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

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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: $2\ NO_2 + H_2O + surface \rightarrow HONO + HNO_3$

Realistic model simulations of HONO levels are difficult

- **HONO measurements are generally sparse in time because mainly resulting from field campaigns**

Continuous MAX-DOAS measurements of HONO 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

MAX-DOAS retrieval algorithm

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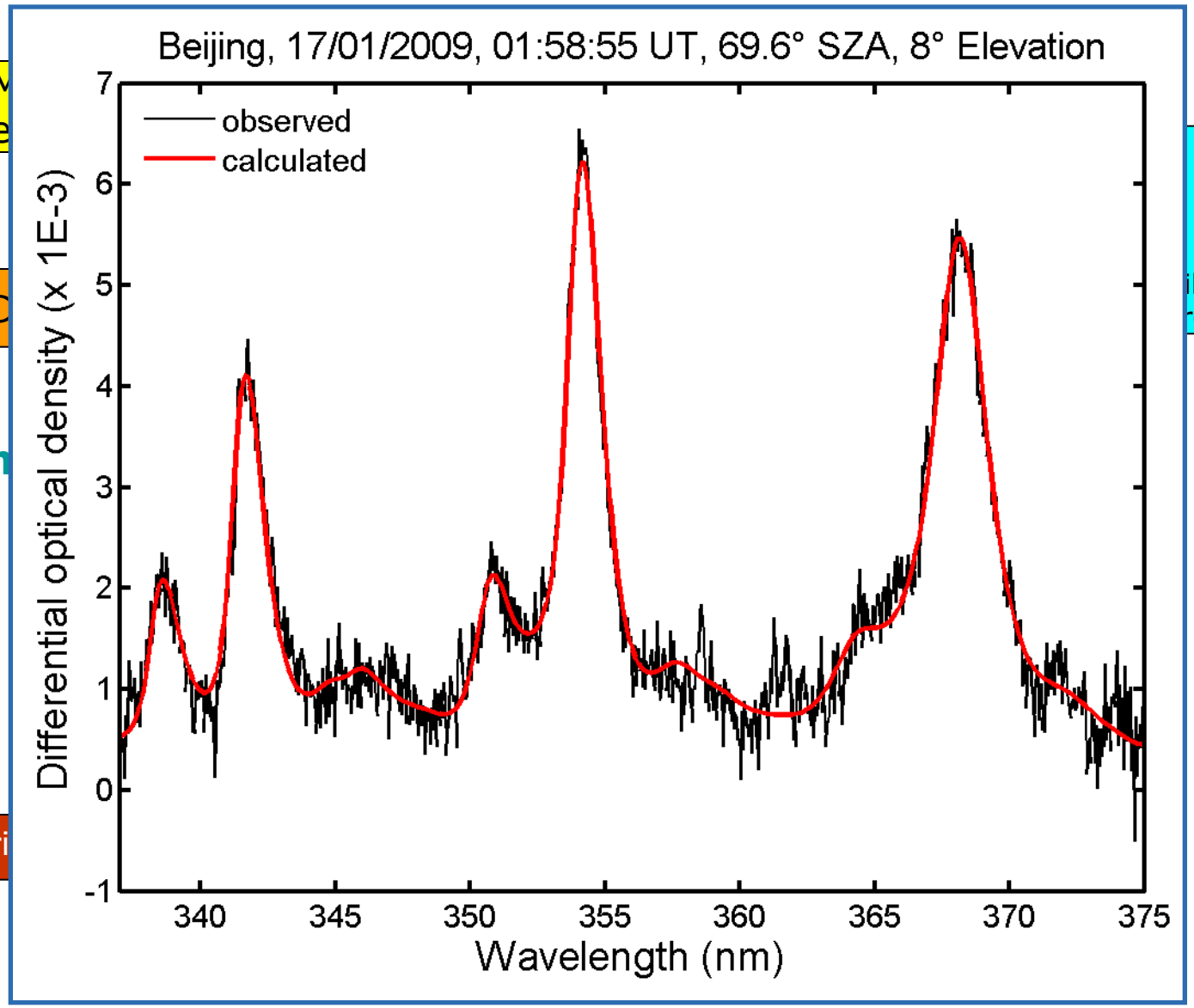
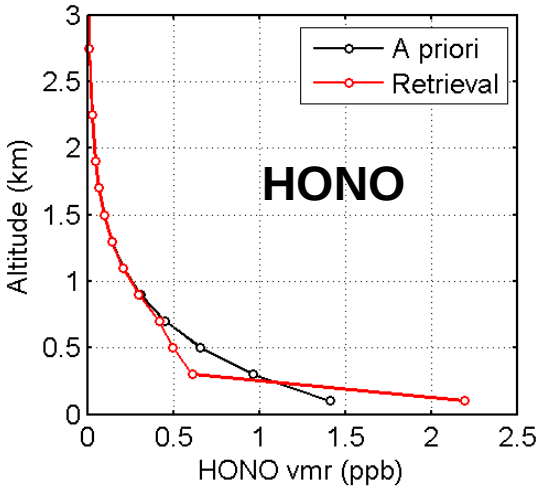


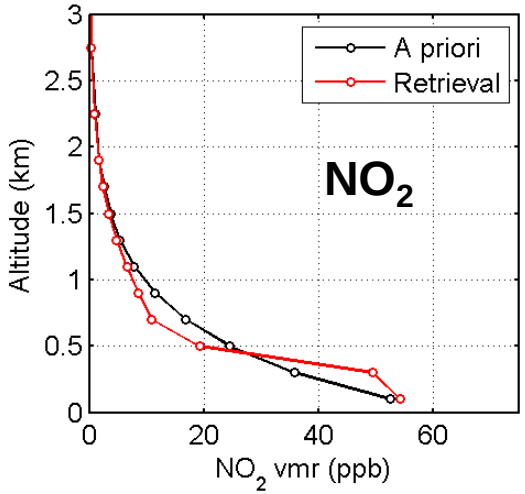
Examples of HONO and NO_2 vertical profile retrievals

Beijing 21/01/2009 ~10:15 AM

Uncertainty on HONO VCD and surface VMR:

