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# MEASUREMENT OF NITROUS ACID (HONO) AND THE IMPLICATIONS TO PHOTOCHEMICAL POLLUTION

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**Department of Civil and Environmental Engineering** 

# MEASUREMENT OF NITROUS ACID (HONO) AND THE IMPLICATIONS TO PHOTOCHEMICAL POLLUTION

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A thesis submitted in partial fulfillment of the

requirements

for the Degree of Master of Philosophy

**March 2015** 

### **CERTIFICATE OF ORIGINALITY**

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it produces no material previously published or written, nor material that has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text.

ZHA Qiaozhi

### Abstract

Nitrous acid (HONO) plays significant roles in atmospheric chemistry; it can be the dominant source of hydroxyl radical (OH) in urban area after early morning and an important daytime source of nitric oxide (NO) in rural and remote regions. Despite its importance, the formation mechanism of HONO is not completely understood. Many field HONO measurements have been conducted in different locations of the world since 1979, which have improved the understanding of HONO formation in terrestrial environment. However, there have been very few HONO measurements in the marine boundary layer (MBL). Considering the fact that many cities are located in the coastal regions, it is of great importance to know the abundance and sources of HONO in the MBL environment and to investigate the impact of HONO on photochemistry. Information on ambient HONO concentrations are also needed to validate and improve current global and regional chemical transport models (CTMs).

In this study, continuous measurements of HONO were performed using a long-path absorption photometer (LOPAP) instrument at a coastal background site (Hok Tsui) in Hong Kong during September-December 2012. Meteorological parameters and other related pollutants such as nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), total reactive nitrogen (NO<sub>y</sub>), ozone (O<sub>3</sub>) and carbon monoxide (CO) were also measured. Analysis of the overall data and the selected cases reveal following

major findings:

An averaged diurnal pattern with two HONO peaks is observed at Hok Tsui, which is different from the typical HONO pattern (with only a single nighttime peak). The first peak (with a mean concentration of 0.155 ppbv) that occurs before dawn is typical and should be due to the accumulation of nocturnal HONO; the second peak with even higher HONO level (mean concentration = 0.160 ppbv) shortly after sunrise is quite unique and should be related to strong formation of HONO during daytime.

Nocturnal HONO formation is investigated by estimating and comparing the NO<sub>2</sub>-to-HONO conversion rates (C<sub>HONO</sub>) in sea-coming air masses, land-coming air masses, and other studies. The selected air masses are distinguished using back trajectory model (hybrid single particle lagrangian integrated trajectory, HYSPLIT model) and on-site wind. The C<sub>HONO</sub> in the "sea cases" ( $3.17 - 3.36 \times 10^{-2} h^{-1}$ ) were significantly larger than rates determined in "land cases" ( $1.20 - 1.30 \times 10^{-2} h^{-1}$ ) and other studies ( $0.80 - 1.80 \times 10^{-2} h^{-1}$ ).

Daytime HONO production, including both "known" and "unknown" sources, are examined. The source strength of presently known daytime sources is too small to explain the measured daytime peak, suggesting the presence of the "unknown" daytime source. The strength of the unknown source (up to 0.2 pptv/s), which is estimated using a photostationary state (PSS) method, is 4 - 8 times larger than the strength of the known sources (homogeneous reaction ( $NO + OH \rightarrow HONO$ ) and heterogeneous reaction ( $2NO_2 + H_2O \xrightarrow{surface} HONO + HNO_3$ )). The unknown source also shows moderate correlation with NO<sub>2</sub>, and the correlation (R = 0.57) is further enhanced by adding the term of solar radiation, implying that this unknown daytime HONO source may be a photo-enhanced heterogeneous process. HONO is found to be a more important source for OH throughout the entire daytime at Hok Tsui, compared to the contribution from ozone photolysis which is another major source of OH.

