Four years of ground-based MAX-DOAS observations of HONO and NO_2 in the Beijing area

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Atmospheric Chemistry and Physics Discussions

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Nitrous acid (HONO) in the troposphere

- **HONO is a source of OH radicals through its photolysis, especially in the early morning:**

$$HONO + h\nu \rightarrow OH + NO$$

- **Formation mechanisms still not well understood and poorly quantified, especially during daytime**

Main source of HONO: $2\,NO_2 + H_2O + surface \rightarrow HONO + HNO_3$

- **HONO measurements are generally sparse in time because mainly resulting from field campaigns (LOPAP and LP-DOAS)**

Continuous measurements of HONO throughout the year can be highly valuable

Observation sites

Institute of Atmospheric Physics (06/2008 - 04/2009)

(03/2010 till now)

-Elevation angles: 2°, 4°, 6°, 8°, 8°, 10°, 12°, 15°, 30°, 90° (zenith)

-Measurements from ~85°SZA sunrise to 85°SZA sunset

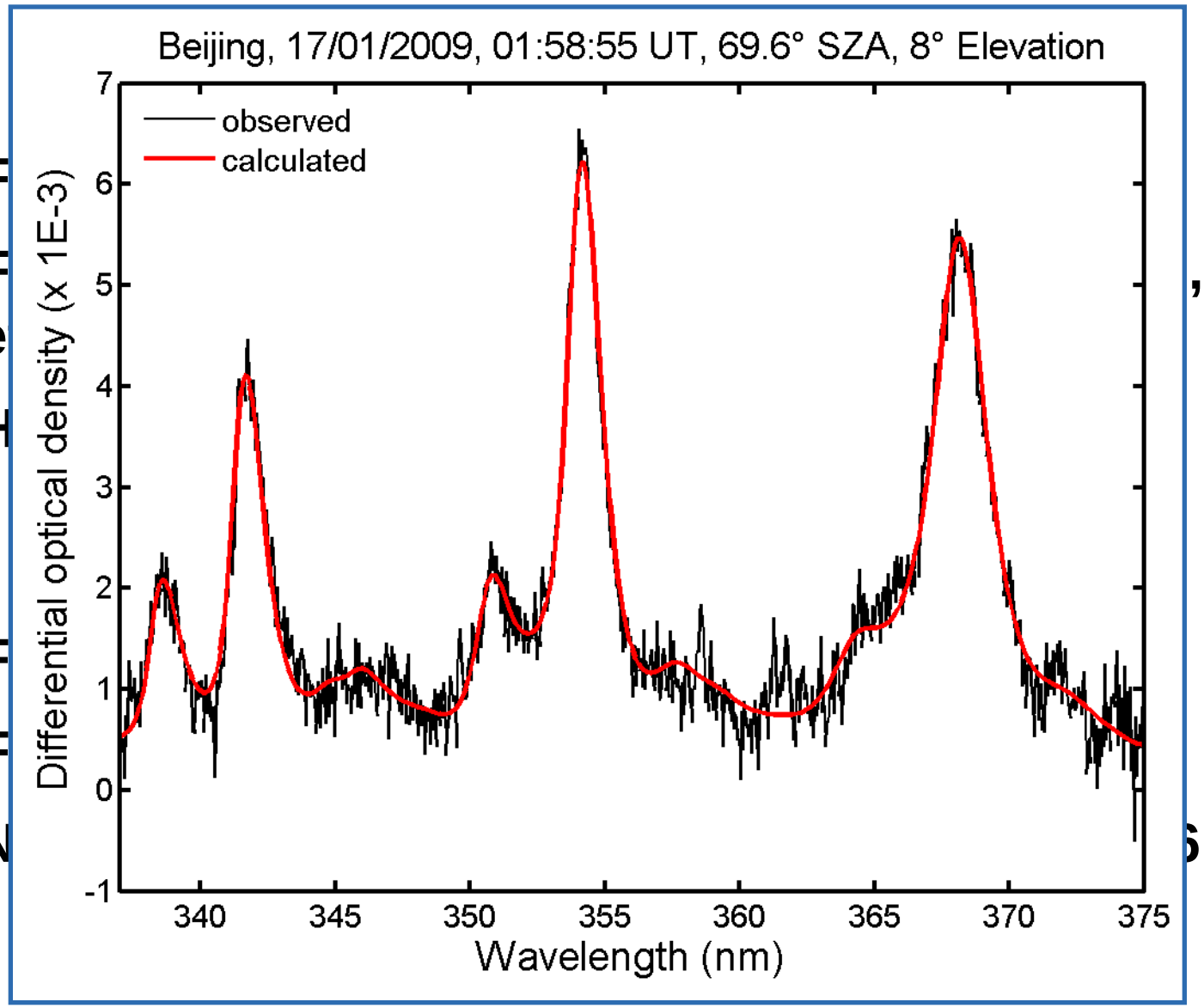
-15' per scan

DOAS settings

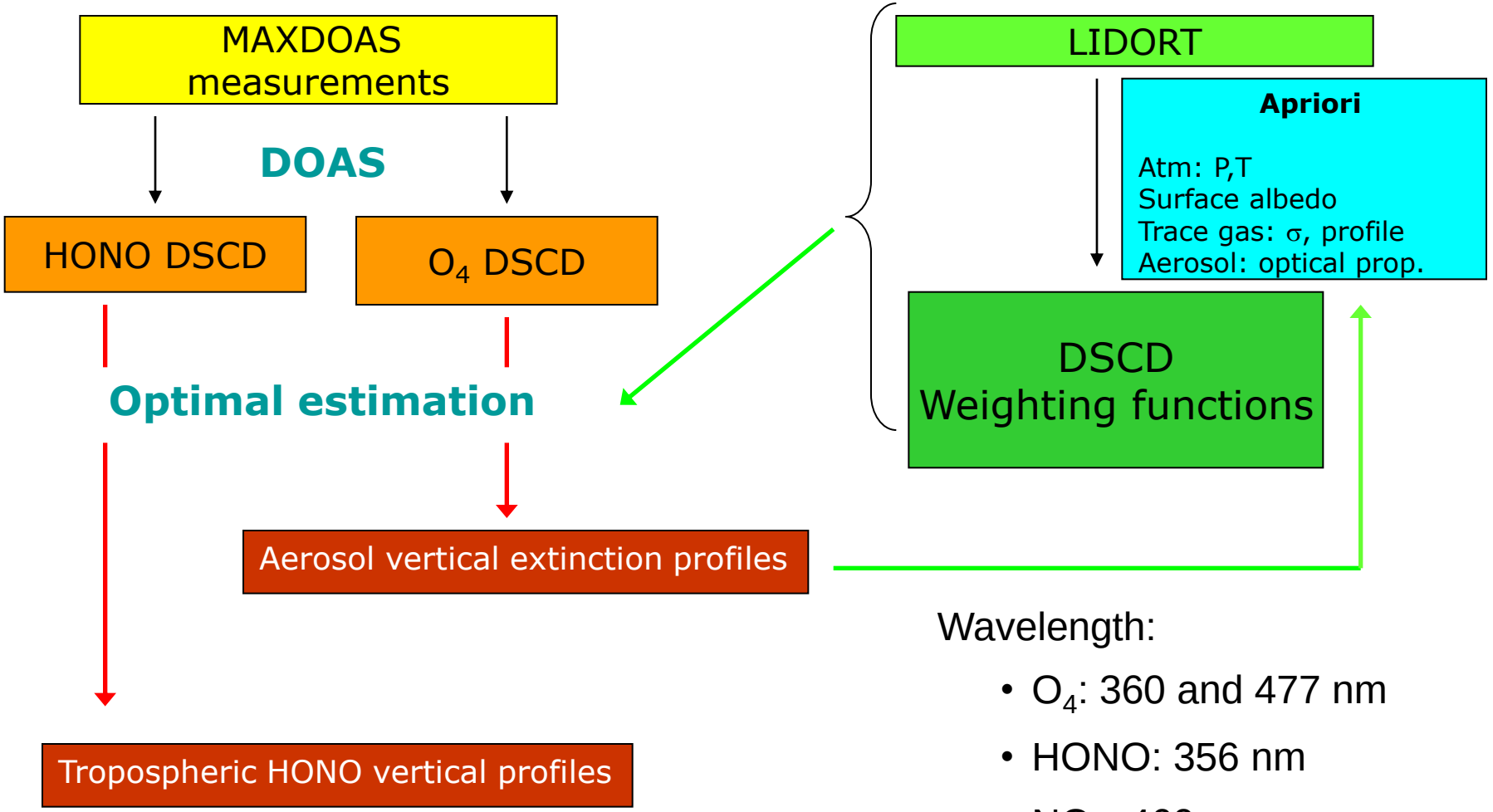
- **HONO:**
  - F
  - F
  - e
  - H
- **NO_2:**
  - F
  - F
  - N

