In situ monitoring of atmospheric nitrous acid based on multi-pumping flow system and liquid waveguide capillary cell

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ABSTRACT

In the last four decades, various techniques including spectroscopic, wet chemical and mass spectrometric methods, have been developed and applied for the detection of ambient nitrous acid (HONO). We developed a HONO detection system based on long path photometry which consists of three independent modules i.e., sampling module, fluid propulsion module and detection module. In the propulsion module, solenoid pumps are applied. With solenoid pumps the pulsed flow can be computer controlled both in terms of pump stroke volume and pulse frequency, which enables the attainment of a very stable flow rate. In the detection module, a customized Liquid Waveguide Capillary Cell (LWCC) is used. The customized LWCC pre-sets the optical fiber in-coupling with the liquid wave guide, providing the option of fast startup and easy maintenance of the absorption photometry. In summer 2014, our system was deployed in a comprehensive campaign at a rural site in the North China Plain. More than one month of high quality HONO data spanning from the limit of detection to 5 ppb were collected. Intercomparison of our system with another established system from Forschungszentrum Juelich is presented and discussed. In conclusion, our instrument achieved a detection limit of 10 pptV within 2 min and a measurement uncertainty of 7%, which is well suited for investigation of the HONO budget from urban to rural conditions in China.

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Introduction

In the early 1970s, the troposphere was finally understood to be chemically reactive, and the major chemical driver was proposed to be the OH radical (Levy, 1971), of which high OH concentrations were maintained by the photolysis of O3 and the catalytic oxidation of VOCs through NO. One decade later, nitrous acid (HONO) was unambiguously identified and recognized to be a potentially important precursor of OH in the troposphere (e.g., Perner and Platt, 1979; Platt et al., 1980) due to its fast photolysis reaction (R1) in the near UV.

HONO + hv(λ > 420nm) → OH + NO  (R1)

Since then, HONO has received significant global attention in the establishment of tropospheric chemistry, and extensive field studies were thus performed to determine its ambient

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concentrations in a variety of geophysical areas; lab studies were also conducted to explore its production and destruction mechanisms. Progress in achievements in both field measurements and laboratory studies of the HONO budget in 1990s and 2000s was reviewed for example by Calver et al. (1994); Lammel and Cape (1996) and Kleffmann (2007).

In contrast to its atmospheric importance, the source of HONO in the troposphere is still quite a mystery in a variety of geophysical areas such as urban, rural, forest and mountain areas, the residual layer, etc. According to the available kinetic studies of HONO production mechanisms in the lab, it has been shown that the HONO can be produced from the oxidation of NO by OH (R2); or the reduction of NO2 through both gas phase reactions (e.g., R3 (Stockwell and Calvert, 1983), R4 (Li et al., 2008a)) and heterogeneous reactions (e.g., R5 (Finlayson-Pitts et al., 2003), R6 (Stemmler et al., 2006)).

\[\text{NO} + \text{OH} + \text{M} \rightarrow \text{HONO} + \text{M} \quad \text{(R2)}\]

\[\text{NO}_2 + \text{HO}_2 \rightarrow \text{HONO} + \text{O}_2 \quad \text{(R3)}\]

\[\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{OH} \quad \text{(R4)}\]

\[2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \quad \text{(R5)}\]

\[\text{NO}_2 + \text{HC}_{\text{red}} \rightarrow \text{HONO} + \text{HC}_{\text{ox}} \quad \text{(R6)}\]

Moreover, the reduction of higher oxidation state nitrogen compounds such as HN03 (Zhou et al., 2002) and nitro-aromatics (Bejan et al., 2006) to HONO by solar radiation was also proposed. Nevertheless, all the HONO formation mechanisms based on reduction of NO2 and higher oxidation state nitrogen compounds were either not well defined or not important under real atmospheric conditions.

Due to the lack of knowledge on the ambient HONO budget, HONO chemistry is still not correctly represented in both regional or global transport models, which introduces big uncertainties for diagnosis or the prediction of radical concentrations therein. Nevertheless, exploration of HONO chemistry in the troposphere is still difficult since the accurate and precise measurement of HONO is challenging work due to its high surface reactivity and low ambient concentrations (daytime concentration at about the hundred pptV level). In addition, accurate and precise measurements of its major precursors and reaction partners such as NO, NO2, OH, HO2, aerosol, etc. are also difficult and some are even more challenging.