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### **Chapter 1 Introduction**

There has been an increasing interest of atmospheric nitrous acid (HONO) since it was recognized as a key precursor of hydroxyl radical (OH) in 1970s [*Perner and Platt*, 1979]. OH is an extremely reactive compound that plays a central role in photochemistry; it is the major remover of volatile organic compounds (VOCs), methane (CH<sub>4</sub>), and the only loss path for chemicals that do not react or react very slowly in the troposphere (e.g. chlorofluorocarbons (CFC's), nitrous oxide (N<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>)) [*Heard and Pilling*, 2003]. Results of recent studies show that up to 80 % of OH production is contributed by HONO [*Acker et al.*, 2006; *Alicke et al.*, 2003; *Kleffmann et al.*, 2005; *X Li et al.*, 2014], which makes it at the heart of the understanding of OH formation and photochemistry.

Loss mechanism of HONO is quite clear: apart from the physical removal processes (dry and wet depositions), HONO can be removed fast (lifetime of  $\sim$  20min during daytime) by photolysis reaction of (R1.1) and reaction with OH (R1.2).

$$HONO + hv(320nm < \lambda < 400nm) \rightarrow NO + OH$$
(R1.1)

$$HONO + OH \rightarrow NO_2 + H_2O$$
 (R1.2)

The source of HONO is much more complex than its loss mechanism. Though understanding of HONO sources has been significantly enhanced, there is still incomplete understanding of the sources of HONO in both daytime and nighttime HONO formation.

Daytime gas-phase homogeneous between OH NO reaction and  $(OH + NO \xrightarrow{M} HONO)$  used to be considered as the largest HONO source after sunrise. However, more and more recent studies have observed daytime HONO peaks, and source strengths of the known homogeneous reaction are too weak to explain the measured daytime HONO levels [Acker et al., 2006; Kleffmann et al., 2005; Michoud et al., 2014; Wong et al., 2012]. An increasing number of both lab experiments and field measurements have been conducted, and several daytime HONO sources have been suggested, but with no consensus reached [George et al., 2005; X Li et al., 2014; Zhou et al., 2007].

Nocturnal HONO formation is also subject to considerable research. Heterogeneous conversion of  $NO_2$ HONO humid surfaces to on  $(2NO_2 + H_2O \xrightarrow{surface} HONO + HNO_3)$  is recognized as the dominant HONO source that contributes the most to nocturnal HONO [Sorgel et al., 2011a]. The source strength of this heterogeneous reaction is first order to NO<sub>2</sub> concentration, and increases with the surface area density (S/V) and surface water content. Nocturnal NO<sub>2</sub>-to-HONO conversion rates have been determined and compared in different places [Alicke et al., 2002; Alicke et al., 2003; Su et al., 2008b; Wentzell et al., 2010] and for different surface water amount in the terrestrial environment [Stutz et al., 2004]. The large variance in the obtained nocturnal conversion rates

(ranged from  $0.43 - 1.80 \times 10^{-2} \text{ h}^{-1}$ ) implies that HONO production rate of the heterogeneous reaction is strongly influenced by environment conditions. Compared to the ground surfaces in terrestrial environment (including surfaces of soils, rocks, buildings and plants), sea surface in the marine boundary layer (MBL) can be another type of surface for nocturnal (or daytime) HONO heterogeneous formation. The abundant water that provides by sea surface may significantly enhance the source strength of this reaction. However, HONO measurement in the MBL is almost absent except for one study which observed the nocturnal HONO in the polluted nocturnal MBL in Saturna Island, Canada [Wojtal et al., 2011]. Considering ~ 71% of earth's surface is covered by oceans [Pidwirny, 2006] and its potential influence on the coastal area as a HONO source, more studies of HONO behavior in the MBL are clearly needed.. Moreover, due to the lack of data on conversion of NO<sub>2</sub> on ocean surface, current global and regional chemical transport models (CTMs) either use the same parameterization scheme for HONO formation on land and sea [Elshorbany et al., 2012] or exclude the reaction on sea surface in their simulations [Goncalves et al., 2012; Sarwar et al., 2008; Zhang et al., 2012a].

As a densely populated city situated on the South China coast, Hong Kong has suffered from its intense  $NO_x$  emissions and regional ozone pollution. Though comprehensive studies and analysis have been conducted to characterize the photochemical pollution in Hong Kong [*Guo et al.*, 2004; *Wang et al.*, 2003; *Wang et al.*, 2009a; b], the information of HONO is still limited, yet the high-NO<sub>x</sub> environment for this city may make HONO an important source of OH radical.