, Ring

6 K



bePRO profiling tool



Wavelength:

- O_4: 360 and 477 nm
- HONO: 356 nm
- NO_2: 460 nm

Clémer et al., AMT, 2010

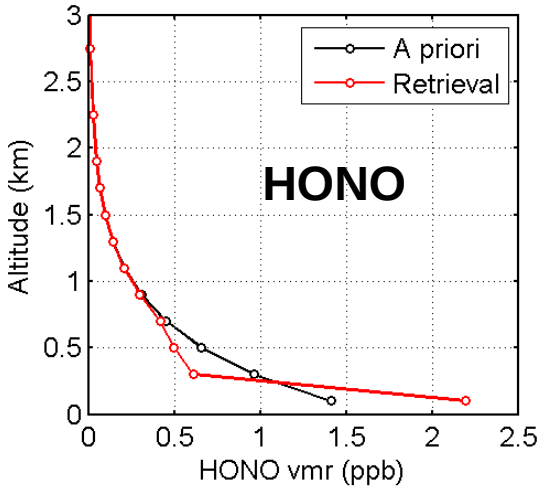
Examples of HONO and NO_2 vertical profile retrievals

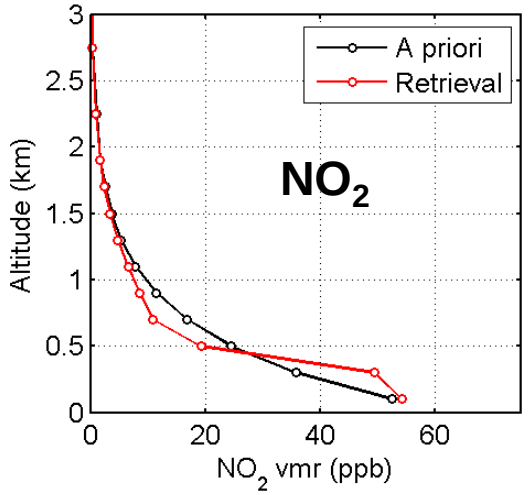
A priori profile:

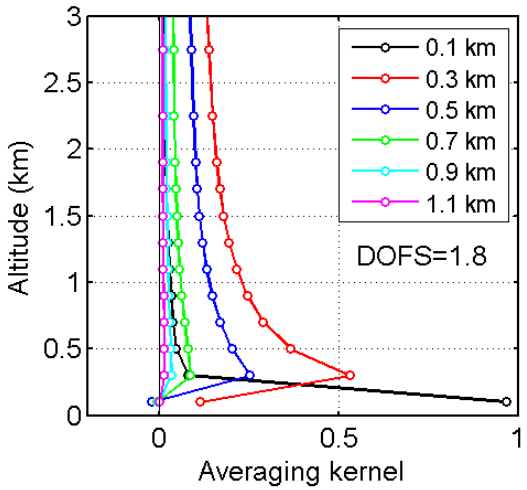
$$\frac{VCD_{HONO}}{SH} e^{-\frac{z}{SH}}$$

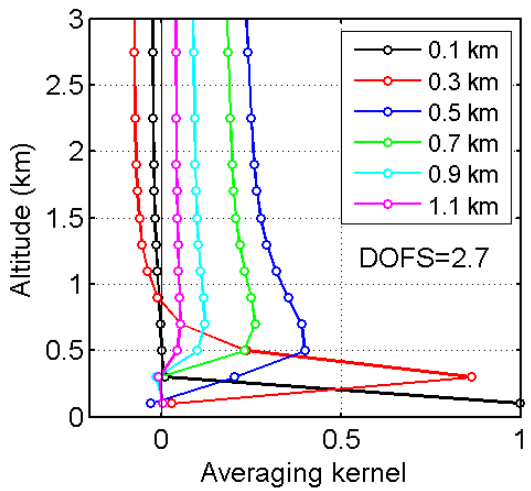
with SH = 0.5 km

Beijing 21/01/2009 ~10:15 AM



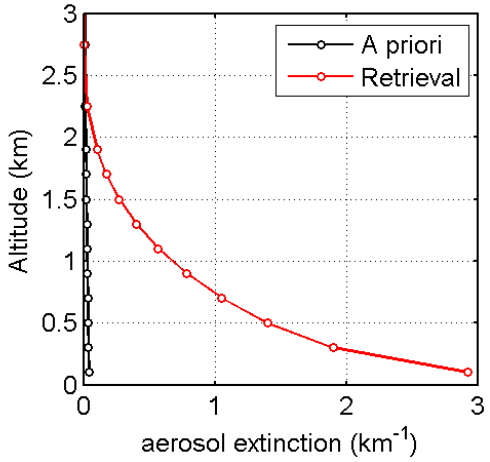


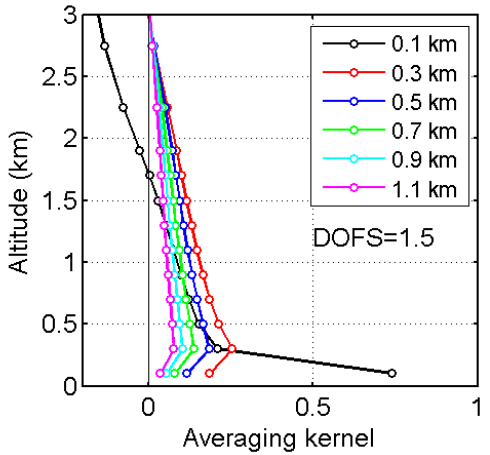




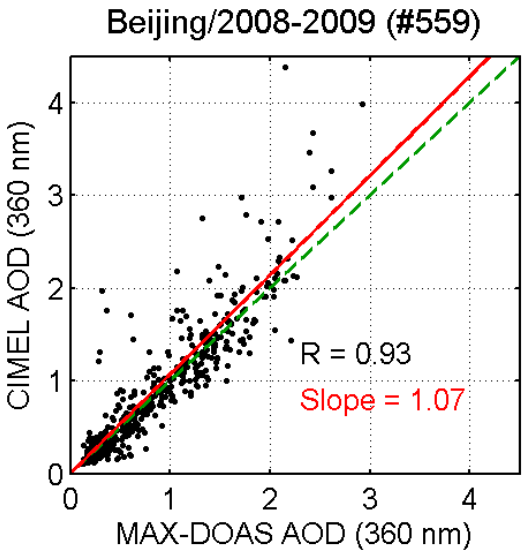
Example of aerosol extinction profile retrievals