In the last four decades, various techniques including spectroscopic methods, wet chemical methods and mass spectrometric methods, have been developed and applied for the detection of ambient HONO concentrations. The first successful technique for the detection of HONO was the differential optical absorption spectroscopic (DOAS) method (e.g., Perner and Platt, 1979; Aliche et al., 2003; Qin et al., 2009). This method is direct and free of interference in principle. However, the HONO detection limit by DOAS is around several hundred pptV for typical aerosol conditions and a light path of 1 km. This high detection limit and large sample volume are the two major drawbacks that have restricted its role in exploring daytime HONO chemistry. To overcome these two major drawbacks of DOAS, wet chemical methods like the denuder system (DS) (e.g., Slanina and Wyers, 1994) were developed. Nevertheless, the DS method is not specific enough for HONO; a significant correction for interference produced by NO2, NO+SO2, etc. is required, and most of the time this correction is very difficult. In China, the DS method has been frequently applied in several intensive field measurements conducted in the Pearl River Delta and Beijing, which gave the first view of the ambient HONO concentrations therein (e.g., Su et al., 2008a, b; Dong et al., 2012; Yang et al., 2014). The most successful technique so far developed for ambient HONO measurement is the azo-dye derivatization of HONO followed by detection with long-path absorption photometry, namely, LOPAP (Heland et al., 2001; Kleffmann et al., 2006). The HONO interference produced from reactive nitrogen compounds is firstly suppressed by acidic absorption solutions and secondly corrected by a second channel. The HONO interference determined in this technique can be also corrected by a denuder system serving as a dynamic zero (Zhou et al., 2011). In recent years, the cavity enhanced-spectroscopic technique (CEAS) for measuring HONO was developed and demonstrated under chamber environments (e.g., Gherman et al., 2008). Since this technique provides direct and absolute HONO measurement like DOAS while having good sensitivity and spatio-temporal resolution, its potential application to ambient HONO concentration and flux measurements as a leading technique is expected. Another technique, namely, the chemical ionization mass spectrometric technique (CIMS), has also been recently demonstrated to be able to detect HONO with high sensitivity and spatio-temporal resolution (Roberts et al., 2010). It is worth noting that peroxy nitrate acid (HONO) was suspected to be an interference of HONO for this technique (Legrand et al., 2014). There have also been a number of other techniques such as tunable diode laser spectroscopy (TDLAS) (Li et al., 2008b), photo-fragmentation/laser induced fluorescence (PF/LIF) (Liao et al., 2006), and thermal dissociation chemiluminescence (TDC) (Pérez et al., 2007), that have been tested for ambient HONO measurement.

Recently, intensive measurements in China were conducted in three Chinese mega-city areas i.e., the Pearl River Delta, Yangtze River Delta and North China Plain. Different techniques were used in these studies and strong unknown HONO sources were determined (as shown in Table 1). As briefly reviewed above, by considering the measurement sensitivity, selectivity, and spatio-temporal resolution of all the available techniques for ambient HONO measurements, we believe that LOPAP, CEAS and CIMS will be the three ideal candidate techniques to be applied in future field studies under various environments. As a continuous effort in developing a HONO measurement instrument based on a wet chemical method, we decided to further develop a PKU-LOPAP system based on our previously developed gas and aerosol collector (GAC, e.g., Dong et al., 2012) and stripping coil-ion chromatograph (SC-IC, e.g., Cheng et al., 2013) systems. In the present paper, we will first introduce our newly developed LOPAP system, which features two improvements over versions previously reported by other groups: one is the application of Solenoid Operated Micro-Pumps, the other is the application of commercialized Liquid Waveguide Capillary Cell (LWCG); secondly, we will
present two measurements demonstrating our new LOPAP system in urban and rural environments in the North China Plain area, with high sensitivity and relatively high time-resolution measurement of HONO.

