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Key Points:

- Strong HONO production in sea-coming air masses
- Air-sea interactions may significantly affect atmospheric chemistry
- Chemical transport models may need to consider HONO production on the sea

Supporting Information:

- Readme
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5

Correspondence to:
T. Wang,
cetwang@polyu.edu.hk

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Large conversion rates of NO_2 to HNO_2 observed in air masses from the South China Sea: Evidence of strong production at sea surface?

Qiaozhi Zha[1], Likun Xue[1], Tao Wang[1], Zheng Xu[1,2], Chungpong Yeung[1], Peter K. K. Louie[3], and Connie W. Y. Luk[3]

[1]Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, China, [2]Environment Research Institute, Shandong University, Jinan, China, [3]Environmental Protection Department, Government of the Hong Kong Special Administrative Region, Hong Kong, China

Abstract Nitrous acid (HONO) plays important roles in tropospheric chemistry, but its source(s) are not completely understood. Here we analyze measurements of HONO, nitrogen dioxide (NO_2), and related parameters at a coastal site in Hong Kong during September–December 2012. The nocturnal NO_2-to-HONO conversion rates were estimated in air masses passing over land and sea surfaces. The conversion rates in the "sea cases" ($3.17–3.36 \times 10^{-2}\,h^{-1}$) were significantly higher than those in the "land cases" in our study ($1.20–1.30 \times 10^{-2}\,h^{-1}$) and in previous studies by others. These results suggest that air-sea interactions may be a significant source of atmospheric HONO and need to be considered in chemical transport models.

1. Introduction

The importance of nitrous acid (HONO) in tropospheric chemistry has been recognized since the 1970s, as it is a key precursor of the hydroxyl radical (OH) [*Perner and Platt*, 1979]; however, the sources of HONO are still not well understood. In addition to known sources such as direct emissions from vehicles [*Kurtenbach et al.*, 2001], gas-phase formation from the OH + NO reaction, and heterogeneous reaction of nitrogen dioxide (NO_2) on surfaces [*Harris et al.*, 1982], recent laboratory and field studies examining the elevated HONO concentrations observed during daytime have proposed several new sources [*Aubin and Abbatt*, 2007; *George et al.*, 2005; *Li et al.*, 2008; *Li et al.*, 2014; *Zhou et al.*, 2003].

The heterogeneous conversion of NO_2 to HONO on wet surfaces (R1) has been identified as a source of atmospheric HONO for some time [*Harris et al.*, 1982]. Laboratory studies have found that the rate of this reaction is first order to NO_2 concentrations and also increases with surface area density and surface water content [*Finlayson-Pitts et al.*, 2003].

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \qquad (R1)$$

Field studies have attempted to determine the source strengths of this reaction on land surfaces based on the observed NO_2-to-HONO conversion rates at night under stable meteorological conditions. During nighttime, the NO_2 heterogeneous conversions on ground surface are thought to be much more important than on the surface of aerosol in the atmosphere because of 1 or 2 orders of magnitude higher surface area density for typical ground compared to aerosol in the shallow nocturnal boundary layer [*Sorgel et al.*, 2011] and in view of strong nocturnal HONO vertical gradient [*Wong et al.*, 2011]. Previous studies have found NO_2-to-HONO conversion rates of $0.43–0.49 \times 10^{-2}\,h^{-1}$ in urban areas [*Kleffmann et al.*, 2003; *Lammel*, 1999] and $0.80–1.80 \times 10^{-2}\,h^{-1}$ in rural areas [*Acker et al.*, 2005; *Alicke et al.*, 2002, 2003; *Su et al.*, 2008; *Wentzell et al.*, 2010]. To the best of our knowledge, there are no published results on the production rates of HONO on the sea, except one field study of HONO in the marine boundary layer (MBL) in Canada [*Wojtal et al.*, 2011] which did not specifically calculate the conversion rates of HONO.

During September–December 2012, HONO and several related parameters were measured at a coastal site in Hong Kong to better understand severe photochemical pollution in southern China during the autumn season [*Wang et al.*, 2009]. We examined the production rates of HONO in air masses passing over land and sea surfaces and found much higher production rates in sea-coming air. The results suggested that the sea may be an important interface for the production of HONO.