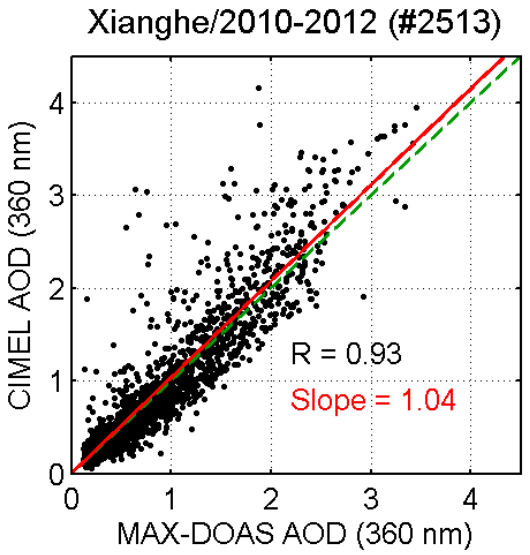
Beijing 21/01/2009 ~10:15 AM





Comparison with AERONET

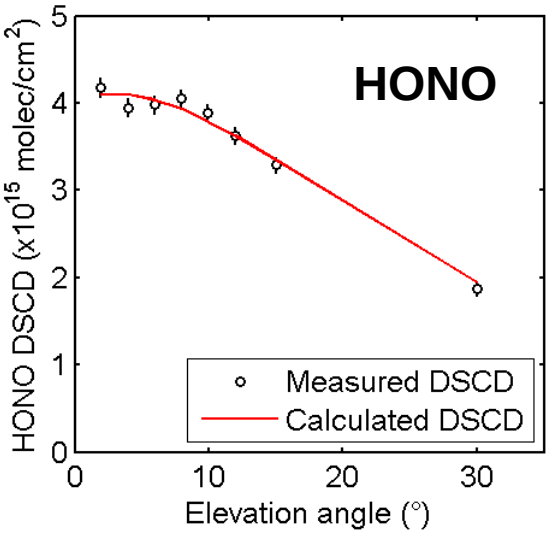


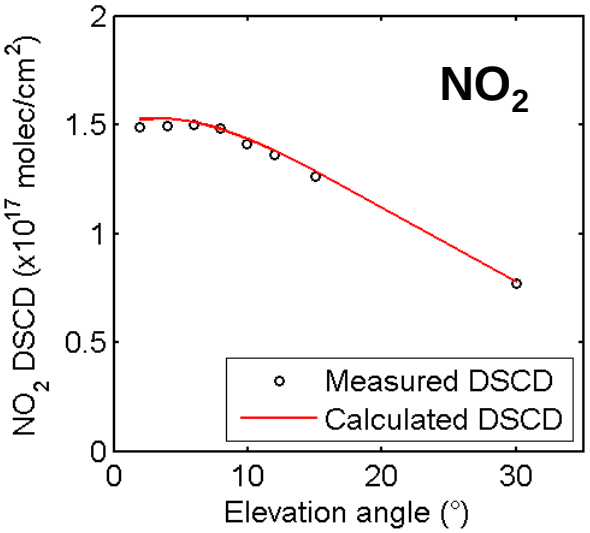


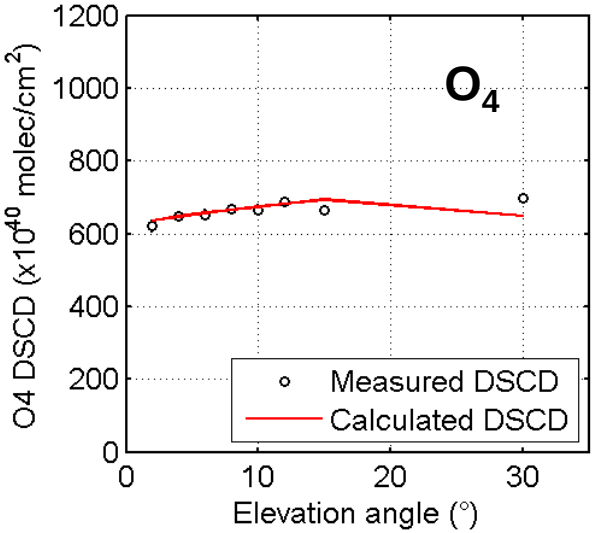
Consistent with Clémer et al., AMT, 2010 (R=0.91 and slope=1.1)

Selection of 'good' MAX-DOAS scans

Beijing 21/01/2009 ~10:15 AM







-RMS of fit results below a threshold value

-DOFS > 0.7

-To be compared to the cloud screening approach based on the CI (cf. C. Gielen's presentation)

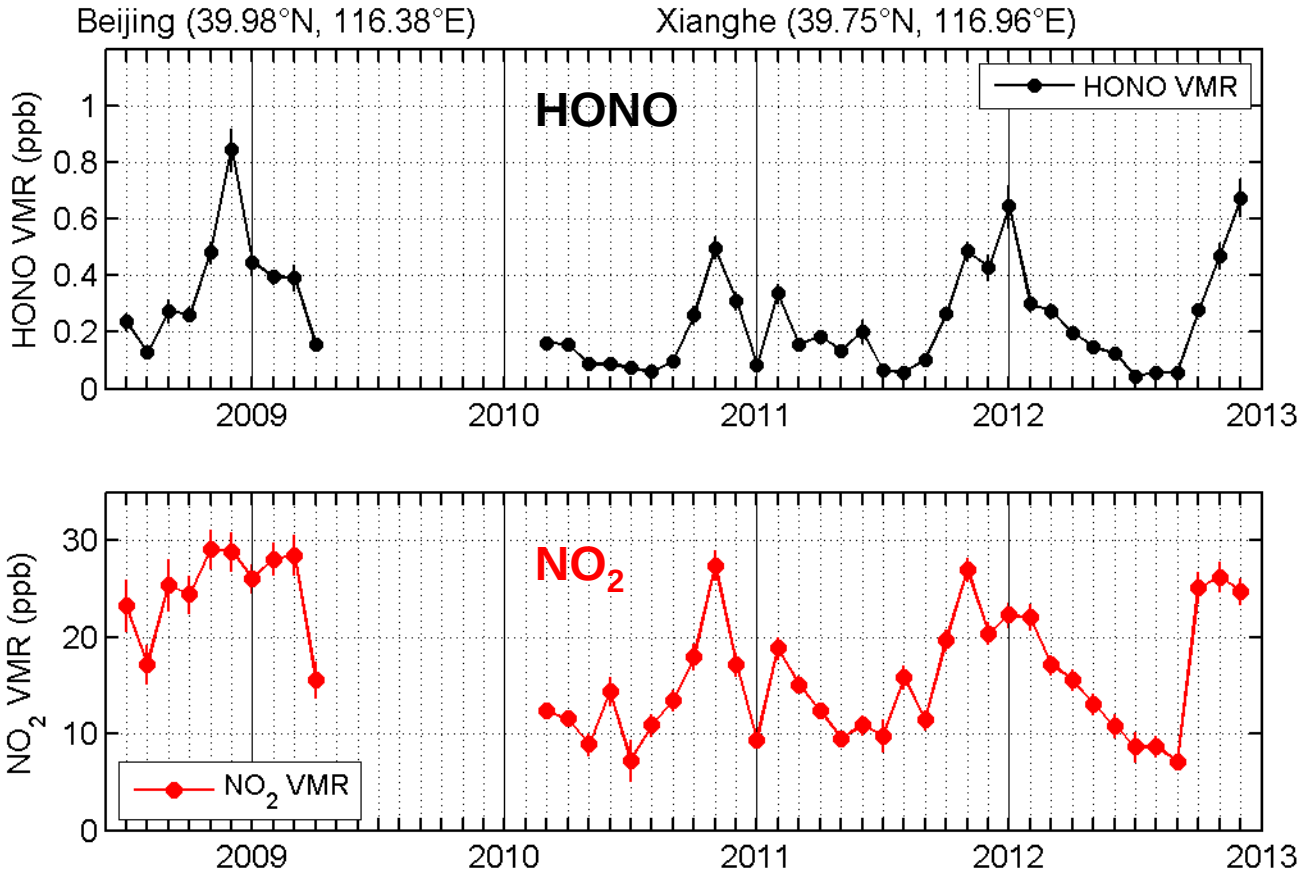
Error budget

Table 1. Error budget of the retrieved HONO and NO_2 near-surface (0–200 m) concentrations and vertical column densities (VCD). The total uncertainty is calculated by adding the different error terms in Gaussian quadrature.