### 1. PKU-LOPAP instrument

#### 1.1. Experimental setup and new modifications

**1.1.1. Measurement principle**

The measurement of nitrous acid in the PKU-LOPAP (Peking University Long Path Absorption Photometer) instrument is achieved by a Griess colorimetric method (Saltzman, 1954), which is also a widely used method to determine nitrite concentrations in waters and foods as well as ambient NO2 concentrations. The exact recipe of the chemical reactions follows the reactions described by Heland et al. (2001). We used 60 mmol/L sulfanilamide (SA) in 1 mol/L HCl as R1 to strip the ambient HONO into a diazonium salt (see reaction R7), and then 0.8 mmol/L N-(1-naphthyl) ethylenediamine dihydrochloride (NEDA) as R2 was added to make the final azo-dye product (see reaction R8). The color development time for R2 is about 2 min (Shinn, 1941) which more or less defined the fastest response time that can be achieved by our method.

\[
\text{SA} + \text{HONO} + \text{H}^+ \rightarrow \text{SA} \cdot \text{N}_2^+ \quad (R7)
\]

\[
\text{SA} \cdot \text{N}_2^+ + \text{NEDA} \rightarrow \text{SA} - \text{N} = \text{NEDA} \quad (R8)
\]

**1.1.2. Experiment setup**

The experimental setup of our LOPAP instrument is shown in Fig. 1. According to the new advances in LOPAP techniques (Kleffmann et al., 2006; Häseler et al., 2009) and fast developing techniques in the field of flow analysis (e.g., Santos et al., 2007; D’Sa et al., 1999), we recognized that the new generation of LOPAP instruments should fit three requirements i.e., modular configuration, easy operation, and simple control and maintenance. Following these guidelines, we designed our instrument to consist of three independent modules i.e., the sampling module, the fluid propulsion module and the detection module. The central part of the sampling module is a glass coil reactor, which is an open glass tube (inner diameter 2 mm, 18 cm long) coiled in three spiral turns (coil diameter 20 mm). At the beginning of this coil, there is a flow manifold to mix the ambient air flow and the stripping solutions. At the end of this coil, it is further connected to a gas–liquid separator. In our setup, two such coils were connected sequentially and enclosed in a double wall glass cylinder so that the coils could be temperature controlled with cycling water. The fluid propulsion module includes an array of eight fixed-displacement diaphragm micro-dispensing solenoid micro-pumps (Bio-Chem Valve Inc., Boonton, NJ, USA) to drive and regulate the liquid flow, and a diaphragm air pump (KNF Neuberger, Inc., Freiburg, Germany) with a mass flow controller (Bronkhorst High-Tech B.V, Ruurlo, Netherlands) to control the air flow. Two mixers, debubblers, filters and several chambers that host the Griess reagents are also included in this module. The detection module consists of two LEDs (Ocean Optics), two LWCCs (World Precision Instrument, FL, USA), and two spectrometers (Ocean Optics, FL, USA) for the long path photometry detection. The detection module was temperature-controlled by air-conditioning of the field containers or laboratories. Currently, both the fluid propulsion module and detection module can be computer controlled.

**1.1.3. Highlights of new modifications**

The major modification of our setup compared to previous LOPAP setups as reported by Heland et al. (2001), Kleffmann et al. (2006), Häseler et al. (2009) and Cheng et al. (2013) is the replacement of the peristaltic pumps with solenoid pumps. According to Lapa et al. (2002), Santos et al. (2007) and Pérez-Forrest et al. (2009), we acknowledged that the use of solenoid pumps could be a significant improvement for flow injection analysis compared to peristaltic pumps. The flow of peristaltic pumps cannot be controlled very precisely due to the aging of the transmission lines, and eventually the lines have to be changed from time to time, which requires a lot of maintenance work. In contrast, with solenoid pumps the pulse flow can be computer controlled both in terms of pump stroke volume and pulse frequency, which enables the attainment of a very stable flow rate (nevertheless, routine calibrations are still required, as we will explain in the field application discussion). In addition, the performance of the solenoid pumps should be stable for years. In short, by using the solenoid pumps, we can approach a more stable and automatic LOPAP instrument. In addition, the variation in
flow rate during the ON/OFF switching of the solenoid pump generates greater turbulence in the solutions than that caused by the pulsating flow delivered by the peristaltic pump, which results in fast and efficient mixing of the air sample and Griess reagent. The other modification of our setup is the use of the customized LWCC manufactured by World Precision Instrument Inc., which offers a versatile path length between 2 and 500 cm. The customized LWCC pre-sets the optical fiber in-coupling with the liquid wave guide, providing us the option of fast startup and easy maintenance of the absorption photometry.