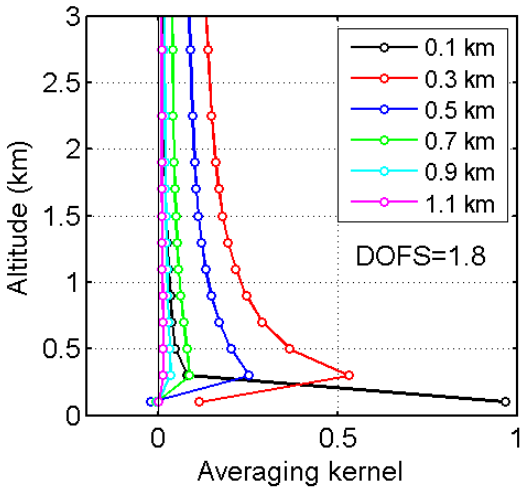
20-25%

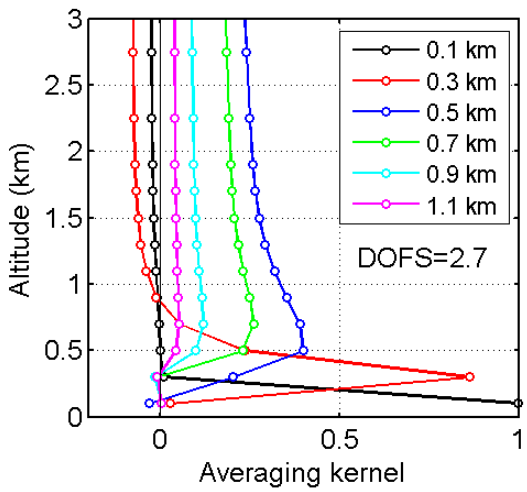




Uncertainty on NO_2 VCD and surface VMR:

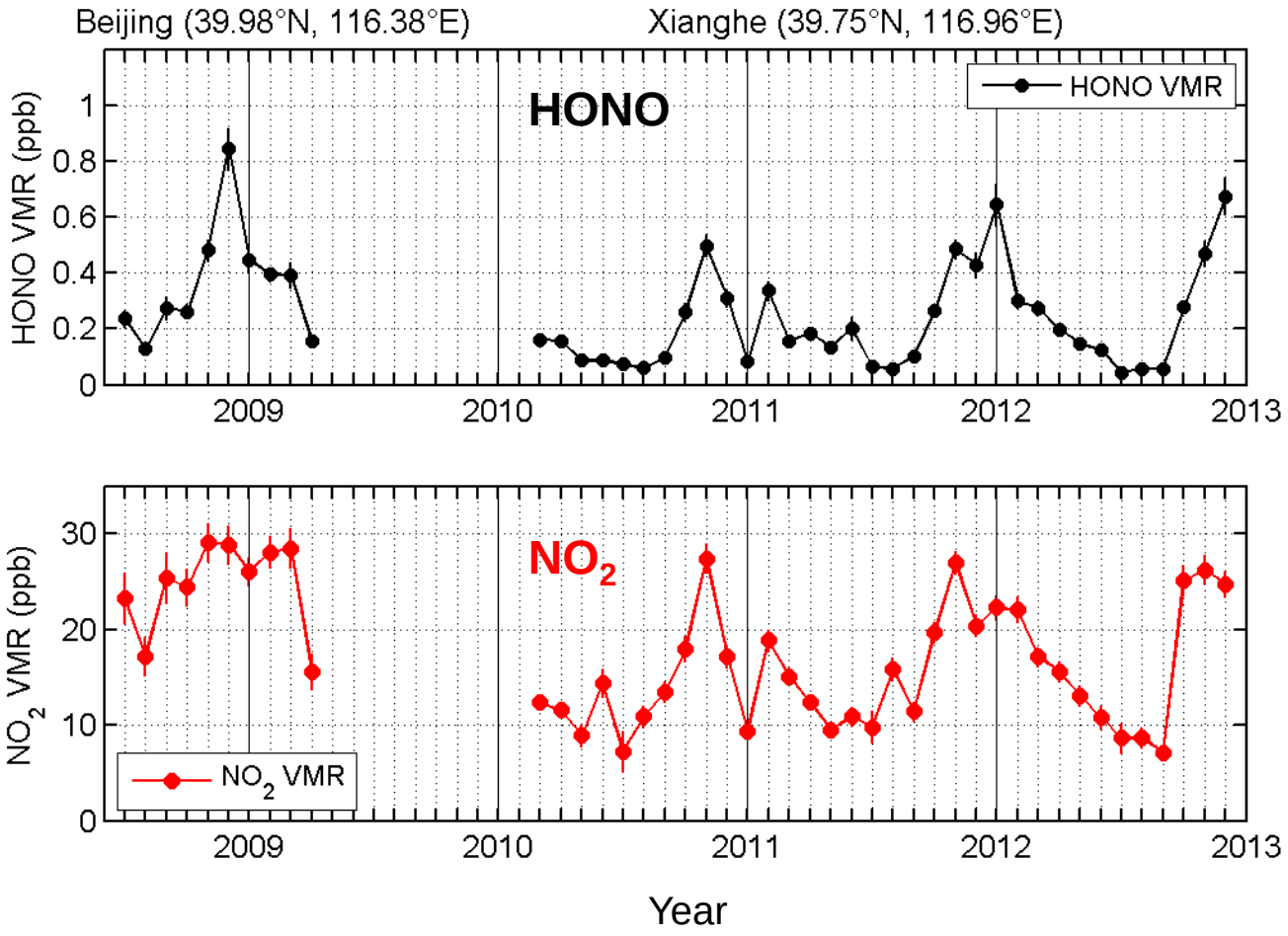
10-15%



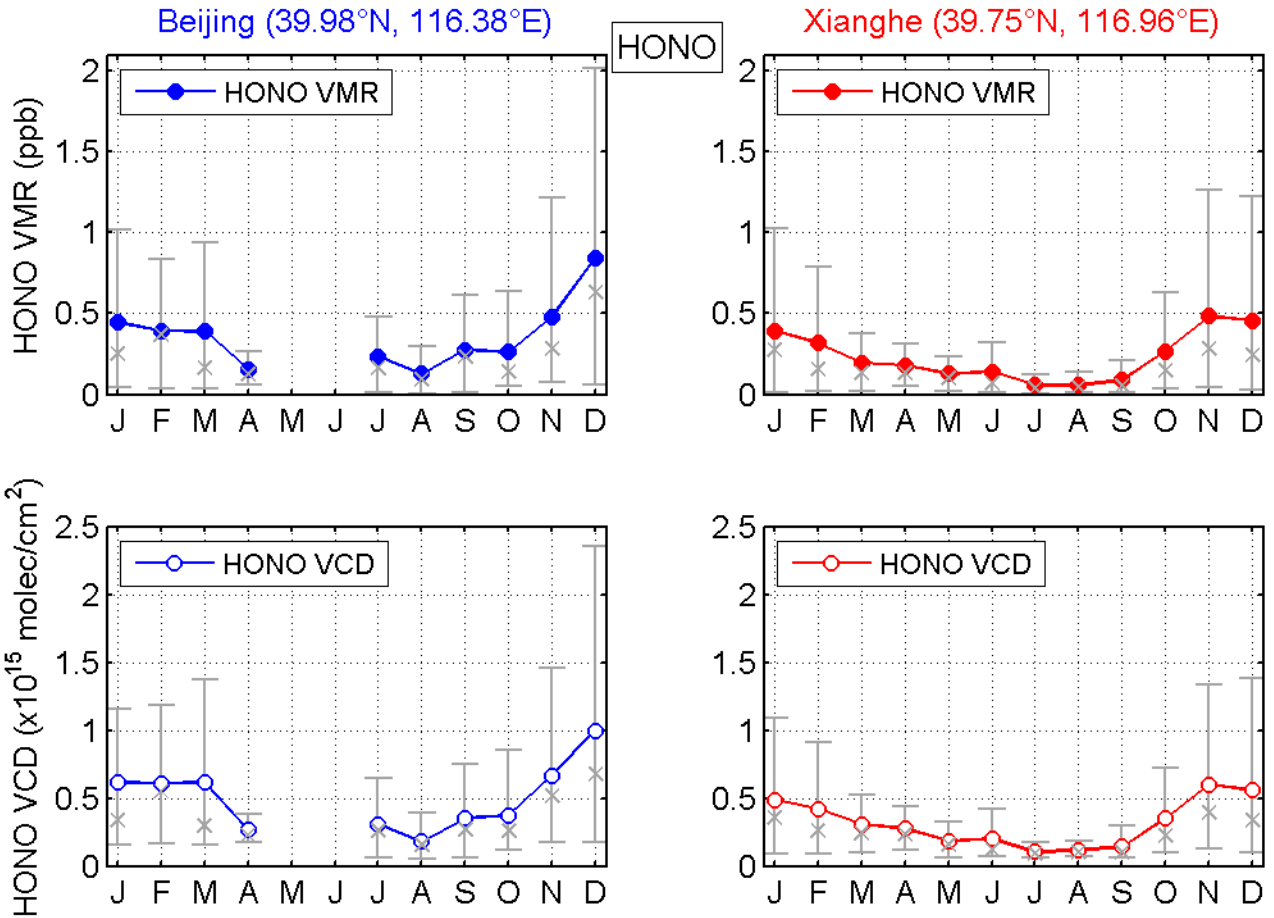


Seasonal variation of HONO and NO_2

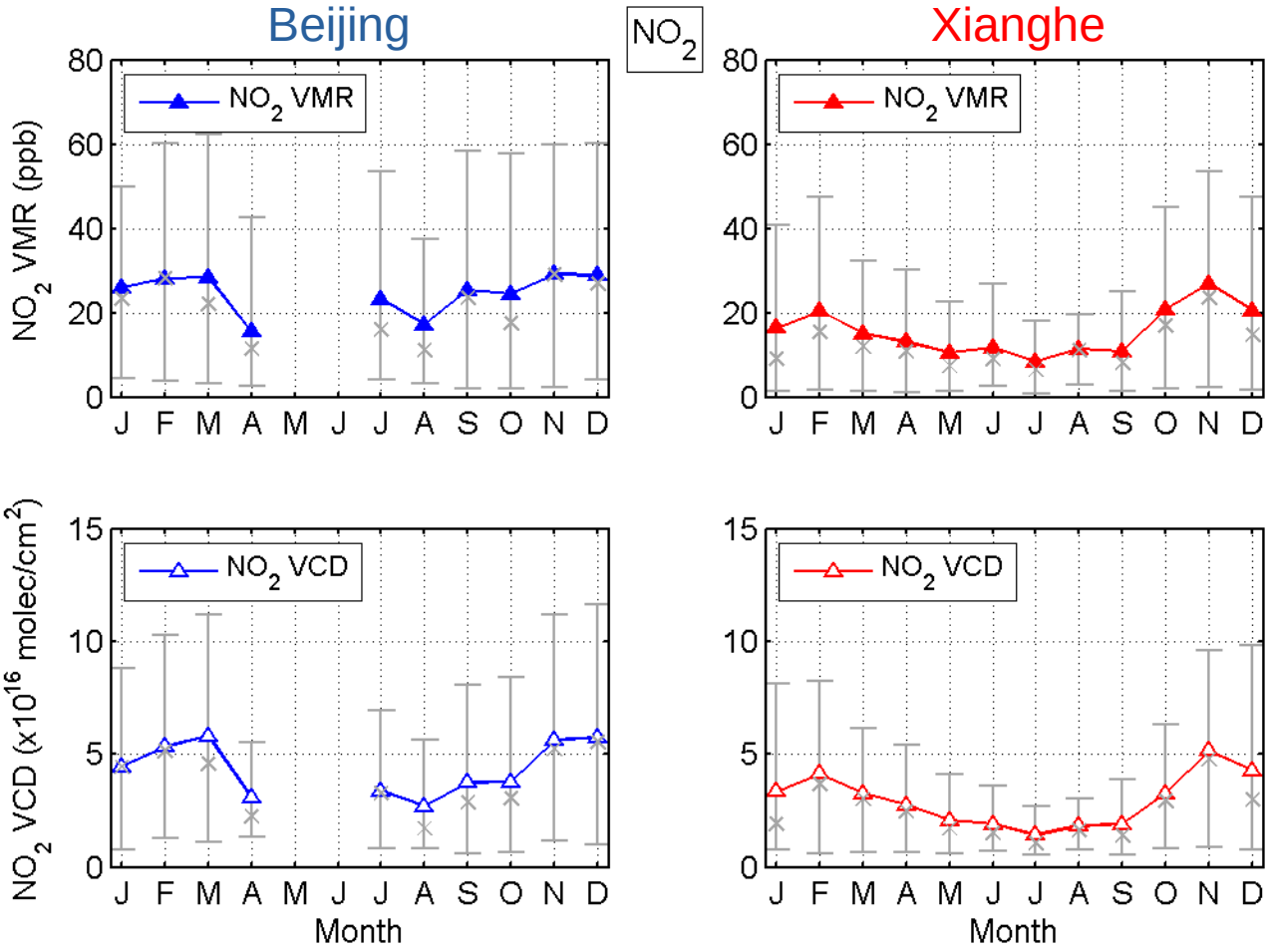
Near-surface (0-200m) concentration (ppb) at local noon