	Beijing				Xianghe			
	0–200 m		VCD		0–200 m		VCD	
	HONO	NO_2	HONO	NO_2	HONO	NO_2	HONO	NO_2
Total retrieval error (%)	19	4	8	2.5	23	8	10	2.5
Uncertainty related to the a priori (%)	7	10	20	10	11	14	23	10
Uncertainty on HONO or NO_2 cross sections (%)	5	3	5	3	5	3	5	3
Total uncertainty (%)	21	11	22	11	26	16	26	11

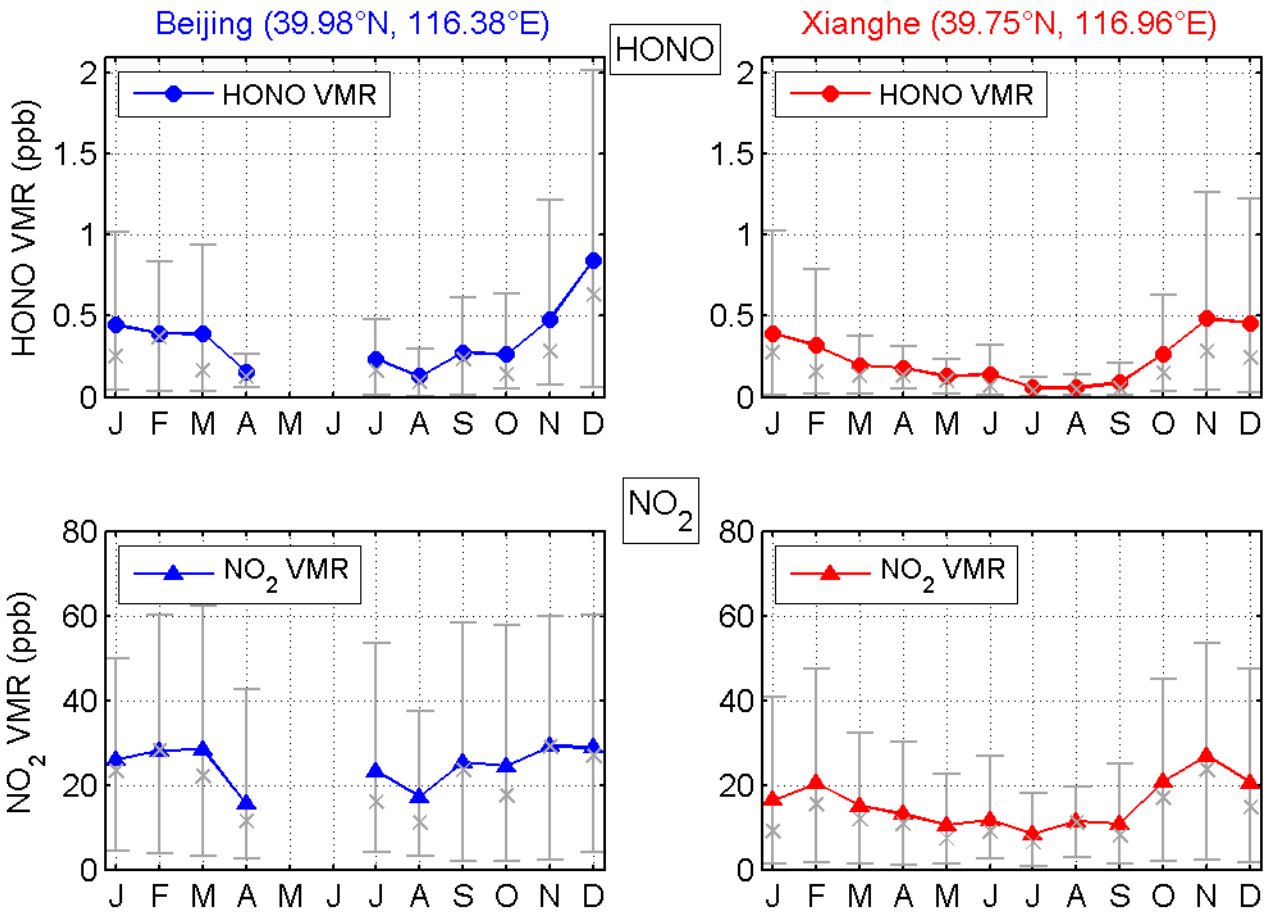
Time-series of HONO and NO_2 surface concentration

