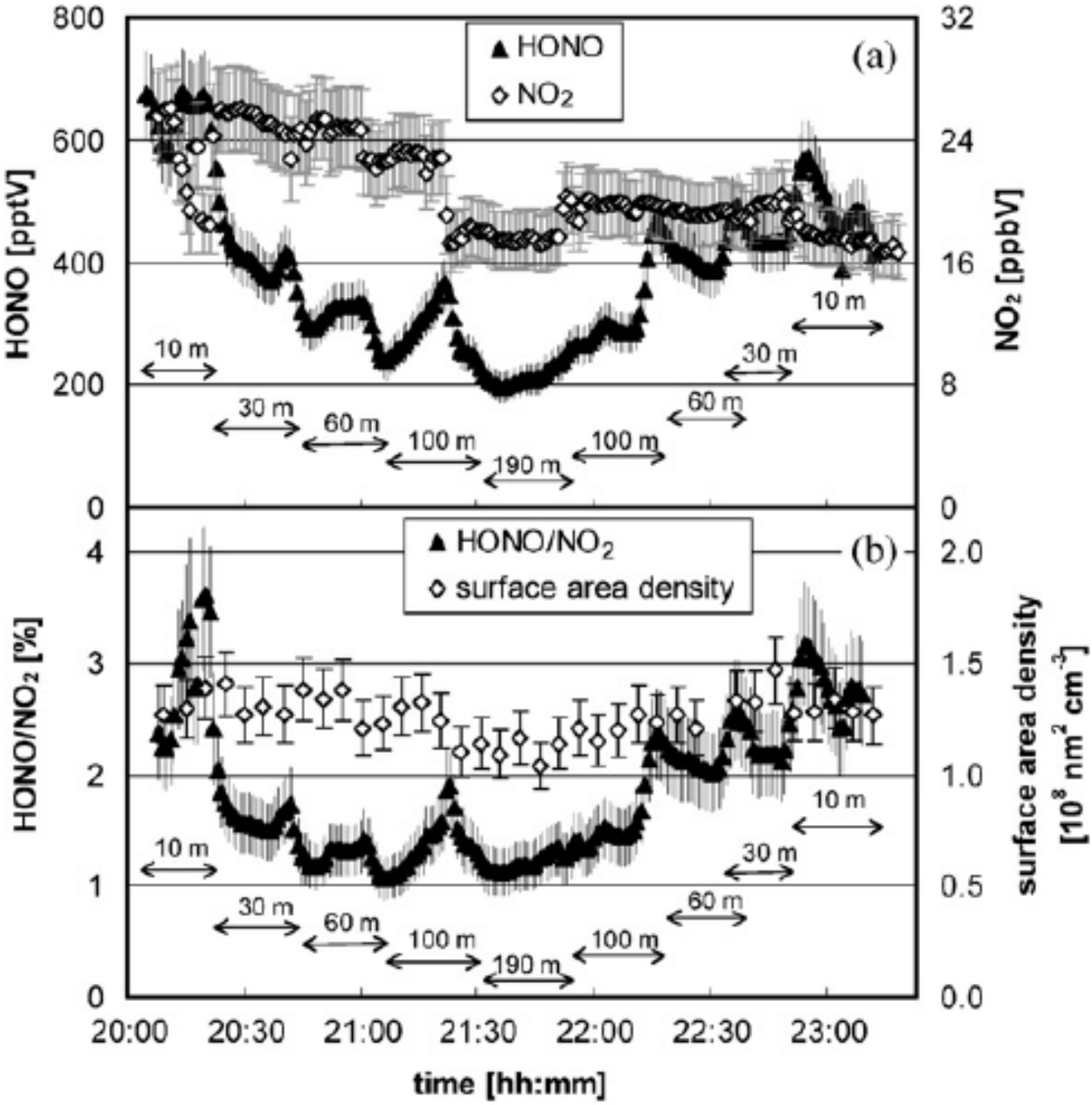
Veitel et al., Environ. Sci. Pollut. Res., 2002