1.2. Characterization and optimizations

1.2.1. Setup of the flow manifold

The fluid propulsion system is designed by mathematical estimation of the reaction time (ca. 2 min) required for the diazonium salt and NEDA. The transmission line between the sampling module and the mixing point of NEDA is kept as short as possible. After the mixing point of NEDA, we used a combination of transmission line, debubbler and particle filter to achieve the required mixing time, and finally the colored azo dye is delivered through the LWCC detection module. The response time-scale of the flow manifold is characterized by a transient HONO concentration pulse generated by quick switching (about 5–10 s) between the ambient air sampling and the high purity N₂ gas for different liquid flow rates (0.5, 0.4, and 0.3 mL/min) of the Griess reagents. The response time of the flow manifold was calculated from 10% of the full signal to 90%. Different liquid flow rates for the Griess reagents only make a slight difference in the response time of the flow manifold. Our flow manifold’s response time is about 2 min if we choose 0.4 mL/min.

1.2.2. Detection sensitivity

The detection of the azo dye quantitatively derived from nitrous acid is based on well-established UV/Vis spectrophotometry. However, we used a liquid waveguide (100 cm, 250 cm) instead of the traditional cuvette (1 cm) as the absorption cell. By this means, the measurement sensitivity of the target species was amplified by a factor of several hundred times according to the Lambert–Beer law. In principle, our detection sensitivity in the liquid phase is the product of the absorption coefficient of the Azo dye at the measurement wavelength and the absorption light path.

LED lamp spectra and absorption spectra (referred to a zero calibration performed by injection of high-purity N₂) of Azo dye for 1 ppb nitrite absorption spectra are shown as Fig. 2. It can be found that the derived azo dye showed its maximum absorption around 544 nm, which is similar to that reported by Heland et al. (2001). To achieve better measurement accuracy and precision and remove the background absorption, dual-wavelength ultraviolet spectrophotometry is used in the subsequent data analysis (the dark signals were corrected by an on-line linear fit of the spectrum data of 390–400 and 750–800 nm). By this approach, we assume that the background absorption is the same for the measurement and reference wavelengths, and therefore the difference
of the absorbance at both wavelengths can be expressed as Eq. (1),

$$\ln \frac{I_m}{I_r} = (k_m - k_r) \times l \times c$$  \hspace{1cm} (1)

where, $I$ denotes absorption path length, $m$ is defined as measurement and $r$ is reference.

This equation can be further rearranged to Eq. (2) to fit better with experimentally determined parameters.

$$\ln \frac{I_r}{I_m} = k \times l \times c + \ln \frac{I_{0r}}{I_{0m}}$$  \hspace{1cm} (2)

where, $k$ is the absorption coefficient of the azo dye, $l$ is the length of LWCC and $c$ is the concentration of nitrite.

For our experimental setup, we chose the integrated value from 650 to 660 nm as the reference signal, and the integrated value from 530 to 560 nm as the primary measurement signal. With a gradient of liquid nitrite standard, we determined our instrument sensitivity factor ($k$, absorption coefficient of the azo dye in Eq. (2)) to be $3.0 \times 10^4$ L/(mol·cm) with this analysis algorithm. Since the absorbance determined by the LWCC proved to be linear over a range of 0.0001 to 1.6, the corresponding nitrite measurement range is 0.001–22 ppb in liquid standard with a 100 cm LWCC. The actual dynamic range of the instrument would be slightly worse than the predicted range, mainly due to the noise of the spectrometer.

Calibrating the setup uses nitrite liquid standard from the National Institute of Metrology, China. The standard is prepared shortly before use by serial dilution of the nitrite liquid standard with R1 solution in brown volumetric flasks. During the calibration setup with the nitrite liquid standard, the liquid flow rates were managed to be the same as that for ambient measurements. In particular, a low concentration liquid standard should not be stored for a long time. When new R1 and R2 solutions are prepared, calibration should be carried out on the setup again in order to ensure data quality.

Sulfanilamide (SA) and N-(1-naphthyl) ethylenediamine dihydrochloride (NEDA), which are used for the R1 and R2 solutions we chose, are produced by Sinopharm Chemical Reagent Co., Ltd. instead of MERCK in order to reduce the cost of setup maintenance by a factor of 10. We used the nitrite liquid standard to compare the two kinds of reagent, and found that both had good correlations (Fig. 3).

