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Nitrous acid (HONO) in a polluted subtropical atmosphere: Seasonal variability, direct vehicle emissions and heterogeneous production at ground surface

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HIGHLIGHTS

- Seasonal variation of HONO is reported for the first time in the PRD region.
- Direct emission from vehicles is an important source of HONO during rush hours.
- HONO emission ratios from vehicles positively correlate with freshly emitted BC.
- A low average conversion rate of NO_2 to HONO at ground (0.52% h^{-1}) is derived.

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ABSTRACT

Although nitrous acid (HONO) plays an important role in the chemistry of polluted atmospheres, its atmospheric abundances and sources are still not well understood. This paper reports ambient measurements of HONO taken over four select months in different seasons at a suburban site in Hong Kong. The data were analyzed to elucidate the seasonal characteristics, emission ratios and rates of heterogeneous production. The monthly averaged HONO concentrations ranged from 0.35 ± 0.30 ppbv in late spring (May) to 0.93 ± 0.67 ppbv in late autumn (November). The similar variation patterns of HONO, NO_x, and traffic flow from midnight to rush hours suggest that the HONO concentration was strongly influenced by vehicle emissions. The emission ratios ($HONO/NO_x$) were derived from an analysis of 21 fresh plumes ($NO/NO_x > 0.80$), with the range of 0.5–1.6%. The large variability in the emission ratios is attributed to the reaction of NO_2 on black carbon (BC) emitted from vehicles, based on a strong correlation between the $HONO/NO_x$ and concurrently measured BC. The mean conversion rate of NO_2 to HONO on ground surface during nighttime estimated on nine select days was 0.52×10^{-2} h^{-1}, which is relatively low compared with other reported values. This paper highlights a large variability in vehicle emission ratios and heterogeneous conversions of NO_2 at ground surface. Photochemical models must consider this variability to better simulate the primary sources of HONO and subsequent photochemistry in the lower part of the troposphere.

1. Introduction

Nitrous acid (HONO) has received considerable attention in the past few decades due to its important role in the HO_x cycle (Kleffmann et al., 2005). HONO sources in the atmosphere can be classified into two categories: direct emissions and chemical formation. Direct emissions include the release of HONO from fossil fuel combustion (Kurtenbach et al., 2001) and the microbial activities of soil (Su et al., 2011, 2008b). For vehicular emissions, Kessler (1984) reported $HONO/NO_x$ emission ratios smaller than 0.15% in engines with no catalytic converters, based on the direct sampling of exhaust from a stationary engine. Measurements taken from

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tunnels in Wuppertal, Germany (Kurtenbach et al., 2001) and San Francisco, U.S. (Kirchstetter et al., 1996) yielded ratios of 0.3–0.8% for vehicles equipped with catalytic converters. Similar emission ratios (0.4–0.8%) were observed in fresh traffic plumes at a semi-rural site in Karlsruhe (Kleffmann et al., 2003). A recent study at a highway junction in Houston (Rappenglück et al., 2013) showed a mean emission ratio of as high as 1.7%. The larger emission ratios in this recent study are possibly due to emissions from heavy-duty diesel vehicles in Houston or difference in emission characteristics of newer vehicles compared to older models. This is a need for more studies of HONO emissions in other cities around the world in view of the possible different types of fuel, engines and emission-control devices installed.

The other category of HONO source is chemical formation, including homogeneous (gas-phase) reactions of NO + OH and heterogeneous processes on surfaces (Harrison and Collins, 1998; Longfellow et al., 1999). Laboratory studies have found that HONO can be rapidly formed from the redox reaction of nitrogen dioxide (NO_2) on black carbon (BC) and semi-volatile species (R1) (Ammann et al., 1998; Aubin and Abbatt, 2007; Gutzwiller et al., 2002; Kalberer et al., 1999; Lelièvre et al., 2004; Nienow and Roberts, 2006; Stadler and Rossi, 2000). Although soot particles (or BC) provide a large, active, specific surface area on which NO_2 can be reduced, these surfaces are deactivated rapidly under atmospheric conditions (Aubin and Abbatt, 2007; Khalizov et al., 2010; Rappenglück et al., 2013). Therefore, the reaction rates of R1 can be subject to large variations.

$$NO_2 + \{C-H\}red + surface \rightarrow HONO + \{C-H\}ox \quad \text{(R1)}$$

In addition to soot surfaces, the heterogeneous conversion of NO_2 to HONO on wet surfaces (R2) is a HONO source and is often the dominant source of nocturnal HONO (Kleffmann, 2007). Laboratory results have indicated that the relevant stoichiometry relies not only on NO_2 concentrations, but also on surface area density and water content (Finlayson-Pitts et al., 2003).

$$2NO_2(g) + H_2O(adsorbed) \xrightarrow{surface} HONO(g) + HNO_3(adsorbed) \quad \text{(R2)}$$

The source strengths of this reaction on land surfaces have been evaluated in field studies yielding NO_2-to-HONO conversion rates of $0.88–1.80 \times 10^{-2}\ h^{-1}$ in rural areas (Acker et al., 2005; Alicke et al., 2002, 2003; Wentzell et al., 2010) and $0.43–0.49 \times 10^{-2}\ h^{-1}$ in urban areas (Kleffmann et al., 2003; Lammel, 1999). A recent study at a coastal site in Hong Kong reported a large rate of $3.3 \times 10^{-2}\ h^{-1}$ in air traveling over the oceans (Zha et al., 2014).