Near-surface (0-200m) concentration (ppb) at local noon

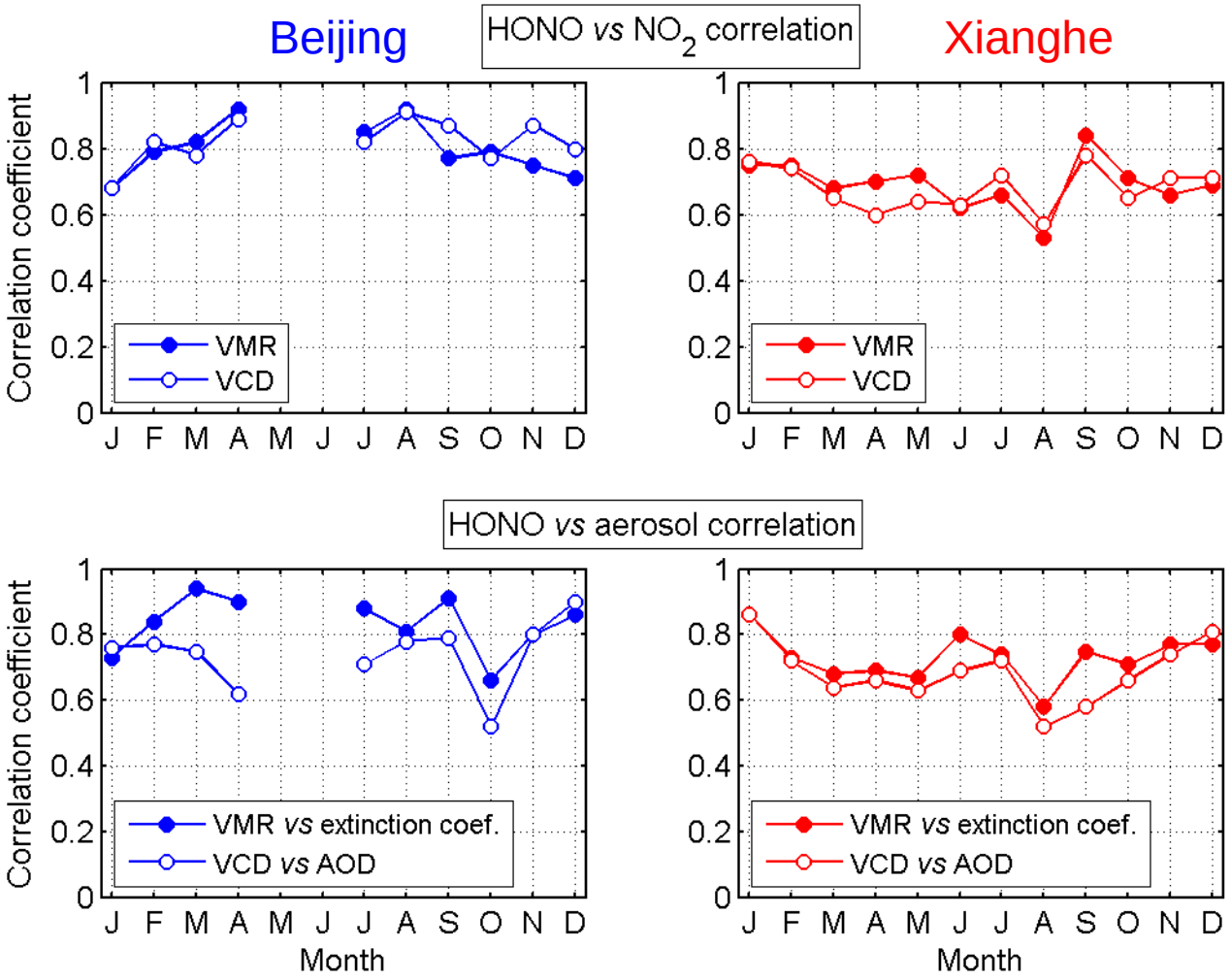


Seasonal variation of HONO and NO_2 concentrations at local noon

Near-surface (0-200m) concentration (ppb) at local noon

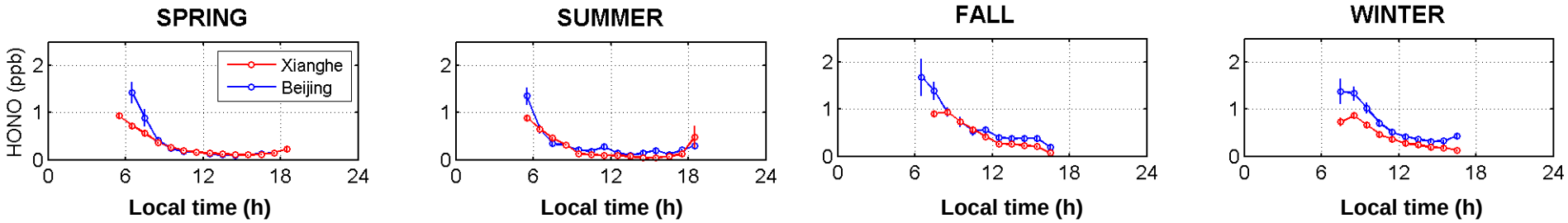


HONO vs NO_2 and HONO vs aerosols correlations at local noon

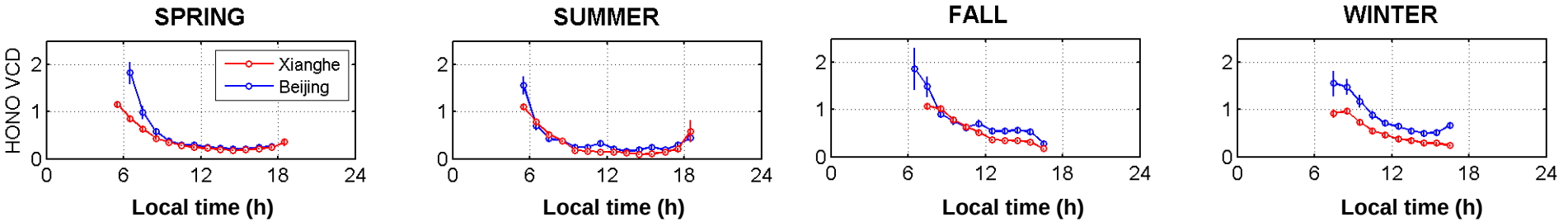


Diurnal variation of HONO

Near-surface (0-200m) concentration (ppb)



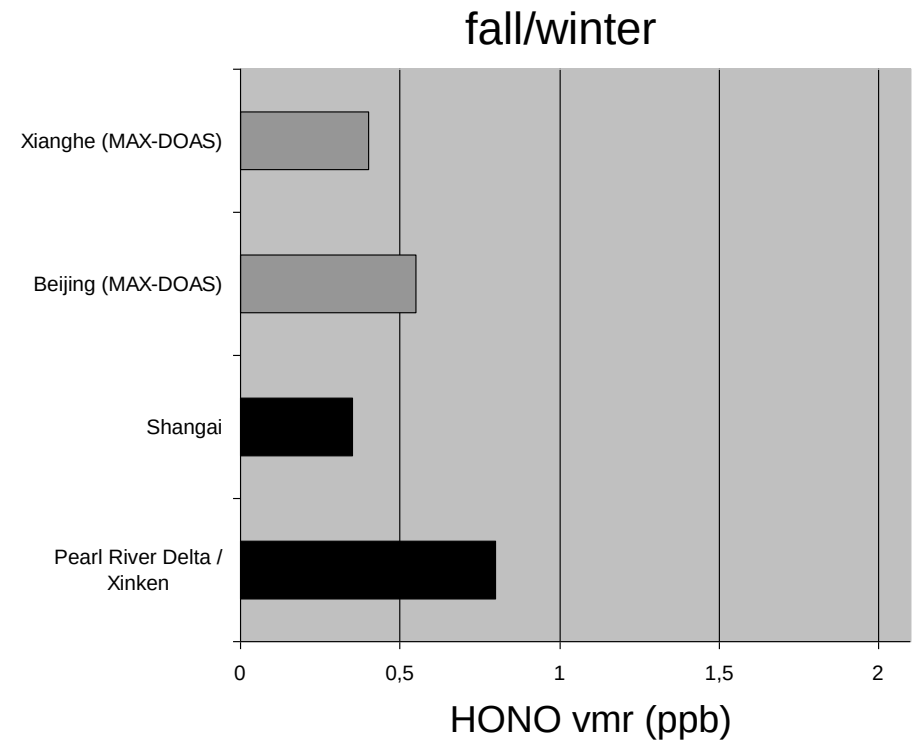
Vertical column density (x10^{15} molec/cm^2)

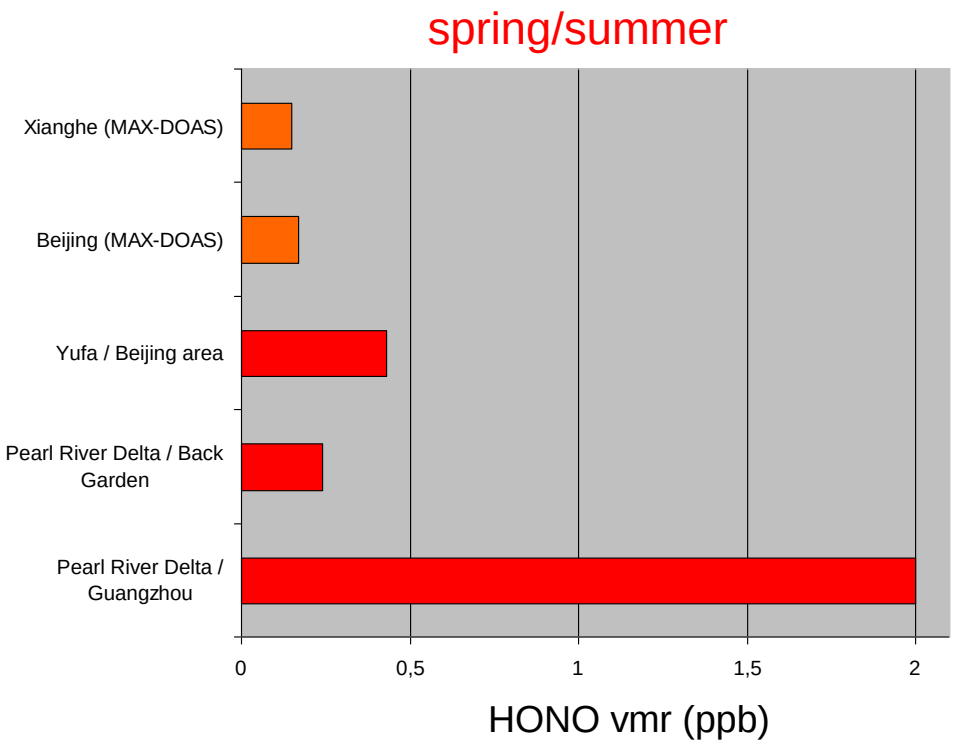


- **HONO concentration and vertical column have very similar diurnal cycle**

Diurnal variation of HONO surface concentration likely mainly driven by photochemistry, not by dilution effects