In order to gain reliable results, we must pay attention to the purity of the water and hydrochloric acid used. The pure water was produced by a Milli-Q system, with conductivity of 18.2 Ω M. The hydrochloric acid is another critical reagent, e.g., even analytical grade material would show a significant nitrite signal for baseline measurement. The hydrochloric acid we used is guaranteed reagent grade, which is produced by Sinopharm Chemical Reagent Co., Ltd.

![Fig. 2 - Data analysis of the nitrite derivative absorption spectrum. (a) LED lamp spectra for Milli-Q water ($I_0$) and Azo dye for 1 ppb nitrite standard ($I$), and the background signal ($I_{dark}$) obtained by a linear fit of the data of 390–400 nm and of 750–800 nm. (b) Corresponding absorption spectra of azo dye for 1 ppb nitrite standard ($I$), In($I_0/\ln(I_{dark})/I_{I_{dark}}$). The data window used for $I$ and $I$, is 530–560 and 650–660 nm, respectively.](image)

![Fig. 3 - Comparison of the calibration results with R1 (sulfanilamide) and R2 (N-(1-naphthyl) ethylenediamine dihydrochloride) from MERCK or from Sinopharm.](image)
1.2.3. Sampling efficiency

The sampling efficiency of a coil reactor is generally determined by the geometry (e.g., aspect ratio of coil tube diameter to coil diameter), gas and liquid flow rates, the nature of the liquid flow, and concentration of the target gases. In the ideal case, we expect to reach maximum sampling efficiency with the smallest liquid flow and shortest coil tube, which means we can achieve the highest sensitivity for the smallest air-liquid contact time.

The sampling efficiency ($\gamma$) of our LOPAP coil sampler was determined experimentally in the lab. Stable and high purity HONO gases were generated by a HONO generator (Kleffmann et al., 2004) and then sampled by two identical tandem coil reactors. Our HONO generator is an improvement of an earlier bubbling solution to obtain HONO. The ionization constant of nitrite is $4.5 \times 10^{-4}$ at 25°C, and when pH < 3, nitrogen will be present as nitrite in the solution. When the HONO concentration is lower than the Henry balance constant, nitrite in the liquid will be released to the air as HONO. HONO was first generated in acidic solution and then carried out by purified N2. The liquid generation module included a stripping-coil reactor, reaction solution and water bath. The stripping-coil is a three-spiral glass coil with a coil diameter of 2 cm (id 2 mm). The reaction solution is a mixture of the nitrite standard and sulfuric acid, with solution pH of ~1 in order to guarantee nitrite will be present in the solution; the concentration of the nitrite standard liquid is 10 ppm, and the solution is kept in a brown glass bottle in water bath at 0°C. A peristaltic pump and 1/16’ PFA-tubing for fluid propulsion are used to transfer the nitrite standard liquid into the stripping-coil, and transfer waste liquid out from the same coil. The carrier gas is high-purity nitrogen, and a mass flow controller is used to control the gas flow into stripping-coil at 2 L/min. The key parameters of the HONO generator are liquid flow rate, concentration of acidic solution, gas flow rate and temperature of acidic solution. The HONO concentration and above key parameters have a positive correlation, and we could change the HONO concentration easily by changing any of the key parameters of the HONO generator.

The sampling efficiency is deduced by the HONO concentrations observed in both coil reactors according to Eq. (3).

$$r = \left(1 - \frac{C_2}{C_1}\right) \times 100\%$$  \hspace{1cm} (3)

where, $C_1$ denotes the concentration of HONO observed in the first coil and $C_2$ denotes that of the second coil.

Due to the fast reactive uptake of HONO by reaction R7, high $\gamma$ was reported to be achieved with a short coil (Kleffmann et al., 2006). We followed this design as described in the Introduction. We optimized the gas flow rate and liquid flow rate by orthogonal array testing experiments, with stable HONO concentrations delivered from our gas phase HONO generator. The gas flow rate was varied between 1 and 1.5 L/min and the liquid flow rate was varied between 0.2 and 0.5 mL/min.