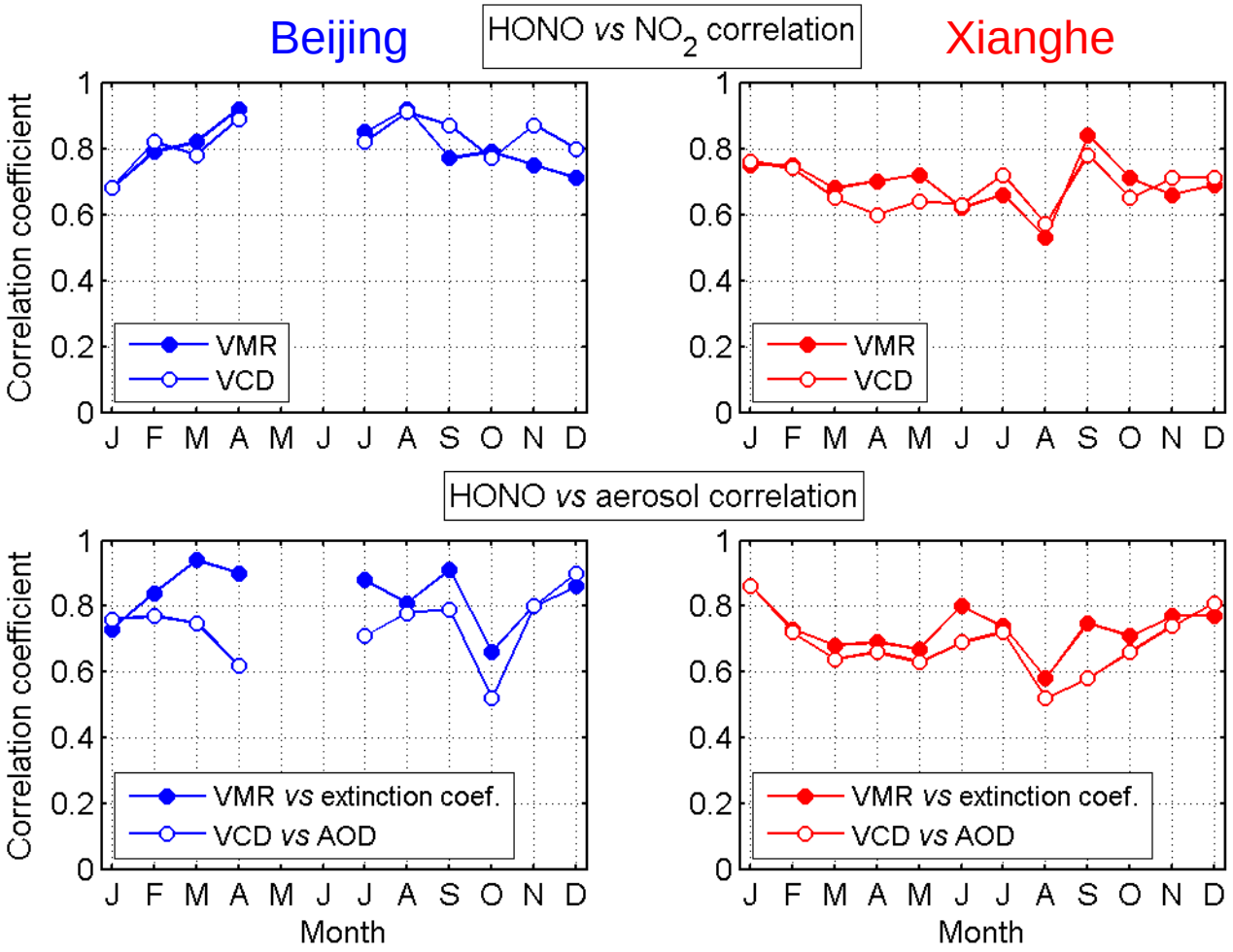
Seasonal variation of HONO at local noon



Seasonal variation of NO_2 at local noon



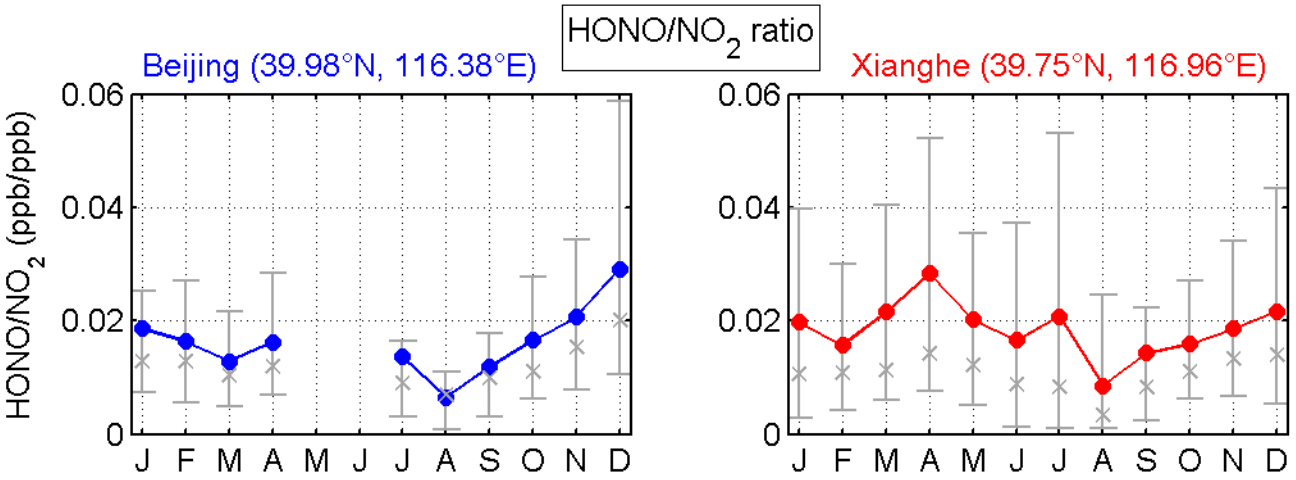
HONO vs NO_2 and HONO vs aerosols correlations at local noon