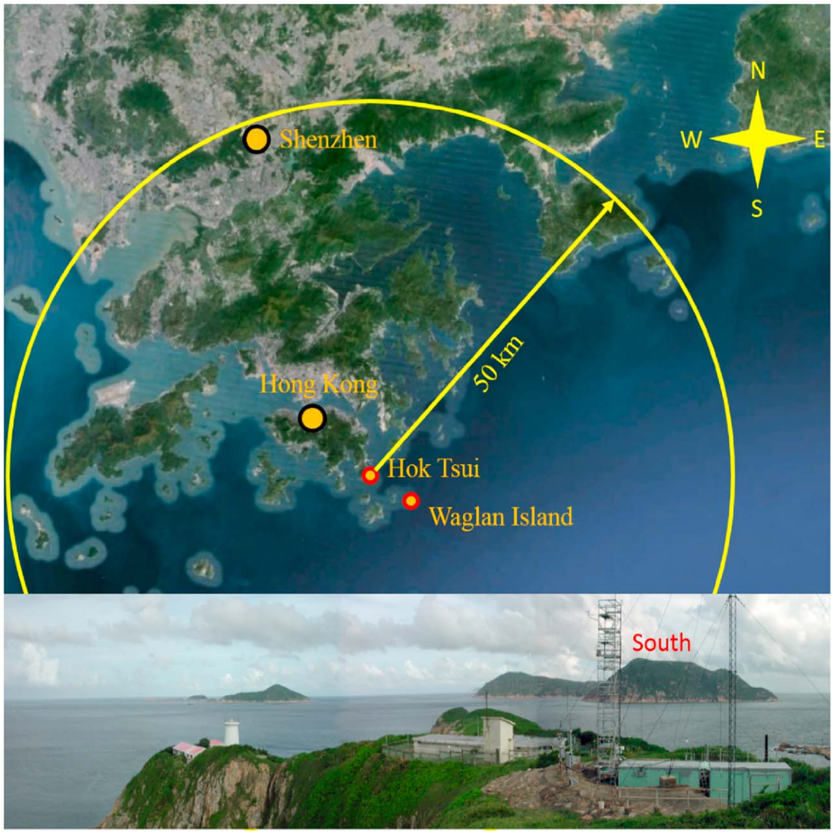

Figure 1. Map from Google Earth showing the observation site in relation to neighboring regions.

2. Experiment

The measurement site was located in a relatively clean coastal area of Hong Kong (Hok Tsui, 22°13′N, 114°15′E) [*Wang et al.*, 2009], approximately 10 km southeast of downtown Hong Kong Island. There were no strong emission sources in the vicinity; the closest source was the international shipping lane about 6 km south of the site. The station was located on a 60 m high cliff and had a 240° sea view; the open sea extended out from northeast to west of the site, which was otherwise surrounded by land (see Figure 1). The field campaign was carried out from 1 September to 19 December 2012.

HONO was measured in real-time using a Long Path Absorption Photometer. The external sampling unit was mounted at a height of 3 m above ground level (agl). This technique was described in detail in *Kleffmann et al.* [2002] and was validated using the differential optical absorption spectroscopy (DOAS) technique in both smog chamber and ambient atmosphere [*Kleffmann et al.*, 2006]. The detection limit of our HONO measurement is 1–2 pptv at a time resolution of 4 min. During the campaign, the baseline of the instrument was checked twice automatically and 2–3 times manually every day by sampling synthetic air from the cylinder, and the calibration of sensitivity was performed every 3 days by sampling 0.01 μg/L and 0.04 μg/L NO_2^- standard solutions. NO and NO_2 were measured with a chemiluminescence analyzer (Thermo Environmental Instruments (TEI), Model 42i) equipped with a photolytic converter (Blue Light Converter, Droplet Measurement Technologies) to reduce NO_2 to NO [*Xu et al.*, 2013]. During the field study, the conversion efficiency was calibrated every 3 days and was found to be stable at around 30%. The detection limit was estimated as 50 pptv for NO and NO_2 at a time resolution of 1 min. Ozone (O_3) was measured by a commercial UV photometric analyzer (TEI Model 49i) and carbon monoxide (CO) by a nondispersive infrared analyzer (Advanced Pollution Instrumentation, Model 300EU) [*Wang et al.*, 2009]. Temperature and relative humidity (RH) were measured by a commercial probe (M. R. Young, Model 41382VC/VF, USA). Wind speed and direction were monitored with a two-axis ultrasonic wind sensor (Gill Instruments, 1405-PK-021, UK), both of which were fixed at a height of 4 m above the ground and had a time resolution of 1 min.