Comparison with other daytime (~12h LT) HONO measurements in China





OH production from HONO and ozone

- **Production of OH from HONO estimated from retrieved near-surface [HONO] and calculated photolysis rate J_{HONO}**
- **Production of OH from O_3 estimated from assumed 30 ppbv O_3, [H_2O] from ECMWF ERA-Interim, and calculated $J_{O3 \rightarrow O1D}$**

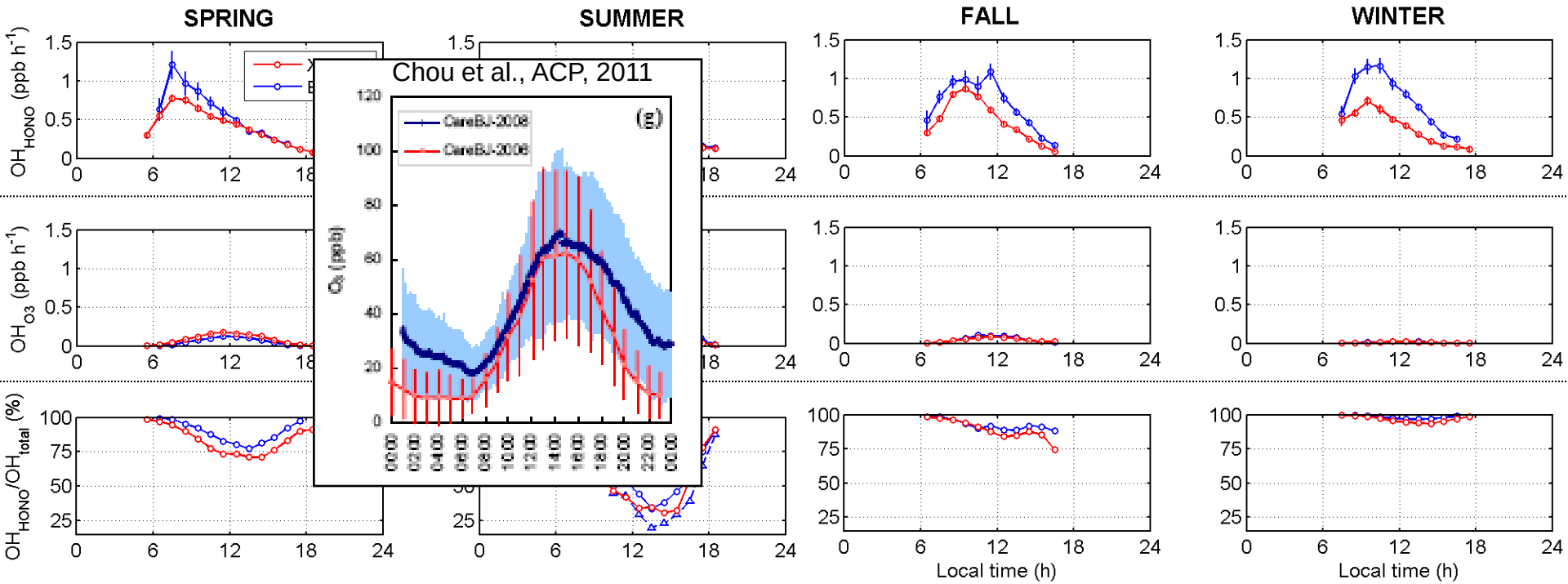
$$O_3 + h\nu\ (\lambda<340\ nm) \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow 2\ OH$$

- **Photolysis rates calculated using the TUV package including the SDISORT radiative transfer code, with**
  - **No cloud**
  - **MAX-DOAS AOD, SSA=0.9, asymmetry parameter=0.7**
  - **Albedo=0.05 except over snow (0.5)**
  - **Snow presence and ozone total columns from ECMWF ERA-Interim**

Diurnal variation of OH production

0-200 m layer



- **Maximum of OH production in the morning**
- **Maximum of OH production larger at Beijing than at Xianghe**
- **HONO is by far the largest source of OH radicals except in summer where the contribution of O_3 dominates from mid-morning until mid-afternoon.**

Concluding remarks

- **First measurements of HONO in and in the vicinity of a megacity (Beijing) using a passive DOAS instrument.**

- **The possibility of retrieving HONO near-surface concentration and vertical column by applying an OEM-based profiling tool to these MAX-DOAS measurements has been demonstrated.**

- **The multi-year operation of the instrument allowed the study of the seasonal and diurnal cycles of HONO and its main precursor NO_2 in the Beijing area:**

  - **The HONO and NO_2 seasonal cycles are highly correlated**
  - **The heterogeneous conversion of NO_2 is the dominant source of HONO with a larger role played by the aerosols in the city center**
  - **The HONO seasonal and diurnal cycles mainly driven by the photochemistry, dilution effects likely play only a minor role**
  - **HONO is by far the largest source of OH radicals in winter as well as in the early morning at all seasons, while the contribution of O_3 dominates in summer from mid-morning until mid-afternoon**

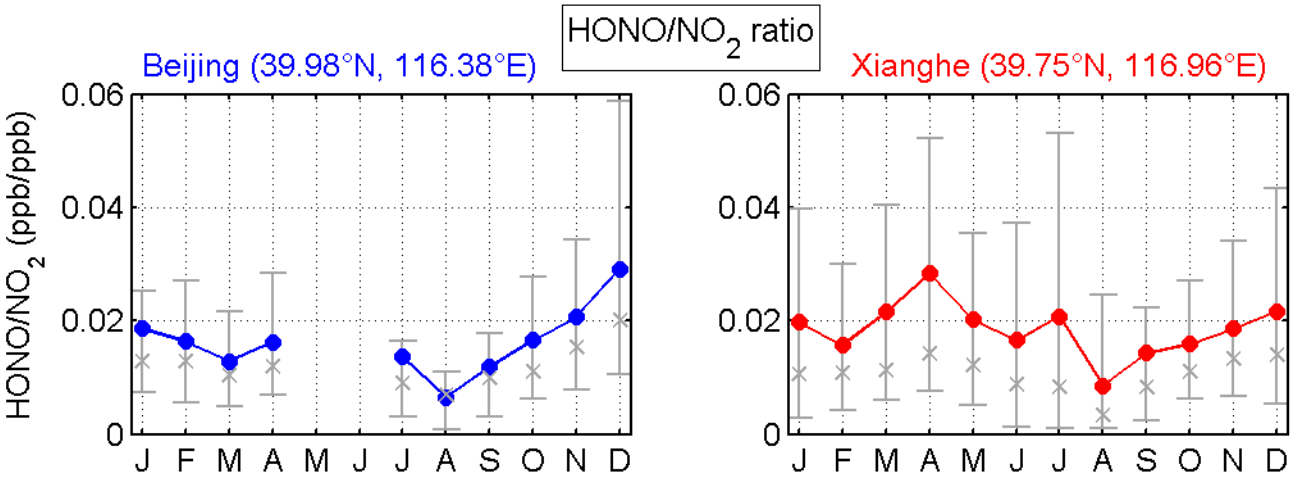
Acknowledgements

- **Belgian Federal Science Policy Office, Brussels (PRODEX contract A3C and AGACC-II project)**
- **EU FP7 projects NORS (contract 284421) and SHIVA (contract 226224)**