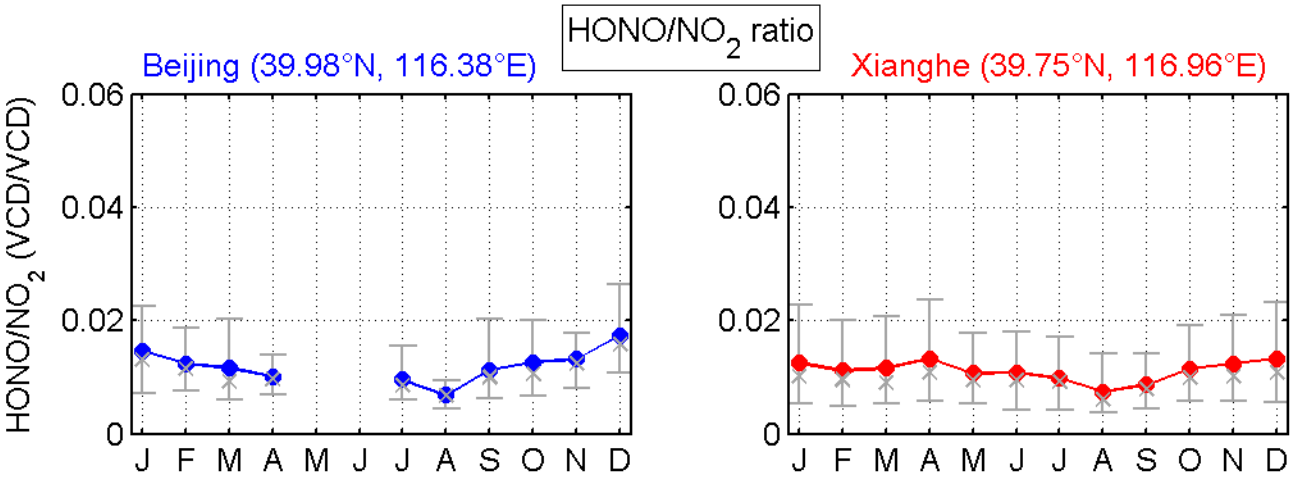
Stronger correlation obtained at Beijing

$HONO/NO_2$ ratio at local noon

VMR/VMR

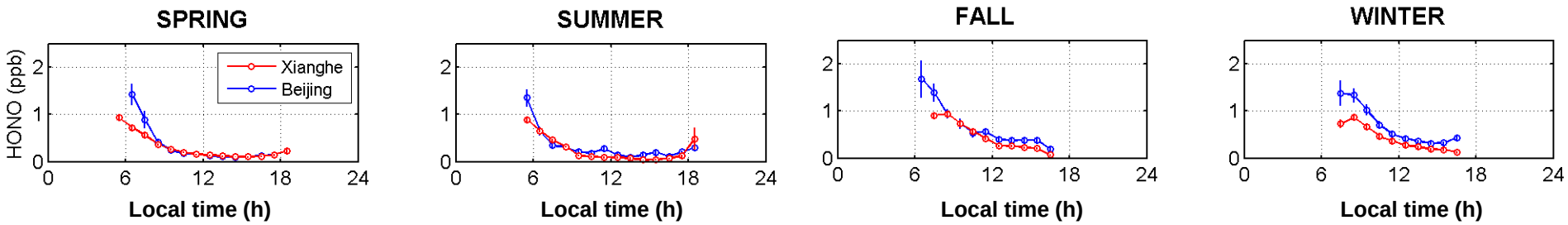


VCD/VCD

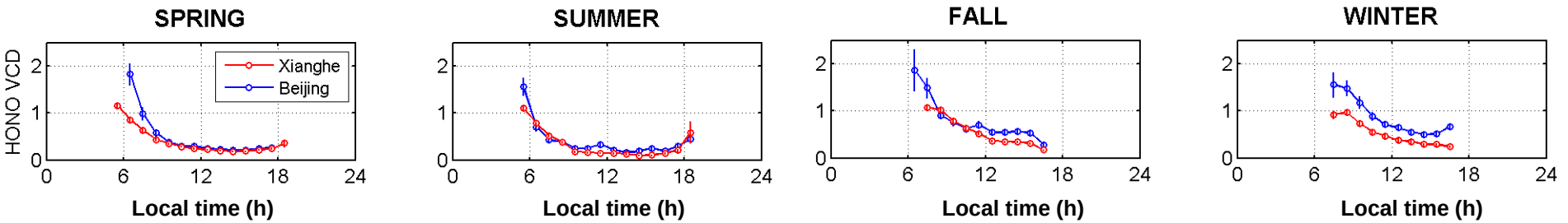


Diurnal variation of HONO

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 not driven by dilution effects

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 $J_{O3 \rightarrow O1D}$**

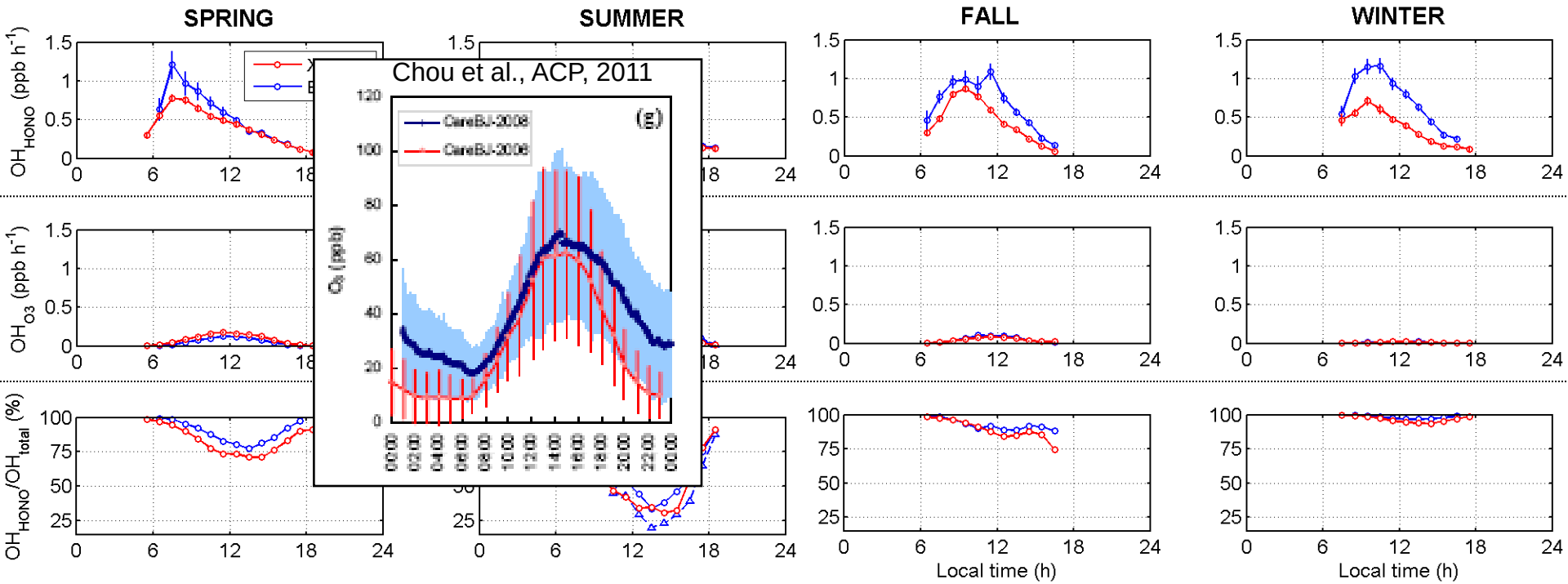
$$O_3 + h\nu\ (\lambda<340\ nm) \rightarrow O(^1D) + O_2$$