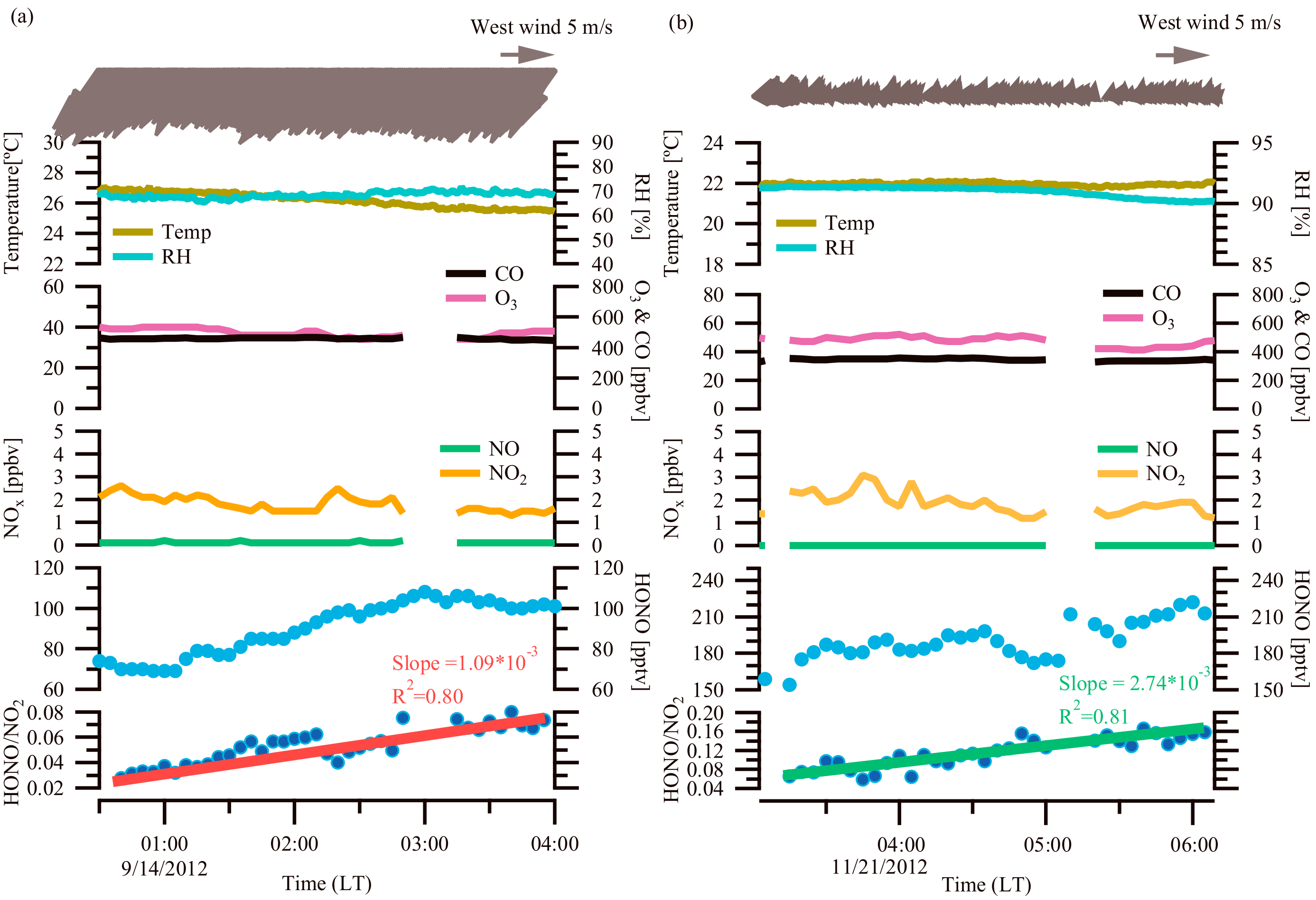

Figure 2. (a) Land case from the night of 13–14 September 2012. (b) Sea case from the night of 20–21 November 2012. Missing data points were due to the instrument's auto calibrations.

3. Results

The weather was primarily sunny and in clear-sky conditions during the study period with an average temperature and RH of 24.3 ± 3.7 (1σ standard deviation) °C and 76 ± 11%, respectively. The mean concentrations of NO, NO_2, and HONO were 0.36 ± 0.79 ppbv, 4.06 ± 3.29 ppbv, and 126 ± 95 pptv. These results indicate relatively clean conditions of the study site.

To investigate the HONO production on land and sea, representative cases were selected using the following criteria. First, only nighttime data were considered so as to rule out complications from daytime photolytic sources. Second, we identified air masses in which HONO concentration showed a steady increase while other gases such as ozone, CO, and NO_x were less variable [*Su et al.*, 2008; *Wentzell et al.*, 2010]; this is to ensure that the increase in HONO was mainly due to production and not change in air masses. Third, 6 h three-dimensional back trajectories computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (version 4.9, model driven by 6-hourly Air Resources Laboratory (ARL) FNL archive data) [*Draxier and Hess*, 1998] indicated air mass