FOUR YEARS OF GROUND-BASED MAX-DOAS OBSERVATIONS OF HONO AND NO_2 IN THE BEIJING AREA

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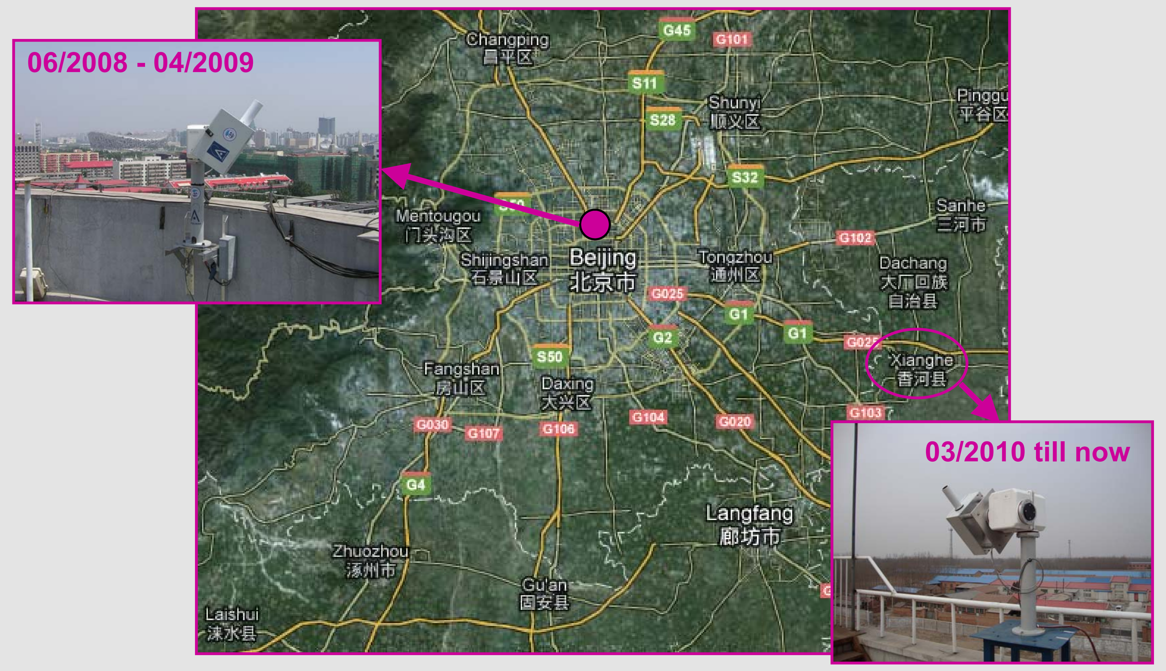
I.INTRODUCTION

Nitrous acid (HONO) is an important trace gas in the atmosphere due to its significant role in the nitrogen oxides (NO_x) and hydrogen oxides (HOx) cycles. For three decades, observations of HONO in the troposphere have been performed at many remote and heavily polluted locations. Although sparse in time because mainly based on field campaigns, they revealed that the HONO photolysis can be a major source of OH radicals, especially during the early morning, when other sources are of minor importance. Recent work has shown also the existence of a strong HONO source peaking around noon at several locations. However, owing to the current uncertainties and lack of knowledge regarding HONO sources, the atmospheric impact of HONO on the global scale, in particular its contribution to the production of OH radicals, remains an open issue.

We present four years of ground-based Multi-Axis (MAX-) Differential Optical Absorption Spectroscopy (DOAS) measurements of HONO and NO_2 in Beijing city center (39.98°N, 116.38°E) and at the suburban site of Xianghe (39.75°N, 116.96°E) located at 60 km East of Beijing. The periods covered by the observations are June 2008-April 2009 in Beijing and March 2010-April 2012 in Xianghe. Combining the MAX-DOAS remote sensing technique with an optimal estimation profiling method allows retrieving information on the vertical distribution of HONO and NO_2 in the 0-1 km altitude range. The diurnal, seasonal, and height variations of the HONO and NO_2 concentrations, HONO/NO_2 ratios, and HONO versus NO_2 correlation at both stations are investigated. We also provide an estimate of the OH production from HONO based on the retrieved HONO concentration and photolysis rates calculated from ECMWF data. The impact of these results on our knowledge about the HONO and OH budgets is discussed.