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

- **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

- **For the first time, the seasonal and diurnal variations of HONO and its main precursor NO_2 has been investigated in and in the vicinity of a megacity using multi-year MAX-DOAS observations.**

- **The very similar seasonal and diurnal cycles obtained for HONO surface concentration and vertical column suggest that these cycles are mainly driven by the photochemistry, while the dilution effects appear to play only a minor role.**

- **The stronger correlation of HONO with NO_2 and also with aerosols observed in Beijing suggests larger role of NO_2 conversion into HONO in the Beijing city center than at Xianghe.**

- **The estimation of OH production from HONO and O_3 photolysis indicates that 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.**

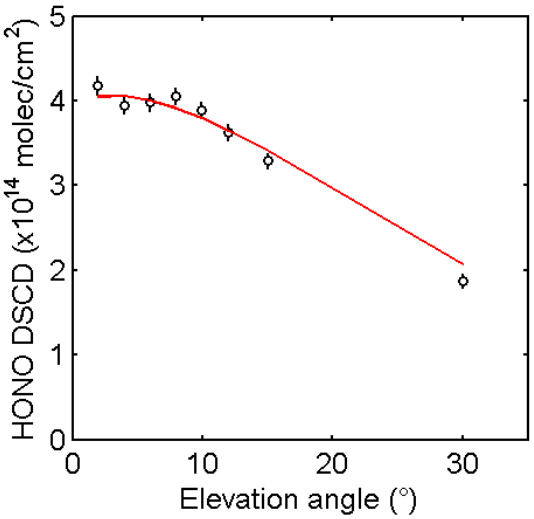
Acknowledgements

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

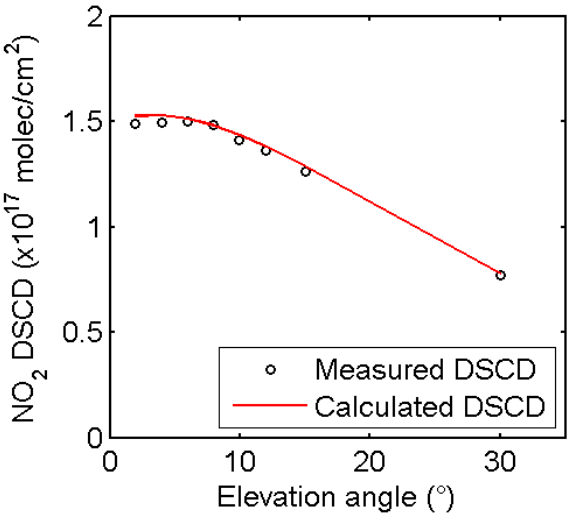
Scans selection based on retrieval fit results