Sampling efficiency changes with the variation of gas and liquid sampling rate, and each measurement period lasted more than 30 min to ensure stable data. Setting the gas sampling rate at 1 L/min is better than 1.5 L/min, giving efficiency higher than 99% in all cases, and stable operation when the liquid flow rate is about 0.4 mL/min. A 1.5 L/min as a sampling gas rate is not the best choice no matter which liquid flow rate is chosen, since its stability and efficiency are lower than that required. According to the above sampling efficiency experiment, we chose 1 L/min as our instrument gas sampling rate, and a liquid flow rate of 0.4 mL/min (Fig. 4).

1.2.4. Detection selectivity

For the setup of our LOPAP system and others, the first coil sampler detects both the HONO and interference signal while the second coil sampler detects the interference signal, which serves as a dynamic zero point. In order to investigate the interference signals, we defined a relative detection sensitivity ($\alpha$) of potential interference gases (NO, NO2, O3, NO2 + O3), $\alpha$, compared to that of HONO.

$$\alpha = \frac{C_1}{C_{HONO}}$$  \hspace{1cm} (4)

We generated different concentrations of NO, NO2, O3 with a dynamic mixer and a Teflon reactor. The determined relative detection sensitivity $\alpha$ values of these potential important interference species are shown as Table 2.

Compared to the results determined by Heland et al. (2001), the response to NO2 is significantly higher in our system, while the others are quite comparable. According to Heland et al. (2001) increasing gas flow rate could reduce the $\alpha$ value of NO2. Nevertheless, we determined in Section 1.2.3 that our best gas sampling flow rate should be 1 L/min and that higher gas flow rate may cause instability in the collection efficiency, which we want to avoid. In addition, the current $\alpha$ of NO2 of our system is reasonably good, given that with an NO2/HONO ratio of 100, the interference signal would be only 15% of the HONO signal per channel, and it can be removed by subtracting the signal of the second channel.
1.2.5. Measurement uncertainty

According to Eq. (5), the measurement accuracy of our LOPAP system is determined by the accuracy of the nitrite (NO$_2^-$) calibration standard (2%, from the manufacturer), the liquid flow rate ($F_l$, 5%), the temperature (T) stability (0.1%), and the gas flow rate ($F_a$, 5%). In total, all these measurement uncertainties accumulated to give a value of 7%. CHONO, C NO$_2^-$, M NO$_2^-$, R, and P denote concentration of HONO, liquid concentration of NO$_2^-$, molecule weight of NO$_2^-$, ideal gas constant and air pressure.

$$C_{\text{HONO}} = \frac{C_{\text{NO}_2} \times F_l \times R \times T}{M_{\text{NO}_2} \times F_a \times P}$$  \(5\)

2. Field application at a rural site in North China Plain

Our PKU-LOPAP was first deployed in a comprehensive summer field campaign conducted at a rural site (Wangdu county, 38.66°N, 115.20°E, in Fig. 5) in the North China Plain in 2014. During this campaign, our instrument was installed in a field container and the sampling inlet was 7 m above the ground. The inlet tube was a 5 m long 1/4′ Teflon tube covered with thermo-isolation materials and aluminum foil. We ran the instrument with an additional drag flow of 4 L/min, and the ambient residence time between the inlet and the stripping coil was about 700 msec. We consider this residence time to be short enough to prevent potential HONO production in the sampling tube. In parallel to our PKU-LOPAP system, Forschungszentrum Juelich also deployed a home-made LOPAP system developed for Zeppelin observations (Häseler et al., 2009; Li et al., 2014); we will denote the Juelich system as FZJ-LOPAP. The FZJ-LOPAP was installed on another container, and its sampling inlet was also 7 m above the ground and 10 m away from PKU-LOPAP. The FZJ-LOPAP set up its sampling coil directly in the outside air and was equipped with a long liquid transport tube. The advantage of this setup is a very short inlet (about 3 cm) but the disadvantage is the 10 min time delay of the ambient sample analysis due to the long liquid transport lines between the sampling coil and the analysis module. The response time of the FZJ-LOPAP was about 3 min while that for PKU-LOPAP was about 2 min. For the comparative analysis in the next section, we used 5 min averaged results from both instruments.