II. OBSERVATION SITES

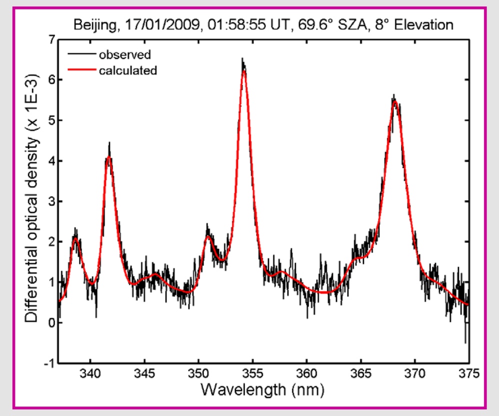
- A MAX-DOAS instrument was installed on the roof of the Institute of Atmospheric Physics in Beijing city center from June 2008 till April 2009. The instrument moved to Xianghe in March 2010.



- The instrument measures sunlight scattered at different elevation angles (2°, 4°, 6°, 8°, 10°, 12°, 15°, 30°, zenith) towards the horizon (~15 minutes per scan)

III. DOAS ANALYSIS

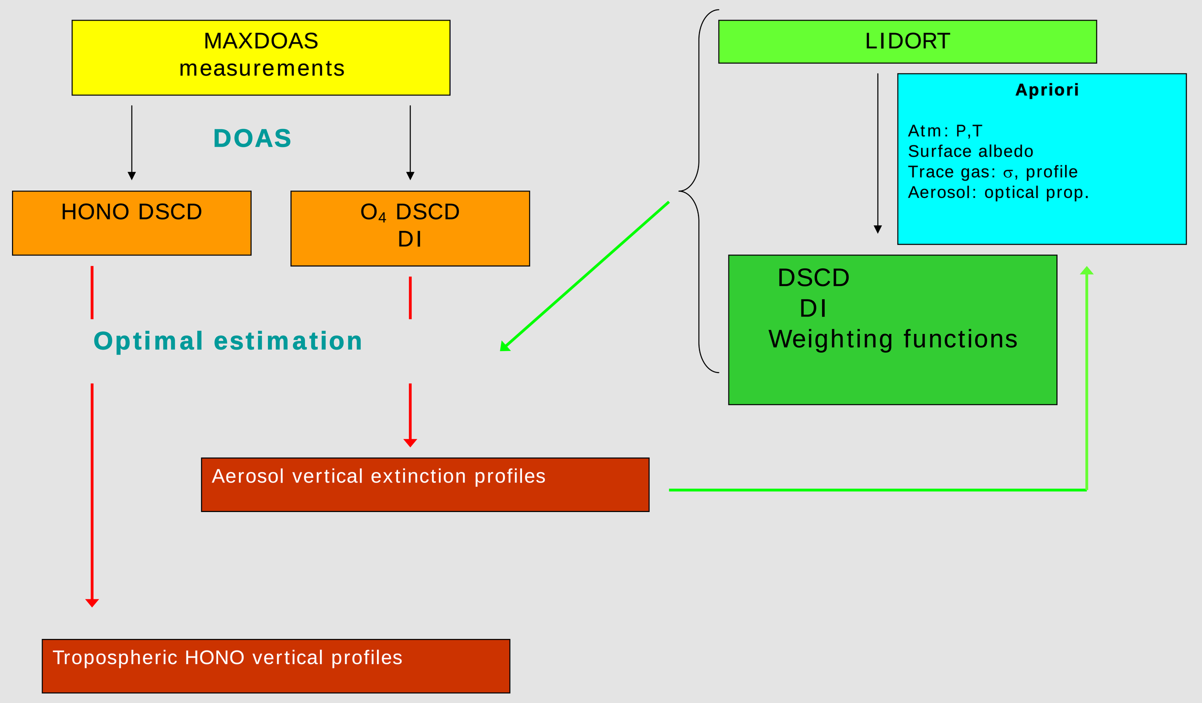
- Use of the QDOAS tool (http://uv-vis.aeronomie.be/software/QDOAS/index.php)
- DOAS settings for HONO:
  - Fitting window: 337-370 nm
  - Fitted species: HONO, NO_2, O_3, O_4, BrO, HCHO, and Ring effect
  - HONO cross-sections: Stutz et al. (2000) at 296 K
  - Example of DOAS fit for HONO:



- DOAS settings for NO_2:
  - Fitting window: 425-490 nm
  - Fitted species: NO_2, O_3, O_4, H_2O, and Ring effect
  - NO_2 cross-sections: Vandaele et al. (1997) at 296K

IV. MAX-DOAS PROFILING TOOL

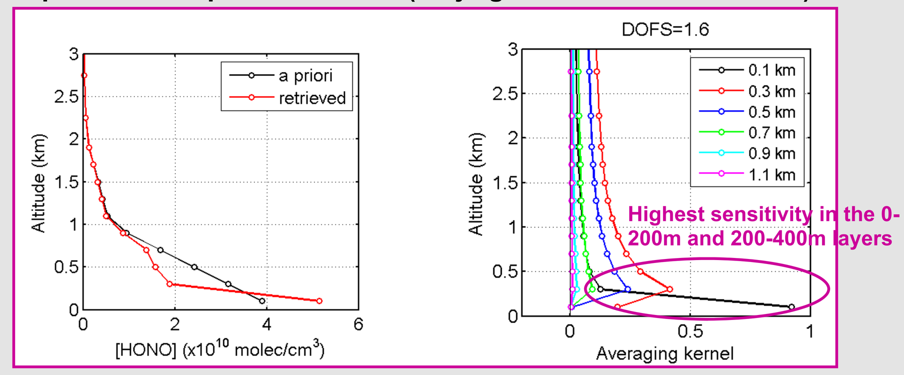
- Use of the bePRO profiling tool (Clémer et al., 2010) based on the Optimal Estimation Method (Rodgers, 2000):



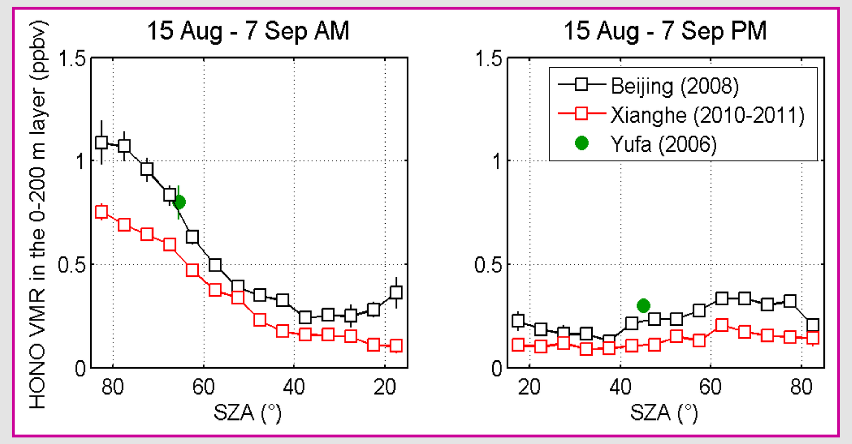
- Use of exponentially decreasing a priori profiles for aerosols, HONO, and NO_2 (scaling height=0.5 km)