Beijing 21/01/2009 ~10:15 AM

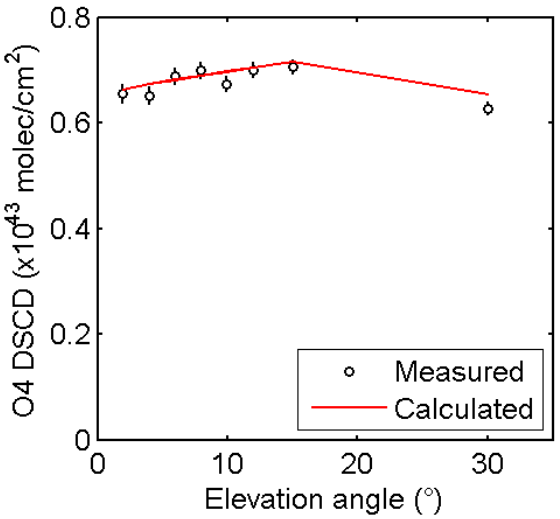
HONO



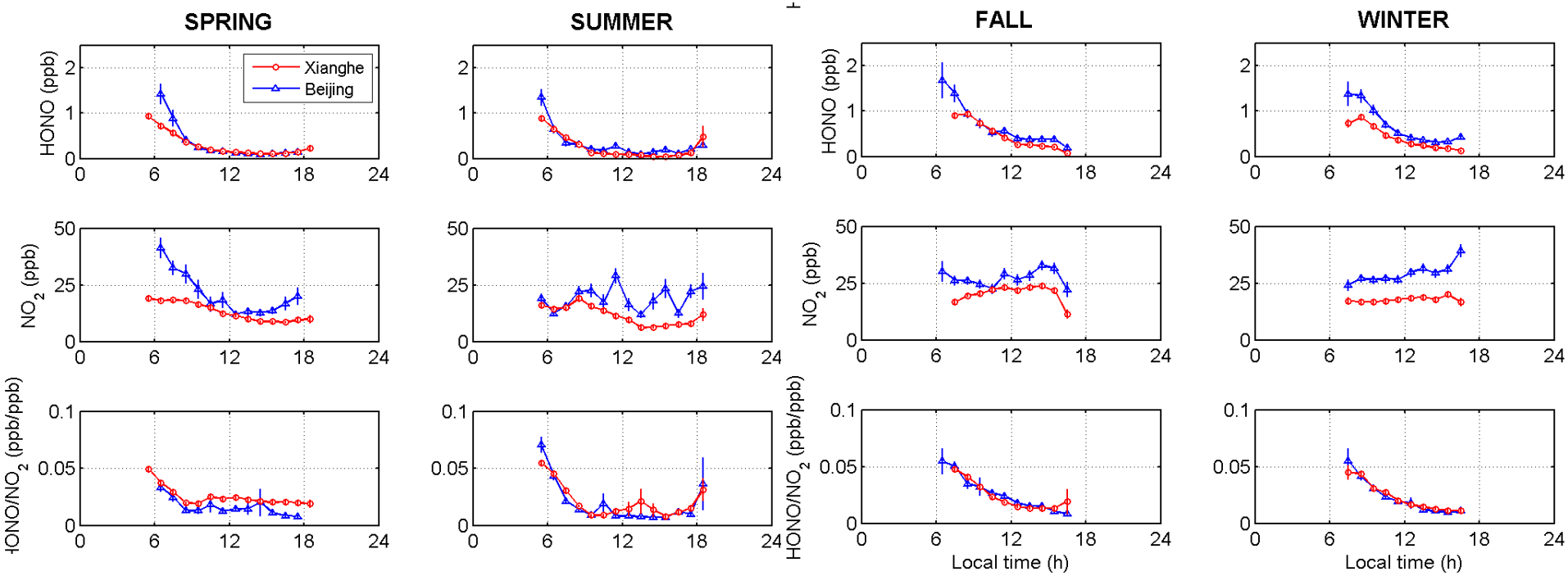
NO_2



O_4



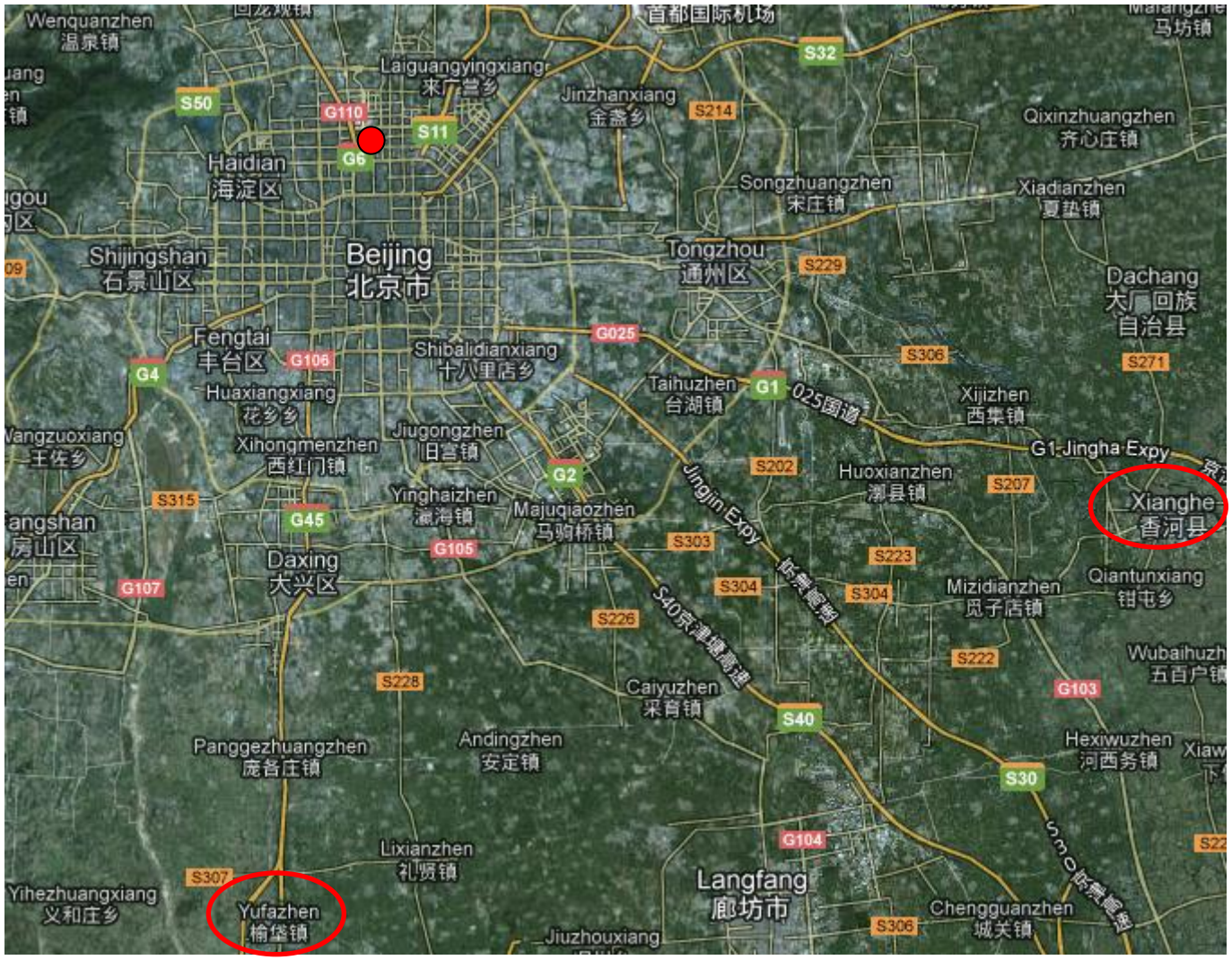
Diurnal variation of HONO and NO_2



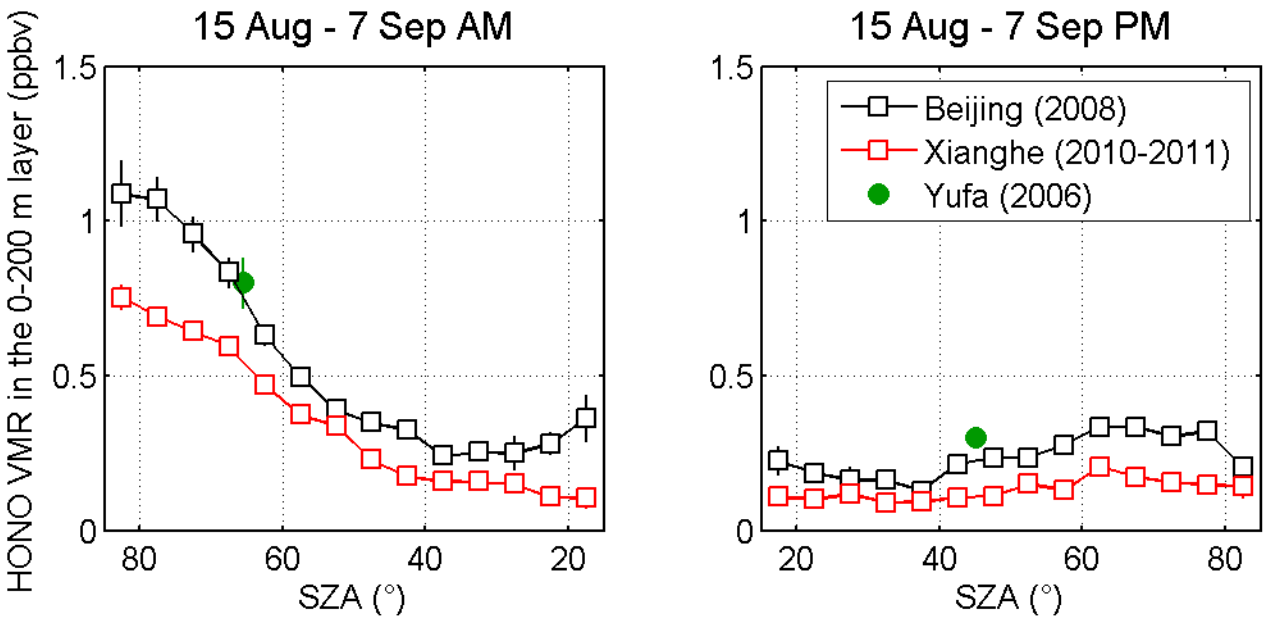
DOAS settings

- The following settings are used for the DOAS analysis:
  - Fitting window: 337-375 nm
  - Fitted species: HONO, NO_2, O_3, O_4, BrO, HCHO, Ring effect
  - HONO XS: Stutz et al. (2000) at 296 K