Stutz et al., JGR, 2002

Kleffmann, Atmos. Environ., 2003

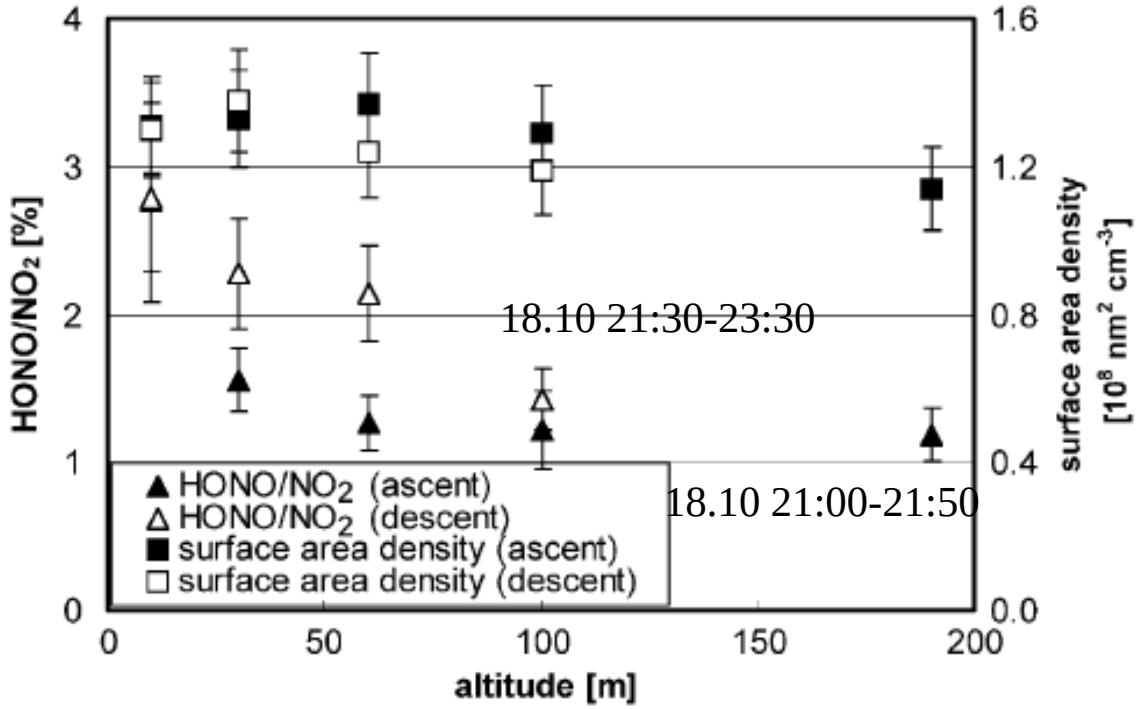
Stutz et al., JGR, 2004

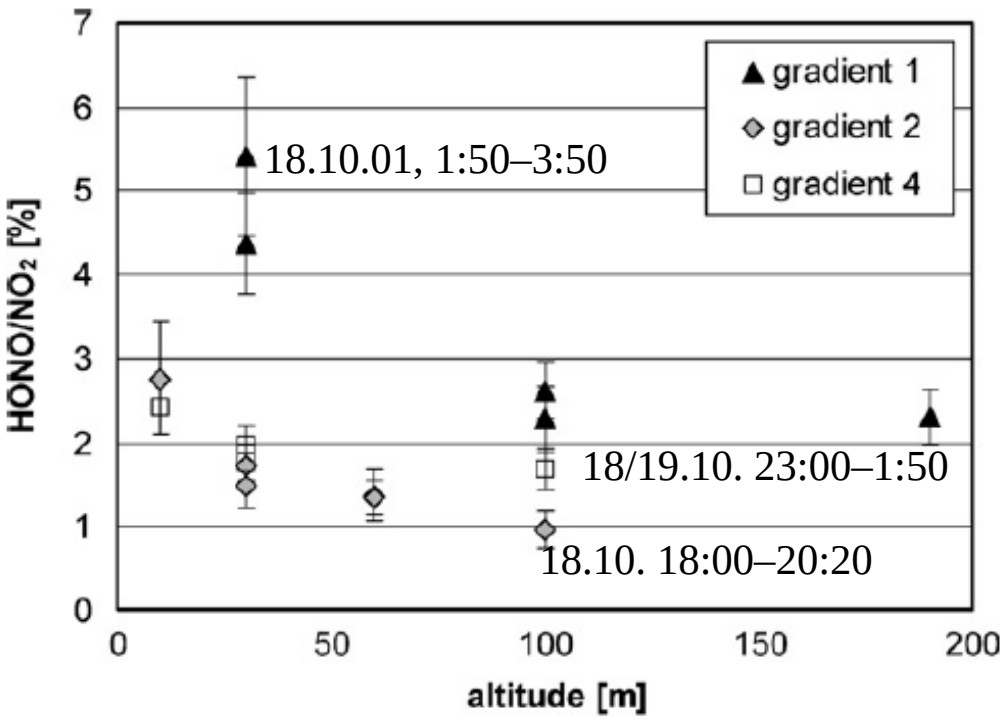
He et al., GRL, 2006.