passing over land or ocean within the boundary layer (see Figures S1 and S2). Note that the height of the starting location of trajectories was set to 50 m agl (the sampling height was 3 m agl) to minimize the influence of topographical condition. Fourth, on-site winds were also examined: the identified cases with persistent (>3 h) surface winds from NE–W (clockwise) were considered as "sea cases," whereas those with winds from W–NE were considered as "land cases." It should be noted that in the land cases, air masses spent a larger portion of time over land during the 6 h prior to the site but may have also inevitably spent little time over the sea during transport. Using these procedures, six cases (three land cases and three sea cases) were chosen, the NO_2-to-HONO

Table 1. Summary of the "Sea" and "Land" Cases

Surface Type	Date	C_{HONO} (10^{-2} h^{-1})	Duration (h)	Wind Direction	Mean NO_2 Concentration (ppbv)	HONO/NO_2 Increment (10^{-2})
Land	13–14 September	1.30	3.0	NNE	1.79 ± 0.34	4.6
	28–29 September	1.20	5.5	NNE	5.13 ± 0.53	7.2
	4–5 November	1.21	4.8	NNE	2.60 ± 1.13	5.4
Sea	21–22 September	3.36	3.0	SW	1.65 ± 0.42	9.9
	19–20 October	3.17	3.3	SW	1.31 ± 0.48	10.8
	20–21 November	3.29	2.8	SW	2.34 ± 1.80	9.3

conversion rate (C_{HONO}) for each case was calculated and further analyzed (see calculation method in the supporting information).