- For each scan, $DSCD_{off\text{-}axis} = SCD_{off\text{-}axis} - SCD_{zenith\ of\ the\ scan\ used\ by\ the\ profiling\ algorithm}$

Comparison to CAREBeijing2006 data (1)



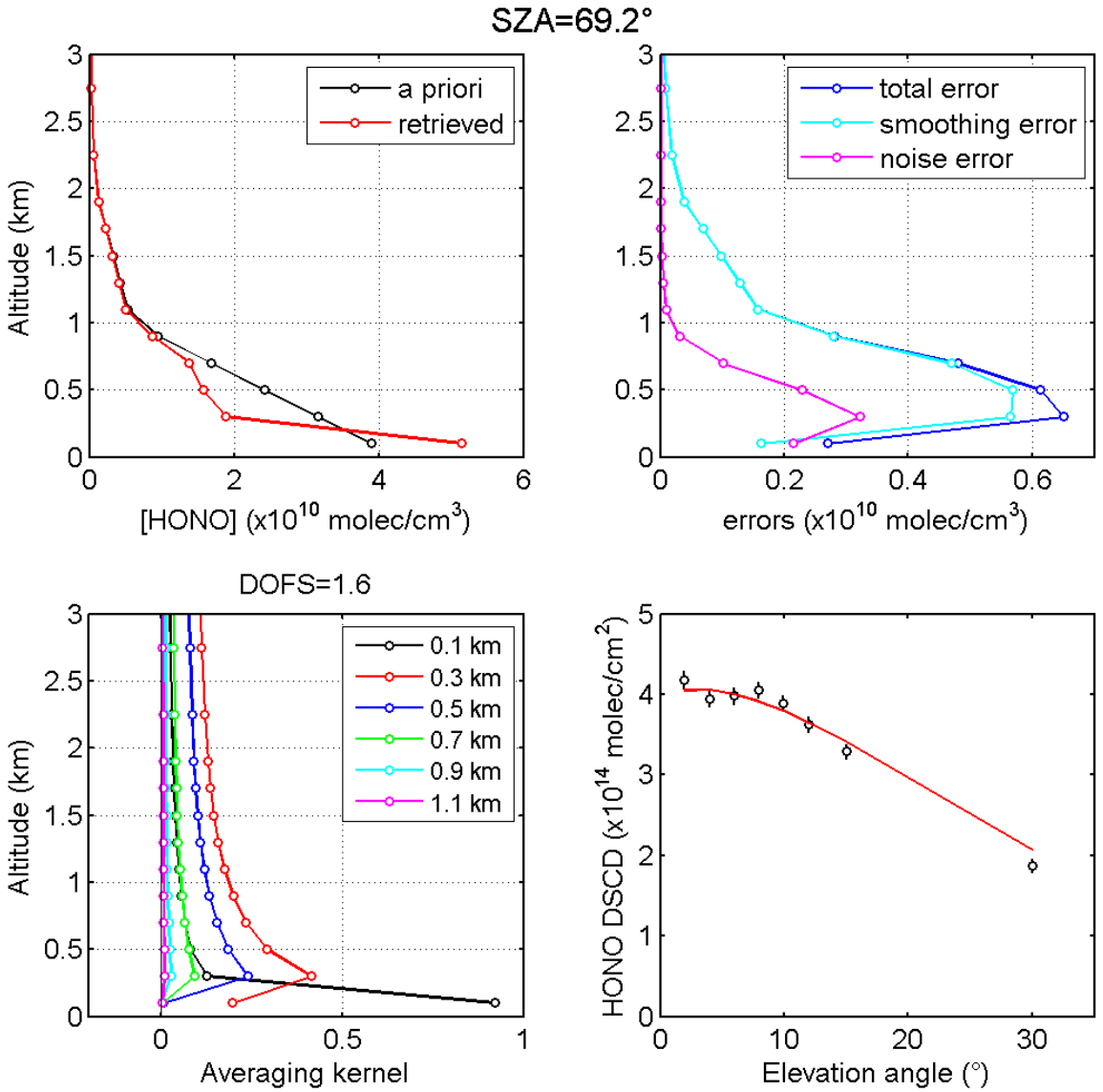
Comparison to CAREBeijing2006 data (2)



CAREBeijing2006 HONO measurements at Yufa: in-situ long-path absorption photometry (LOPAP); see Lu et al., ACPD, 2012

HONO vertical profile retrieval

Beijing 21/01/2009 ~10:15 AM



A priori:

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

with SH = 0.5 km