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# 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 waveguide, 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 O<sub>3</sub> 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.



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 NO<sub>2</sub> 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)).



Moreover, the reduction of higher oxidation state nitrogen compounds such as HNO<sub>3</sub> (Zhou et al., 2002) and nitroaromatics (Bejan et al., 2006) to HONO by solar radiation was also proposed. Nevertheless, all the HONO formation mechanisms based on reduction of NO<sub>2</sub> 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, NO<sub>2</sub>, OH, HO<sub>2</sub>, 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; Alicke 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 NO<sub>2</sub>, NO<sub>2</sub> + SO<sub>2</sub>, 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 peroxyxynitrite acid (HNO<sub>4</sub>) 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 (TDLS) (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 (LWCC); secondly, we will

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