Figure 2a illustrates a typical land case from the night of 13–14 September 2012. In this case, the surface winds blew continually from the NNE at a high speed of 8–10 m/s. The back trajectory (see Figure S1a) indicated that the air mass had mainly moved above land surface (mainly covered with vegetation, see Figure S3) and only passed over sea surface before reaching the study site. The NO_2 concentrations were ~2 ppbv from 00:30 to 03:30 local time (LT), the HONO levels rose steadily from 69 pptv to ~108 pptv, and the HONO/NO_2 ratios increased from 3.14×10^{-2} to 7.35×10^{-2}. As the urban center of Hong Kong is to the northwest direction, the air mass sampled in this case should not be strongly influenced by Hong Kong's urban emissions. The C_{HONO} was calculated by the regression method as 1.30×10^{-2} h^{-1} ($r^2 = 0.79$). Similar land cases were also identified on the nights of 28–29 September and 4–5 November (see Table 1 and Figure S4) with C_{HONO} values (1.20×10^{-2} h^{-1} and 1.21×10^{-2} h^{-1}) comparable to the first case. We note that the three cases were observed in different months and should therefore be representative of the heterogeneous HONO production on the land surface around the study site. These C_{HONO} values were within the range of $0.88–1.80 \times 10^{-2}$ h^{-1} derived from ground surface in other rural areas [*Acker et al.*, 2005; *Alicke et al.*, 2002, 2003; *Su et al.*, 2008; *Wentzell et al.*, 2010].

Figure 2b shows the time series of HONO and related parameters for a representative sea case on the night of 20–21 November 2012. In this case, the on-site winds were continuously from the southwest (i.e., from the open sea) at a speed of ~2–3 m/s, which is much smaller than the wind speed in land case. However, the back trajectories did not show significant difference in the speed of movement of large-scale air masses in the land and sea cases. An examination of the wind data from another station (Waglan Island), which is 5 km southeast of Hok Tsui and whose data should be more representative of regional winds due to less effect of terrain than at Hok Tui, also indicates comparable regional wind speeds in this case compared to the previous land case. Thus, the reduced winds at Hok Tsui appear to be a localized phenomenon near the site.

In this case, from 03:00 to 06:00 LT, the NO_2 concentrations decreased slightly from 3.10 to 1.18 ppbv, except for several spikes; the HONO levels increased rapidly from the lowest 154 pptv to the highest 222 pptv, and the HONO/NO_2 ratio increased from 6.55×10^{-2} to 16.85×10^{-2}, giving a C_{HONO} of 3.29×10^{-2} h^{-1} ($R^2 = 0.81$). Similar open sea cases were also observed on the nights of 21–22 September and 19–20 October (see Table 1 and Figure S5), with comparable C_{HONO} values (3.20×10^{-2} h^{-1} and 3.36×10^{-2} h^{-1}). The large conversion rate over the sea can also be inferred from another field study using DOAS technique on Saturna Island, Canada [*Wojtal et al.*, 2011]. Based on their measurement data, we calculated a conversion rate of 3.06×10^{-2} h^{-1} there. In analysis of measurements near Lake Erie, Canada, *Wentzell et al.* [2010] derived the conversion rates in air masses coming from land as well as mentioned higher values in air masses coming over the lake with no detailed result given.

4. Discussion and Implications

Our results indicate that the conversion rates of NO_2 to HONO in air masses passing over the sea are almost 3 times the rates in air passing over the land. A *T* test confirmed that the difference is statistically significant (*P* value < 0.01). As air masses in the land cases may have also spent a small portion of time over the sea before arriving at the study site, the actual conversions on land surface may be lower than our values. It is difficult to explain the apparent larger conversion rates on the sea than on the land. On one hand, much more abundant water of the sea surface may favor a faster production of HONO; on the other hand, the alkaline condition of the sea water would retain acidic HONO. Could it be due to enhanced production of HONO in the sea surface microlayer (first 1000 μm of the sea surface) [*Donaldson and George*, 2012] or to the difference in micrometeorology above land and sea? Clearly, more measurements of HONO and better characterization of boundary layer dynamics in the polluted MBL are needed to verify our results and to find out the reason(s) for the high conversion rates in the air mass coming from the sea.

Nonetheless, our findings have an important implication. Current global and regional chemical transport models that consider the heterogeneous production of HONO on the ground surfaces either do not distinguish sea and land [*Elshorbany et al.*, 2012] or do not consider the HONO formation on the sea at all [*Goncalves et al.*, 2012; *Sarwar et al.*, 2008; *Zhang et al.*, 2012]. Our study indicates that HONO may be produced at a faster rate on the sea; if this finding is confirmed and applicable to other regions, current chemical transport models may need to consider HONO formation on the sea and to adopt different parameterizations for reactions on land and sea.

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