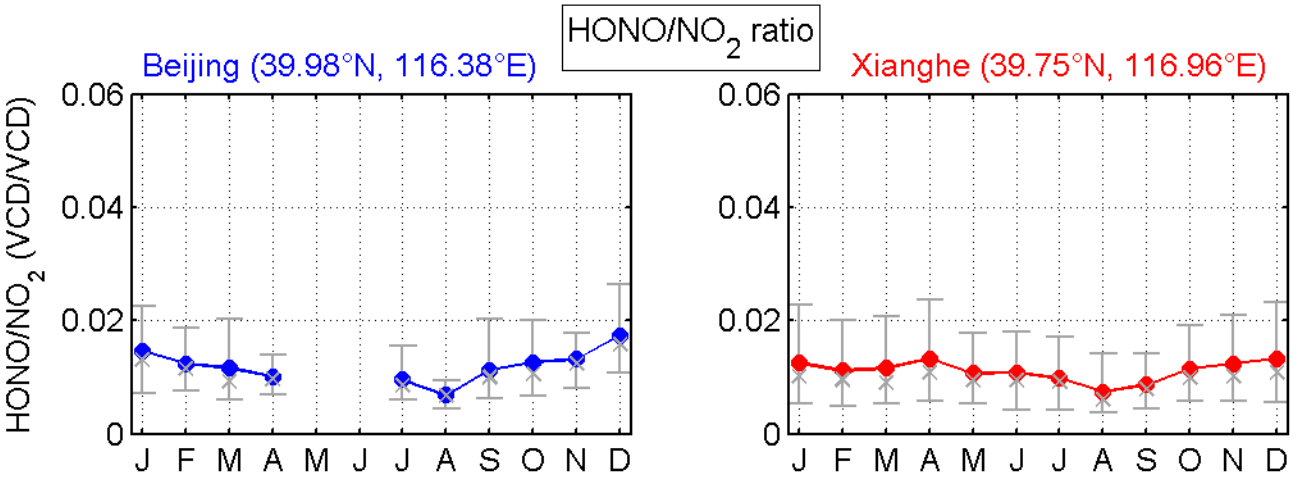
Thank you for your attention !