V. HONO RETRIEVAL VERIFICATION

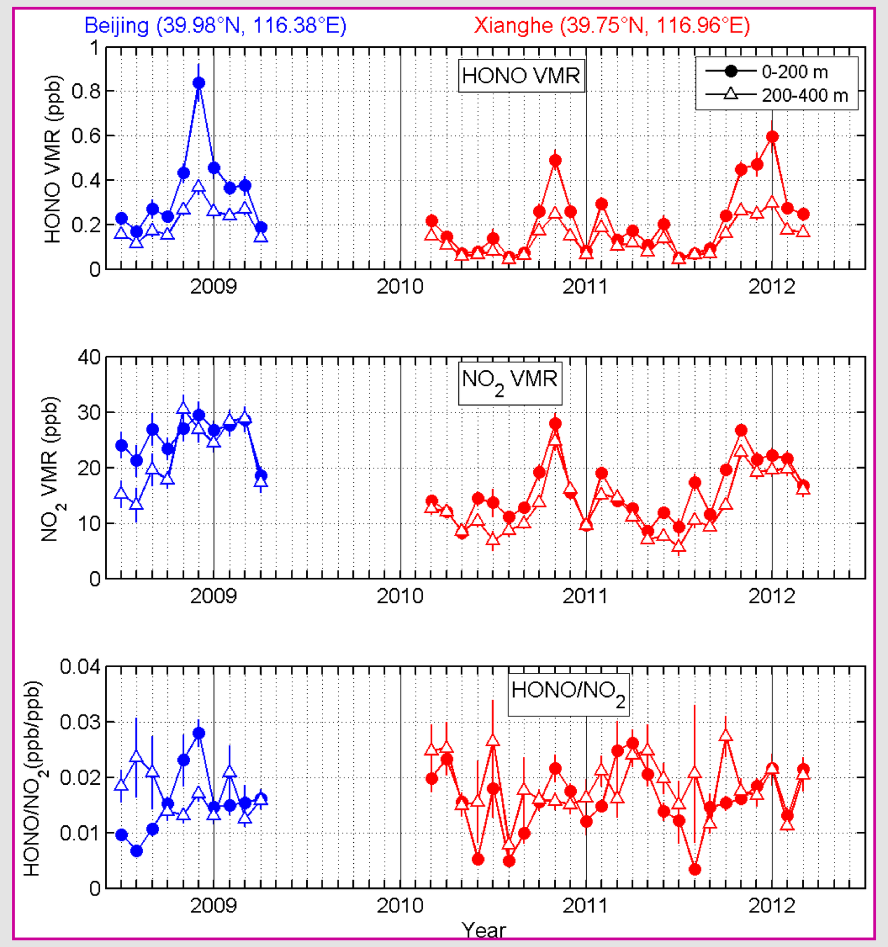
- Example of HONO profile retrieval (Beijing/21-01-2009/69° SZA AM):