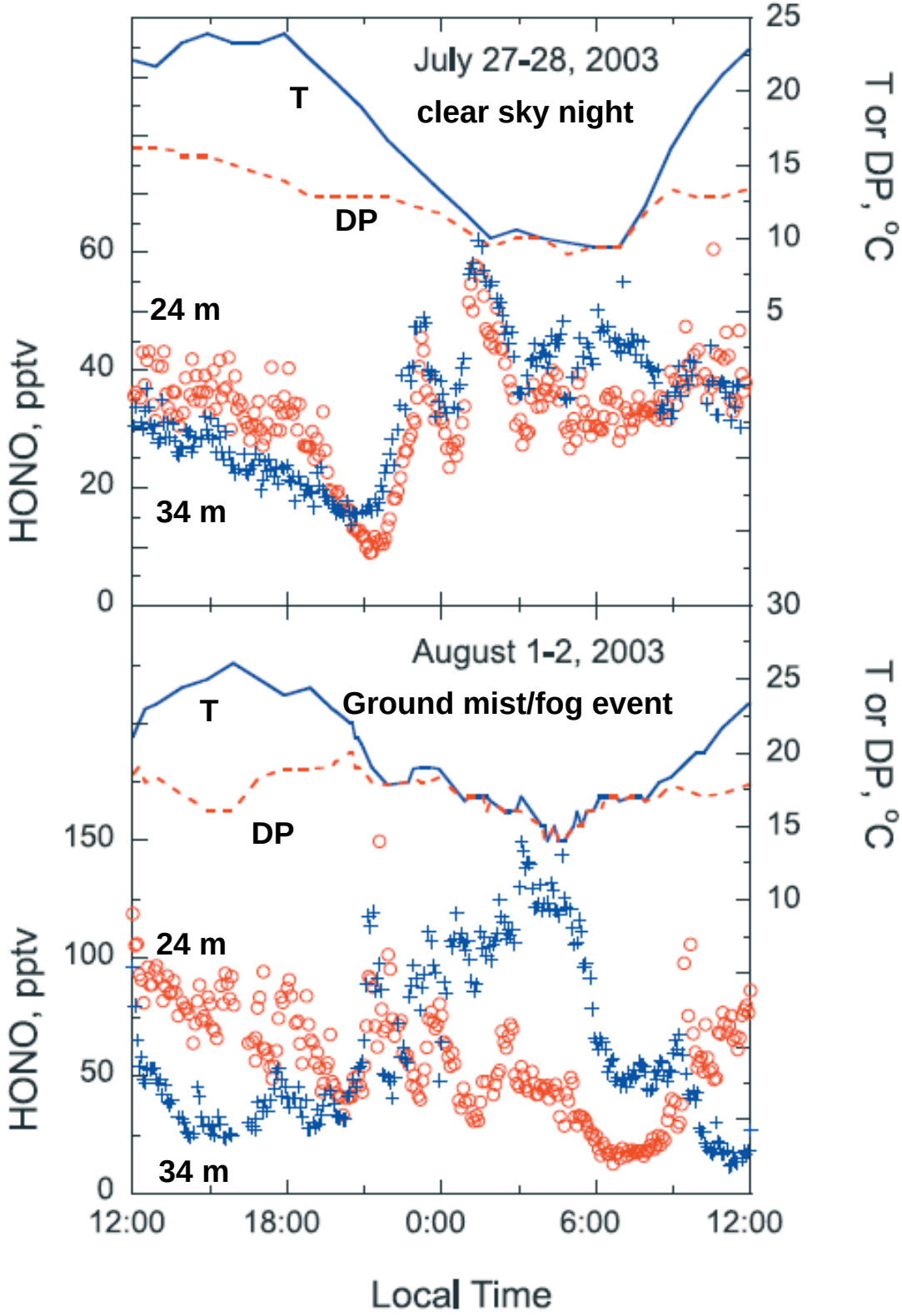
Gradient measurement on the meteorological tower at the Forschungszentrum Karlsruhe in the altitude range 10–190m in the early night of 18 October 2001: (a) HONO and NO2 concentration; and (b) [HONO]/[NO2] ratio and particle surface area density. (*Kleffmann et al.*, Atmos. Environ., 2003)