Another area of active ongoing research has considered elevated daytime HONO concentrations, which cannot be explained by the known homogenous reaction between NO and OH and the sources just mentioned (Acker and Möller, 2007; Czader et al., 2012, 2013; Li et al., 2012; Qin et al., 2009; Sorgel et al., 2011; Su et al., 2008b; VandenBoer et al., 2013). Several potential photo-enhanced sources have been proposed, including light-dependent heterogeneous reactions of NO_2 on aerosol and ground surfaces, photolysis of HNO_3 absorbed on surfaces, the reaction of excited NO_2 with water vapors and the reaction of NO_2 with $HO_2{}^*H_2O$ (Kleffmann, 2007; Li et al., 2008, 2014; Monge et al., 2010; Wong et al., 2012; Zhou et al., 2011). This topic is a hot topic of continuing research.

Due to the important role of HONO in atmospheric chemistry and air quality, ambient HONO has been measured in many places around the world. Several field studies related to HONO sources and chemistry have been conducted in the Pearl River Delta (PRD) region of China, where rapid industrial and urban development has taken place, and regional air quality has been deteriorating. HONO concentrations of up to 3–4 ppbv have been reported in urban and rural areas of the region during the summer and autumn seasons (Li et al., 2012; Qin et al., 2009; Su et al., 2008a). Heterogeneous conversion of NO_2 to HONO on ground surfaces and the sources/processes that contribute to daytime HONO have also been discussed.

During 2011–2012, HONO and its related parameters were measured at a suburban coastal site in the southern part of the PRD during four select months (one month in each season). This paper presents the findings related to the seasonal and diurnal variations and deduces the emission ratios of HONO to NOx and nighttime heterogeneous conversion rates of NO_2 to HONO from the measurements. A more detailed (modeling) analysis of daytime HONO is presented in a separate work currently in preparation. The present paper provides new data related to the seasonal variation of HONO in South China and offers new information on emission and heterogeneous conversion rates that should be useful in improving the general understanding of HONO sources in different environments.

2. Experiments

2.1. Study site

The study site was located at an air-quality monitoring station in Tung Chung (TC), which is operated by the Hong Kong Environmental Protection Department. The site is located in a newly developed residential area in the northern part of Lantau Island, and is about 3 km south of Hong Kong International Airport (see Fig. 1). The measurement site is 80 m south of the TC Expressway which is the only main road connecting Lantau Island (and the airport) to other parts of Hong Kong. The traffic flow is strongly influenced by flights at the airport, and its daily and monthly variations are very small due to the relatively constant number of flights on most days (see Table 1 and Fig. 2). The numbers and composition of vehicles are shown in Table 1, which indicate that the percentage of diesel and gasoline vehicles is 33% and 67%, respectively. In addition to the main highway, there are several local roads around the site, but the traffic flows are much smaller.

The nearby airport is another local source of air pollutants in TC. A previous study (http://www.hongkongairport.com/eng/csr/environmental-management/DraftAOAQSReport.pdf) suggests that aircraft and vehicular activities at the airport contributed 3%–20% of NO_x and less than 5% of CO, SO_2 and hydrocarbons in the ambient concentrations at TC. Apart from these local sources, transport from main urban areas of Hong Kong (in the east direction) and the Pearl River Delta region (in the northwest direction) can also affect the air quality in TC (e.g., Wang et al., 2003).

The terrain surrounding the TC site is complex, with the Lantau Mountain lying in the south with several peaks of 700–950 m a.s.l. (see Fig. 1) and several buildings of around 100 m tall situating to the northeast and southwest. This complex terrain blocks the regional winds resulting in frequent calm conditions at TC according to on-site measurement of winds.

2.2. Measurement period and meteorological conditions

The measurements were taken in four non-consecutive months: August 3 to September 7, 2011 (late summer); November 1 to December 3, 2011 (late autumn); February 3 to March 9, 2012 (late winter) and May 1–31, 2012 (late spring). Table 2 presents the statistics of meteorological data. Hong Kong is influenced by Asian monsoons, which bring in dry, cold continental air in autumn and winter and wet oceanic air in late spring and summer (Lam et al., 2001; Wang et al., 2005). Compared with historical