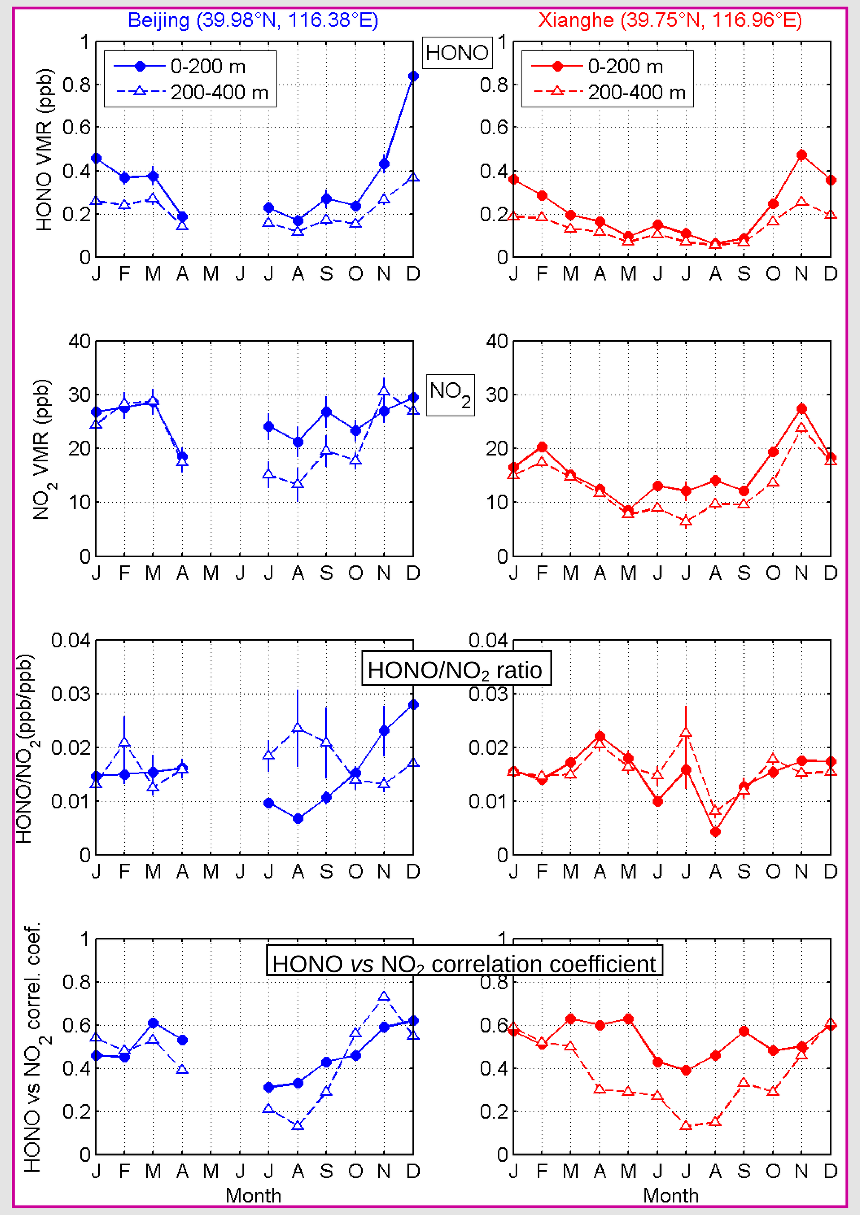


- Comparison to CAREBeijing2006 data (Lu et al., 2012):