Table 2 – Relative detection sensitivity ($\alpha$) of NO, NO$_2$, O$_3$ and NO$_2$ + O$_3$ in our LOPAP.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\alpha$ (Heland et al., 2001)</th>
<th>$\alpha$ (this study)</th>
<th>Concentrations of the gases</th>
<th>Calibration standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>&lt;0.006%</td>
<td>0.00%</td>
<td>50–150 ppb</td>
<td>97.6 ppm</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.06%</td>
<td>0.15%</td>
<td>50–150 ppb</td>
<td>NO</td>
</tr>
<tr>
<td>O$_3$</td>
<td>&lt;0.004%</td>
<td>0.00%</td>
<td>30–100 ppb</td>
<td>NO$_2$</td>
</tr>
<tr>
<td>NO$_2$ + O$_3$</td>
<td>&lt;0.004% + NO$_2$ interference</td>
<td>0.00% + NO$_2$ interference</td>
<td>80 ppb O$_3$ + 150 ppb NO$_2$</td>
<td>NO$_2$ generator</td>
</tr>
</tbody>
</table>

*a* Haikeyuanchang Practical Gas Co., Ltd.
*b* Beijing Nanfei Co., Ltd.
*c* Thermo Electronics 142i.

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**Fig. 5** – Experimental setup of the PKU- and FZJ-LOPAP systems during the Wangdu field campaign. Upper sub-panel shows the location of the Wangdu field site in North China Plain, color-coded by satellite-observed NO$_2$.
2.1. Results

Fig. 6 depicts the time series of the observed HONO concentrations by PKU- and FZJ-LOPAPs, with the corresponding NO$_2$ concentrations shown as reference. Both LOPAP systems operated smoothly over the whole campaign from 8th June to 8th July. There were a few data gaps for the two LOPAPs caused by calibration operations, instrument maintenance and thunderstorms. The ambient HONO data spans over two orders of magnitude from a few tens of ppt to a few ppb, corresponding to a HONO/NO$_2$ ratio of about 1%–60%. Such a large span of the HONO/NO$_2$ ratio indicated quite distinct HONO production mechanisms present during this campaign, which will be analyzed in a future publication. Interference

Fig. 6 – Time series of observed HONO (a) and NO$_2$ (b) concentrations. (a) Red dots present PKU-LOPAP, and blue dots FZJ-LOPAP.

Fig. 7 – Averaged diurnal profile of the HONO interference signal determined by Channel 2 of PKU-LOPAP. (a) Concentration ratio of Channel 2 to Channel 1; (b) evaluation of the HONO interference with estimated relative detection sensitivity of NO$_2$ and NO$_2$ determined by Channel 2 of PKU-LOPAP.
of the PKU-LOPAP HONO data as characterized by the measurement signal of the second channel is further analyzed in Fig. 7. The interference signals determined by channel 2 were about 1%–10% of that from channel 1, which at times was a significant component needing to be corrected. The diurnal analysis showed that such a correction was more important for daytime periods than at nighttime. Moreover, the interference signals determined by channel 2 could be explained by the observed NO₂ and NO₃ (the sum total of all NOₓ oxidation products determined as the difference between NOₓ (total odd nitrogen) and NO₃) times the relative detection sensitivity factors as derived by Heland et al. (2001). According to this result, the interference from NO₂ and NO₃ were considered to be quantitatively removed. Relatively good correlations for the HONO data observed by these two LOPAP types of instruments were achieved over a large dynamic range of concentration (Fig. 8). For our PKU-LOPAP system, the calibration factor based on the liquid nitrite standard was quite stable, with the reproducibility during the last year of observations being within 6%. However, our data may have additional variability deriving from the change of liquid flow rate of the solenoid operated micro-pumps. The viscosity and acidity of R1 is significantly higher than pure water so that the liquid flow rate cannot be as stable as was designed. We estimated the additional variability from the pumps to be ca. 10%. The FZJ-LOPAP might also have suffered from such a problem, that the liquid flow is more variable than expected, but because of the aging of the tubes used by the peristaltic pump. We performed in-situ testing of both LOPAP systems with our gas phase HONO source as described in Section 1.2.3. We produced HONO concentrations of about 0.5 and 2 ppb. Both LOPAP systems agreed for the two HONO concentrations within 10%. Therefore, the scattering of the two HONO data sets shown in Fig. 8 is not fully explained by the known measurement uncertainties of the two LOPAPs. Moreover, these differences could also be caused by the inhomogeneity of the HONO concentrations at the site, which was generated by the direct HONO emission of the wheat field or the change of solar radiation, etc. We further analyzed the differences of the two instruments on a daily basis. It was found that most of the time there were good correlations between the two instruments within one day except for the data of 24th and 27th June. The regression slope for all the days with high correlations and higher slopes is 1.38. The regression slope for all the days with lower slopes is 0.85. Most of the data with lower slopes were those from 3rd to 8th July. There seems to be an experimental factor or an air mass change which caused this deviation from 3rd July on. As shown by Fig. 9, we also explored the causes of the deviation by examining the functional dependence of the relative difference (\(\beta\)) between HONO concentrations measured by PKU-LOPAP and FZJ-LOPAP