$HONO/NO_2$ ratio at local noon

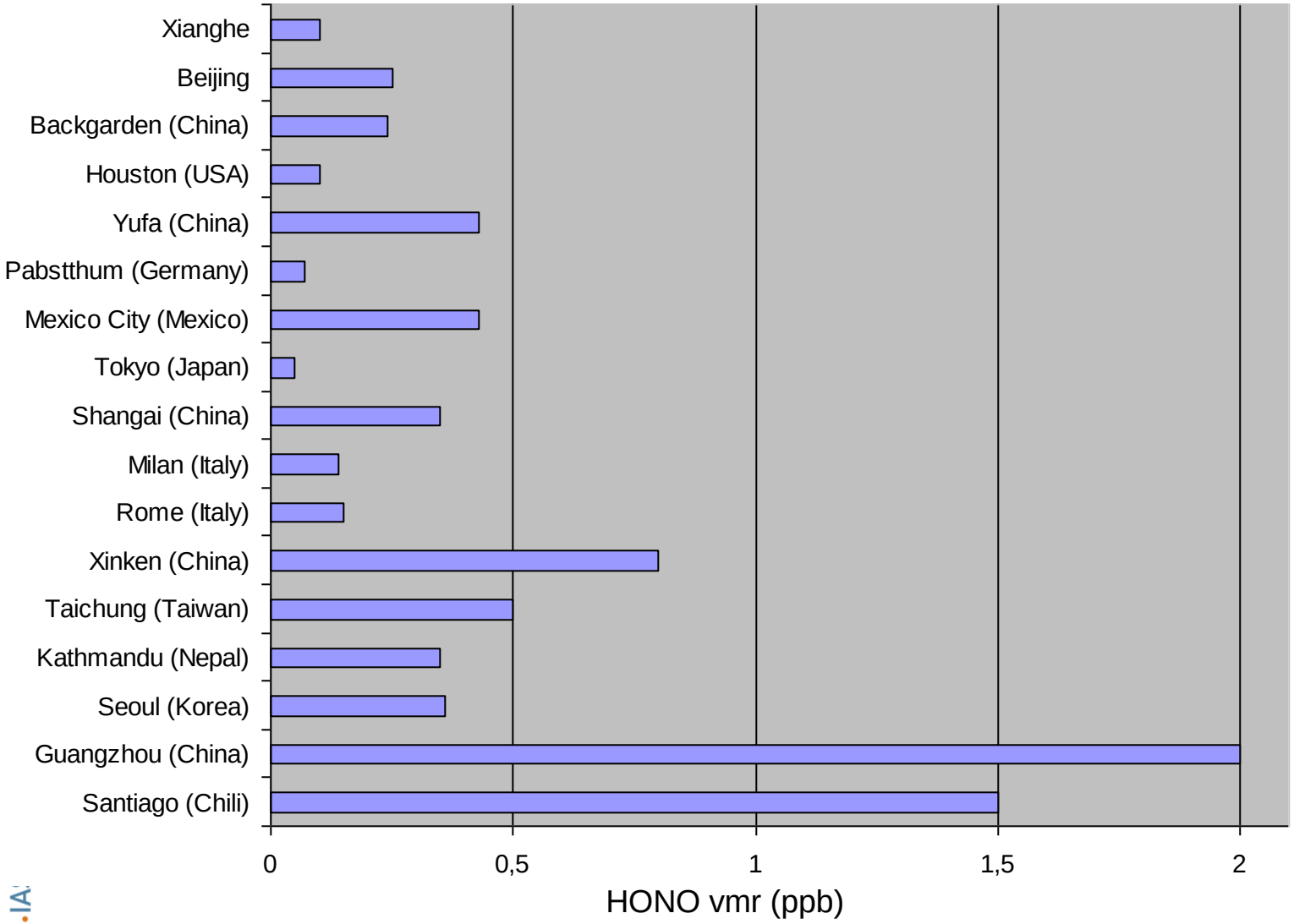
VMR/VMR



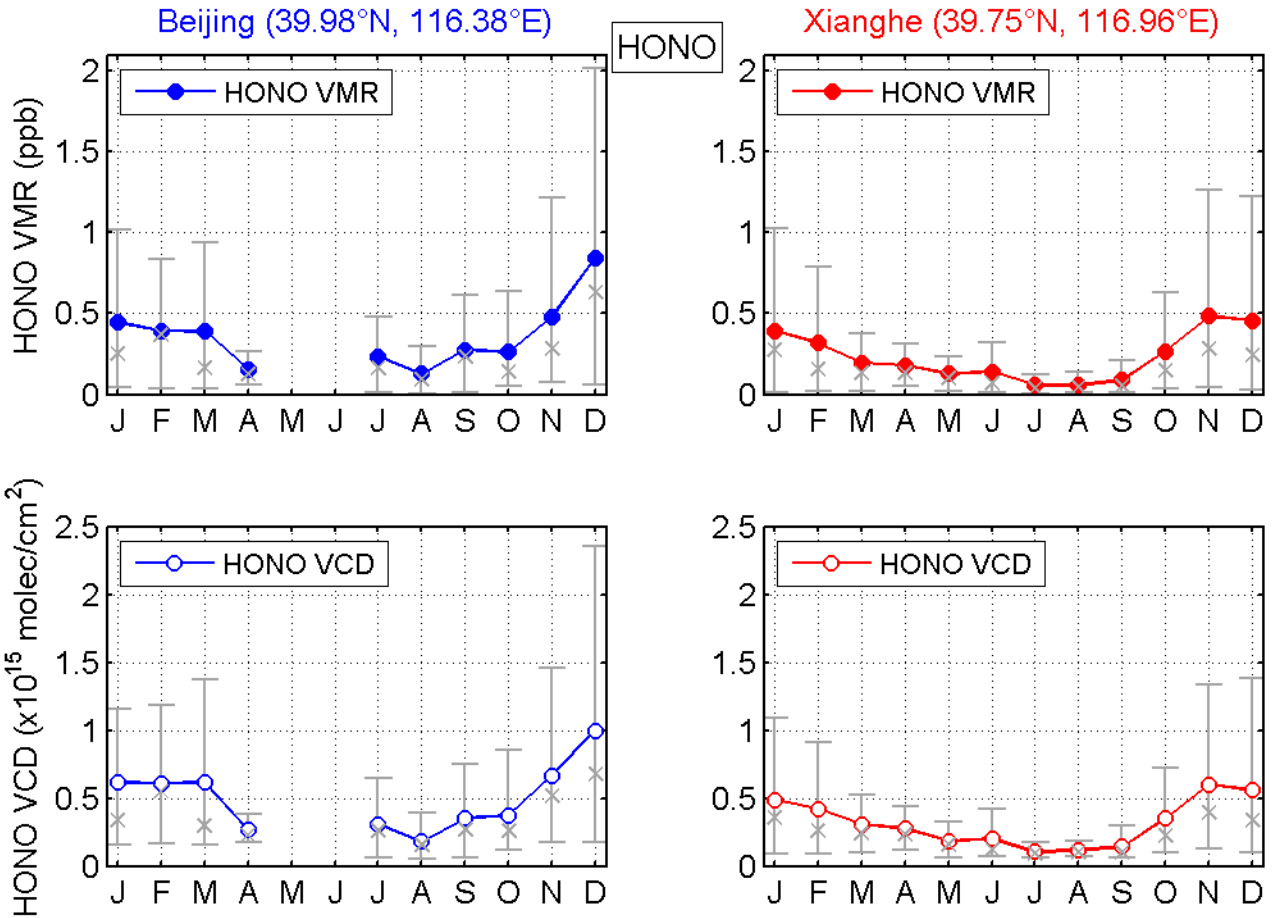
VCD/VCD



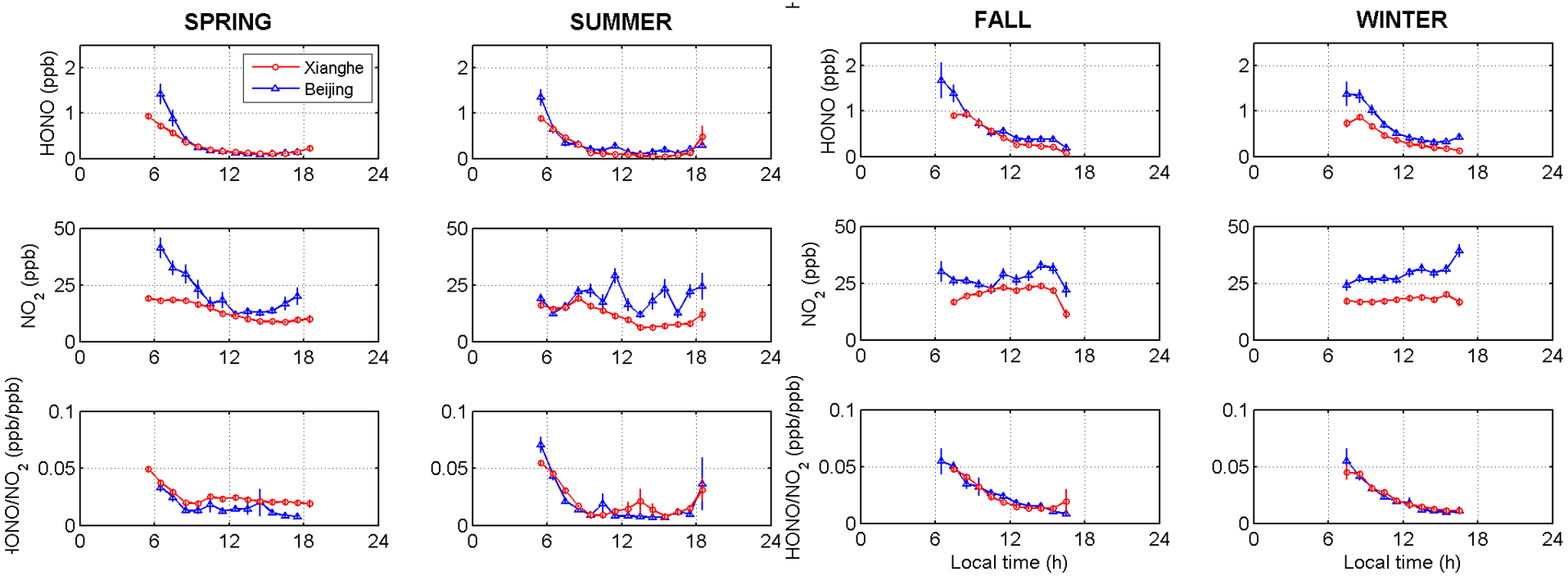
Comparison with other daytime (~12h LT) HONO measurements in China



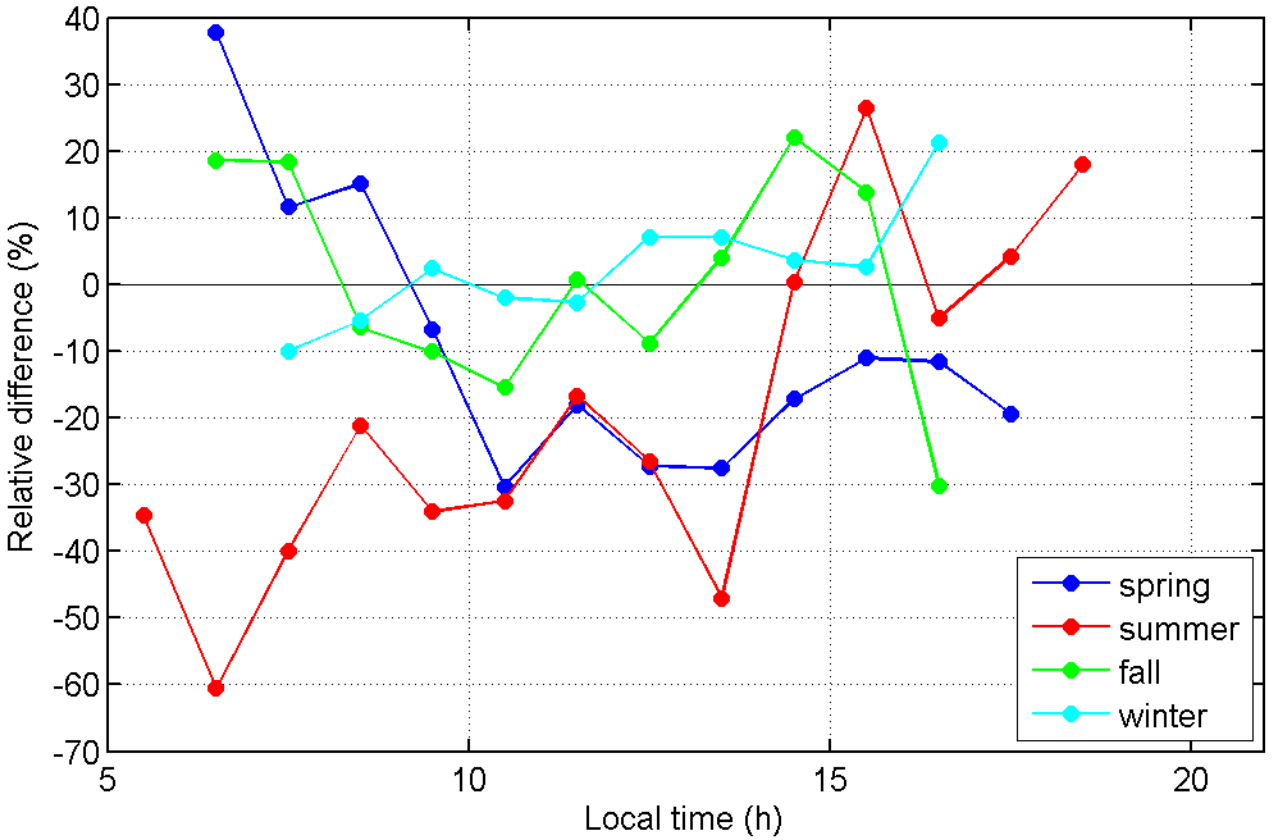
Seasonal variation of HONO at local noon



Diurnal variation of HONO and NO_2



Comparison with Ma et al.



Photolysis rates