VI. SEASONAL VARIATION AT LOCAL NOON

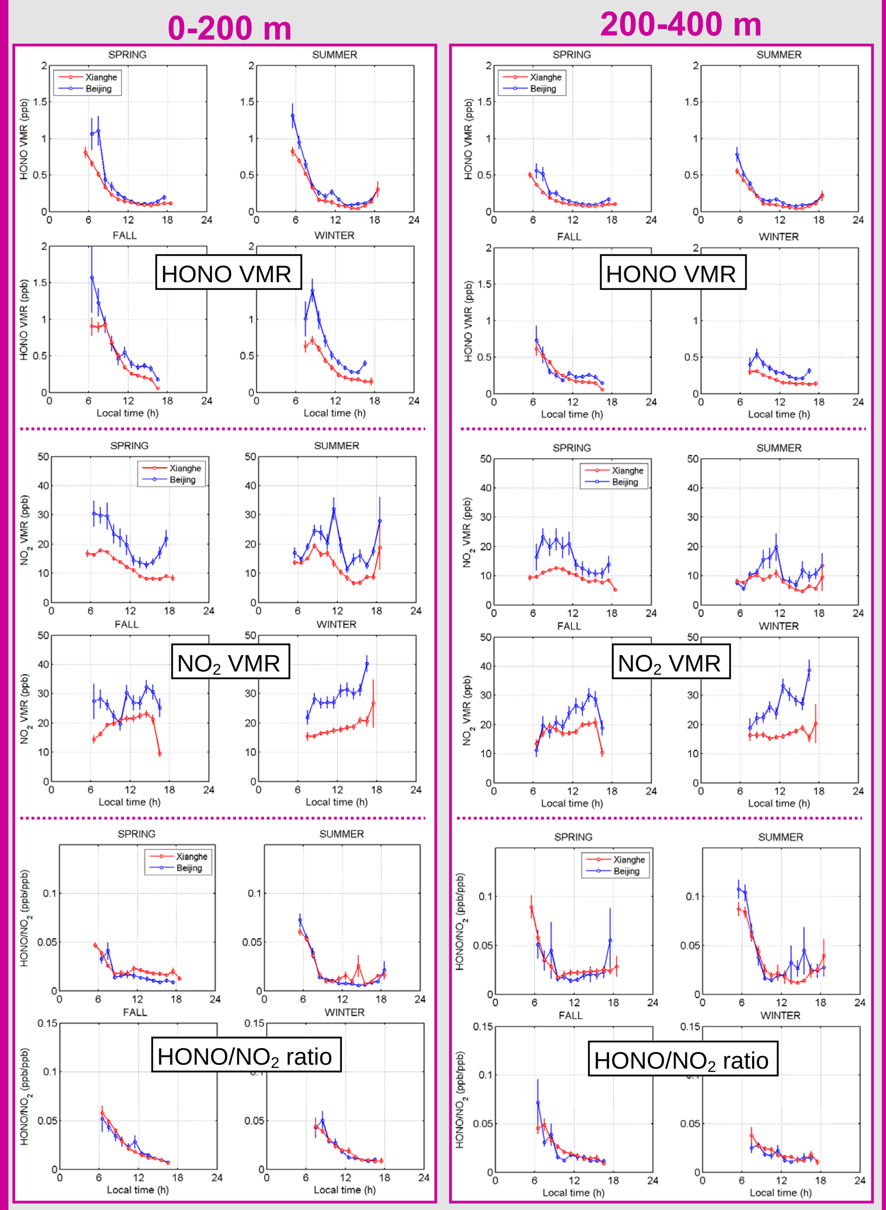




- Larger HONO and NO_2 VMR values at Beijing than at Xianghe, especially in winter in the 0-200m layer.
- Marked seasonality of the HONO VMR (lower values in summer than in winter), especially in the 0-200m layer; more likely related to the more efficient photolysis of HONO in summer and to dilution effect (BLH significantly larger in summer than in winter).
- HONO VMR values in the 0-200m and 200-400m layers are similar in summer, also due to dilution effect.
- The HONO/NO_2 ratio, which is often used to indicate the heterogeneous conversion efficiency of NO_2 to HONO, ranges in average from ~0.003 to 0.03 at both stations. These values are consistent but at the lower limit with respect to those observed in many field studies (Li et al., 2012). These low values suggest the presence of mostly fresh air masses at both locations.

- Similar HONO/NO_2 ratio values in the 0-200m and 200-400m layers, except at Beijing during the summer/fall period.
- Reasonably good correlation between HONO and NO_2 in the 0-200m layer at both locations, with R values between 0.45 and 0.65, except in summer (R~0.3-0.4). Lower R values with more marked seasonality are observed in the 200-400m layer. These results suggest that the heterogeneous conversion of NO_2 is the major HONO source near the surface, especially in winter.