\[
\beta = \frac{\text{HONO}_{\text{PKU}} - \text{HONO}_{\text{FZJ}}}{\text{HONO}_{\text{FZJ}}}
\]

toward HONO, NO₂, j(HONO) and PM₂.₅. It can be found that there were no systematic deviations for different levels of HONO, j(HONO) and PM₂.₅. The negative deviation when the concentration of HONO is higher than 3 ppb is not representative due to the small number of available data points for such concentration levels during this campaign (see Fig. 8). It is worth noting that the j(HONO) also showed the effect of diurnal variations, which means that the difference is not generated by a factor related to the time of day. The zero dependence on PM₂.₅ is also interesting and promising for HONO measurement under high aerosol conditions (20–300 \(\mu g/m^3\)). As was discussed by Kleffmann et al. (2006), the interference of HONO by particles can be either corrected by the two channel approach or is of minor importance. During this campaign, another four HONO instruments were available simultaneously, of which one was a wet-denuder system.
and three were cavity enhanced absorption spectroscopy systems. Among the six instruments, HONO data determined by both LOPAPs were in the same range as that obtained by all of the instruments. More detailed intercomparison for these six HONO instruments will be analyzed in a future publication.

3. Conclusions

Since 2004, nitrous acid has been found to be one of the most important OH primary sources in polluted urban areas in China (Su et al., 2008a, 2008b; Qin et al., 2009; Li et al., 2012; Yang et al., 2014; Hendrick et al., 2014). The investigation of the ROx radical budget in a regional model framework also indicates that an unknown HONO source which supports the observed high HONO concentrations would have a large impact on the simulated aerosols in the developed coastal areas of China (Tang et al., 2015). In a larger theoretical framework, the unknown HONO source mechanism, the unrecognized OH unclassical regeneration mechanism and the undetermined aerosol uptake rates/mechanism of HO2 radical were considered to be the three major sources of uncertainty in the radical budget as well as that of the secondary pollution rates in the mega-city areas in eastern China.

The accurate and precise detection of ambient HONO concentrations is therefore an urgent need for the exploration of secondary pollution at the regional scale in China. At the present stage, ambient HONO measurements at many supersites are still done with wet-denuder systems, which are restricted by the high detection limit and subject to significant interferences from NO2, NO2 + O3, etc. In recent years, LOPAP and CEAS have been considered to be the two best technology concepts available for ambient HONO measurements. As part of continuous efforts in developing wet chemical methods, we have now made an update to the LOPAP experimental concept proposed by Heland et al. (2001). Our new LOPAP system has two notable improvements: one is the application of Solenoid Operated Micro-Pumps, the other is the application of a commercialized Liquid Waveguide Capillary Cell. Solenoid Operated Micro-Pumps could reduce manual operation and
control the liquid flow rate to maintain constant values, which can minimize the system error caused by liquid flow rate. The Liquid Waveguide Capillary Cell, as a commercial product used in our instrument, can solve the air bubble problem, which may affect the signals of the instrument, and different models could be used to satisfy various environmental requirements. Our LOPAP reached a detection limit of about 10 ppt by using a 100 cm LWCC, with a time resolution of 2 min depending on the running conditions. Our LOPAP has been extensively characterized in a laboratory setting for critical interference species like NO₂, NO, O₃, and NO₂ + O₃. Our LOPAP was validated against another well-established LOPAP instrument constructed by Forschungszentrum Juelich (Li et al., 2014) in a summer campaign in the North China Plain in 2014 for about one month of measurements, with relatively good agreement. We therefore conclude that our update of the LOPAP experimental framework has been successful. We plan to apply the updated LOPAP system for the measurement of ambient HNO₃ (Kleffmann, 2007) and HNO₄ (Legrand et al., 2014) with a few modifications or additions.

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