➔ Sourface source for HONO



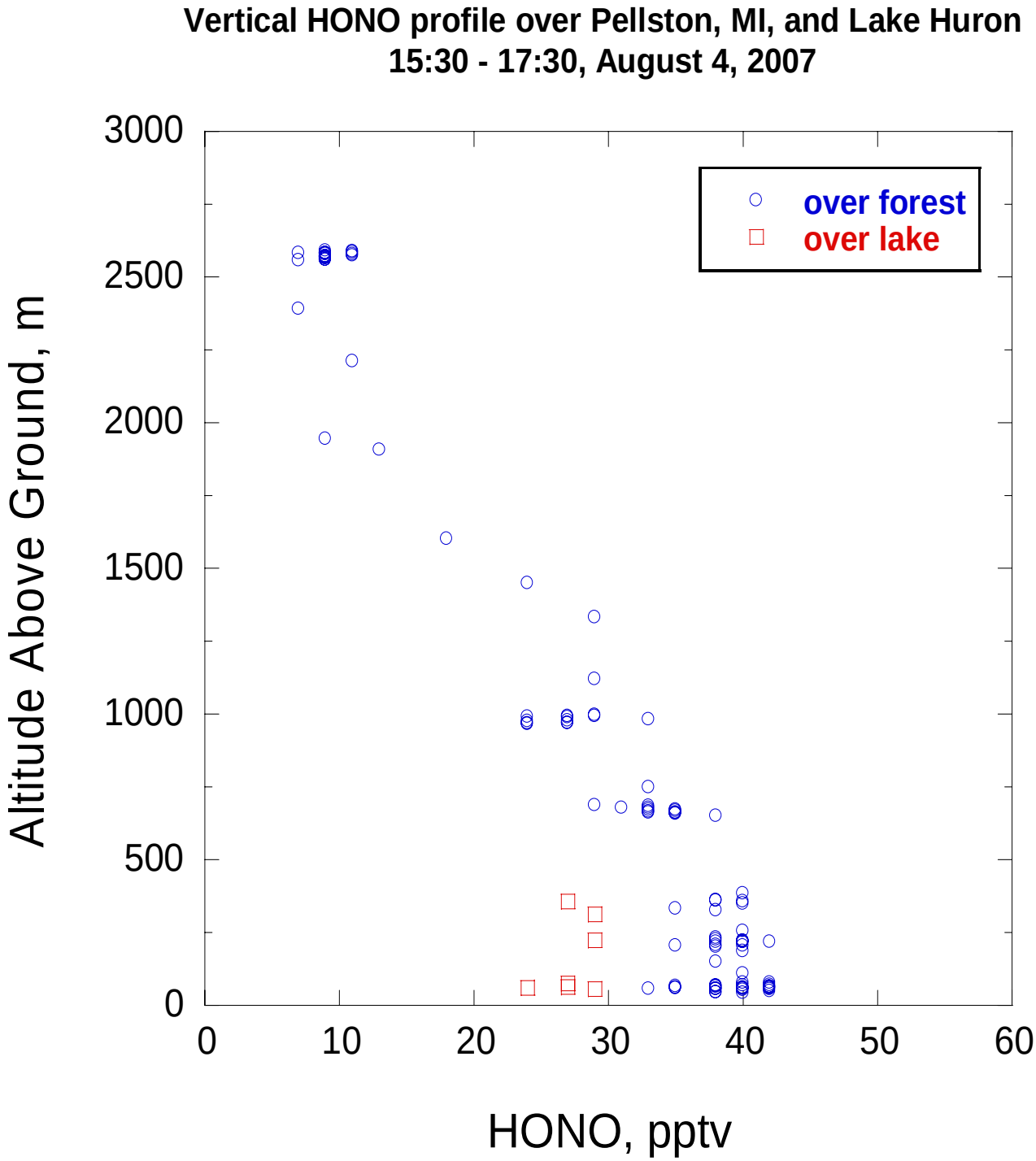


Vertical profiles (*Kleffmann et al.*, Atmos. Environ., 2003)



Diurnal changes in HONO concentration at 24 m and 34 m along with T and DP in summer 2003 study at PROPHET site in Pellston, Michigan. Canopy height was 21 m. (*He et al.*, GRL, 2006)

HONO distribution in the air aloft



➔ In situ production vs transport from ground surface?

➔ Mechanism(s)?

Thank You!