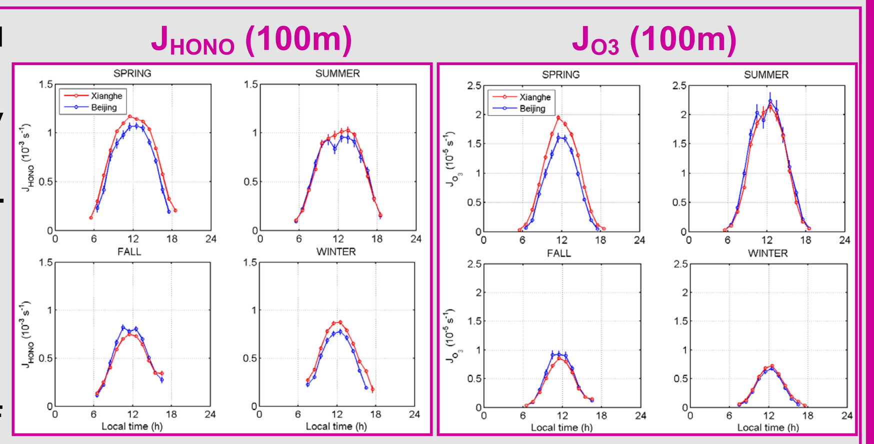
VII. DIURNAL VARIATION



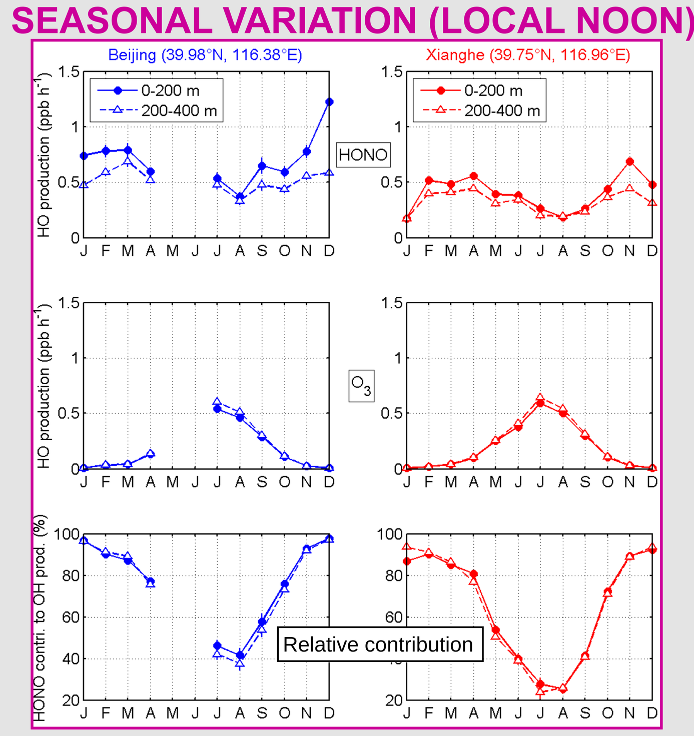
- Larger HONO VMR values in the early morning at Beijing than at Xianghe, especially in the 0-200m layer (more efficient conversion of NO_2 during nighttime at Bejing ?)
- Similar daytime HONO VMR values at both stations, except during the fall/winter period where larger VMR values are obtained at Beijing; could be related to the stronger increase of NO_2 VMR during daytime observed at Beijing during this period and consistent with Ma et al. (2012).
- The HONO/NO_2 ratio shows a marked diurnal cycle which is similar at both stations.

VIII. OH PRODUCTION

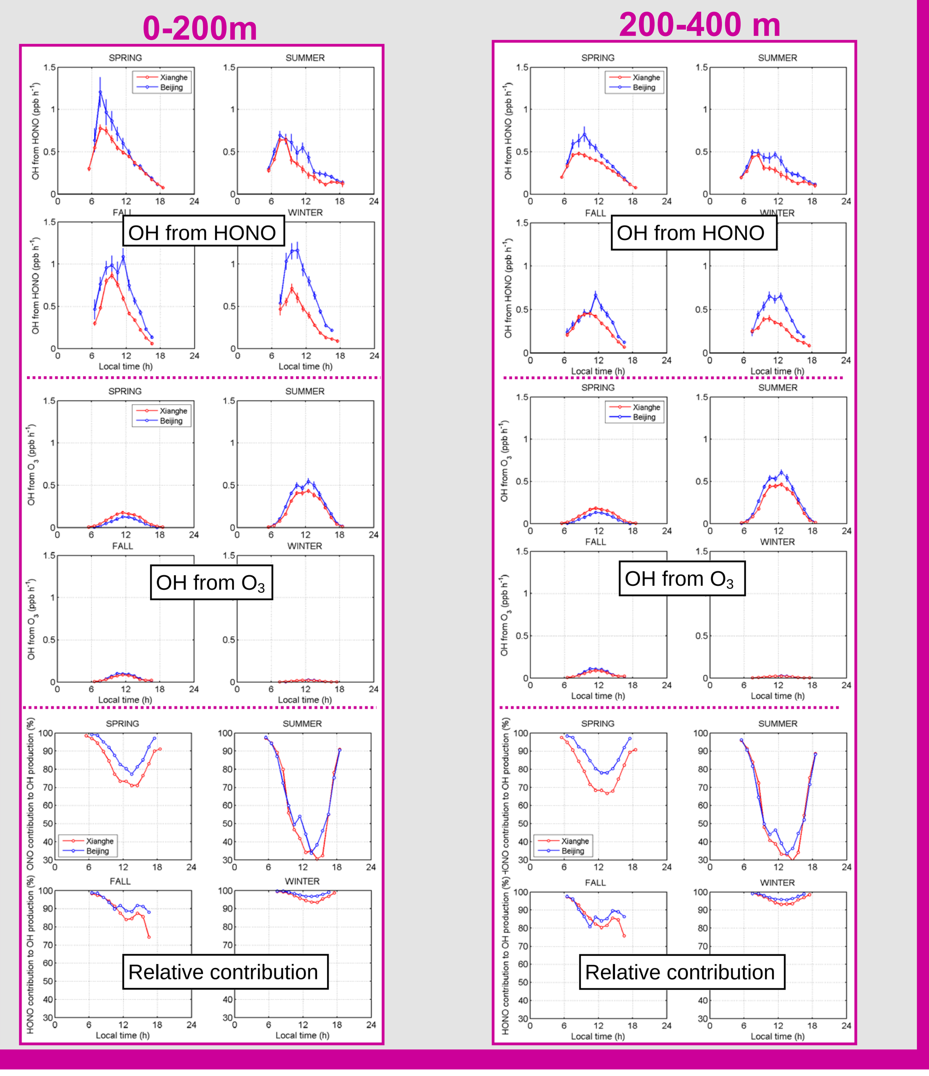
- Production of OH from HONO estimated from retrieved [HONO] and calculated photolysis rate J_{HONO}
- Production of OH from O_3 estimated from assumed 30 ppbv O_3, [H_2O] from ECMWF ERA-Interim, and calculated $J_{O3 \rightarrow O1D}$
- Photolysis rates calculated using the TUV package including the SDISORT radiative transfer code, with
  - No cloud
  - In-situ 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



SEASONAL VARIATION (LOCAL NOON)



DIURNAL VARIATION



- Significantly larger OH production from HONO at Beijing than at Xianghe, especially in the 0-200m layer.
- The HONO contribution to OH production dominates in fall/winter/spring as well as in the early morning during summertime.
- The diurnal variation of the HONO contribution to OH production in the 0-200m layer shows a maximum around 10 am LT, except in spring where it is around 8 am.

IX. CONCLUSIONS

- Four years of MAX-DOAS measurements of HONO in the Beijing area allowed studying for the first time the evolution on a long-term basis of this species in a megacity.
- In the 0-200m layer, retrieved HONO VMR values are most of the time larger in the Beijing city center than at Xianghe (60km East of Beijing), more likely due to a larger NO_2 concentration and a more efficient conversion of NO_2 into HONO in the Beijing city center.
- In the early morning at both stations, HONO VMR shows a strong vertical gradient with values significantly larger in the 0-200m layer than in the 200-400m layer. This feature is also observed at local noon, especially during the fall/winter period where the BLH is the lowest.
- The HONO VMR diurnal cycle in the 0-200m layer shows a maximum in the early morning (1-1.5 ppbv at Beijing and 0.6-0.8 ppbv at Xianghe) then a decrease to 0.1-0.3 ppbv around local noon. This diurnal cycle is similar to the one observed by Li et al. (2012) during the PRIDE-PRD2006 campaign.
- A good correlation (R~0.45-0.65) between HONO and NO_2 VMR is obtained at both stations in the 0-200m layer, suggesting an efficient conversion of NO_2 into HONO close to the ground.
- At both stations and altitude levels, HONO is the main contributor to the OH production, except in summer around local noon where the contribution of O_3 dominates.
- The diurnal cycle of the OH production from HONO shows a maximum in the morning (between 8 and 11 am). In the 0-200m layer, the OH production form HONO is also significantly larger at Beijing (up to 1.2 ppbv h^{-1} observed in spring) than at Xianghe (up to 0.8 ppbv h^{-1} observed in fall). The shape of this diurnal cycle is qualitatively similar to the one observed in Southwest Spain by Sörgel et al. (2011). However, the maximum of OH production from HONO was significantly lower there (0.18 ppbv h^{-1}).
- Modelling studies could certainly help to go one step further in the interpretation of our results.

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