The aim of this study is to investigate HONO formation mechanism in the MBL and the role of HONO in the photochemistry in the coastal area of Hong Kong. The data used in this study were from a 4-month field study conducted at a background coastal site in Hong Kong, 2012. This thesis consists of 7 chapters:

- Chapter 1 presents an overall description of the research background, rationale and outline of this study.
- Chapter 2 gives an extensive literature review of the nighttime and daytime HONO sources, including results of current laboratory studies and field measurements.
- 3) Chapter 3 reviews the principles of instruments that are currently used for HONO measurements, including both absorption spectroscopy technique and wet-chemical technique. The principle for LOPAP instrument, which was used in the present study, is described in detail.
- 4) Chapter 4 describes the objectives and importance of this study.
- Chapter 5 presents the location of the study site, and instrumentation for HONO and other gas pollutants.
- Chapter 6 illustrates the overall measurement results and specific analysis for daytime and nighttime HONO formation.

7) Chapter 7 concludes the main findings and some implications of this study.

### **Chapter 2 Literature Review**

In this chapter, field measurements of HONO in the world and current understanding of HONO sources and formation mechanisms (including direct emissions, homogeneous reaction, heterogeneous processes and other possible daytime sources) and loss pathways are reviewed.

### 2.1 HONO Field Measurements

The first field measurement of atmospheric HONO was conducted in a suburban site in Julich, Germany, 1979 [*Perner and Platt*, 1979] with the observed concentrations of ambient HONO varying from < 0.050 ppbv to  $0.130 \pm 0.070$  ppbv during nighttime. Since then, many measurements of ambient HONO have been conducted in different locations in the world, and the observed HONO levels varied from several pptv (in polar region) [*Villena et al.*, 2011] to hundreds pptv (in remote areas) [*Ren et al.*, 2010; *Zhou et al.*, 2002], and to several ppbv (in polluted environments) [*Qin et al.*, 2009; *Stutz et al.*, 2002; *Yu et al.*, 2009].

HONO typically shows higher concentrations at night than in daytime. For a long time only nocturnal HONO could be quantified (See Figure 2-1) because of the poor detection limit (> 0.050 ppbv) of the measurement instruments. Due to the lack of direct measurement, daytime HONO was assumed to be at very low level (several pptv) and thought to have little contribution to OH concentration during daytime [*Kleffmann et al.*, 2005]. It was also believed that daytime HONO level could be explained with an equilibrium between a homogeneous source and HONO photolysis [*Calvert et al.*, 1994].

With the deployments of new instruments that have detection limit as low as 1 pptv in recent field studies in polluted areas, daytime HONO concentrations up to ~ 2.5 ppbv (Figure 2-2) have been reported since 2000 [*Acker et al.*, 2004; *Acker et al.*, 2006; *Kleffmann*, 2007; *Kleffmann et al.*, 2003; *Kleffmann et al.*, 2005; *Li et al.*, 2012; *Michoud et al.*, 2014; *Qin et al.*, 2006; *Su et al.*, 2008a; *Wentzell et al.*, 2010; *Wong et al.*, 2012; *Zhou et al.*, 2002].



Figure 2-1 HONO diurnal pattern, adapted from *Platt et al.* [1980].

To our knowledge, one of the first measurements of the atmospheric HONO in China was made in the Pearl River Delta (PRD) region in 2004 [*Su et al.*, 2008b].

The ambient levels of HONO in both urban (> 1.0 ppbv) and suburban (~ 0.6 ppbv) environments were found to be much higher than in other studies (See Table 2-1), suggesting a more significant role of HONO in East Asia than in other regions of the world. A more recent field measurement conducted in the urban area of Guangzhou reported a HONO diurnal pattern (Figure 2-2) with a peak level of ~ 3.5 ppbv during nighttime and a constant HONO level of > 2.5 ppbv during daytime [*Qin et al.*, 2009].

			HONO	Type of the	
Campaign	Location	Period	(ppbv)	environments	Reference
HOx Comp	Julich, Germany	June - July,	0 220	Remote	[Elshorbany et
		2005	0.220		al., 2012]
Santiago 3	Santiaga Chila	November,	1.440	Urban	[Rubio et al.,
Santiag0_5	Santiage, Chile	2009	1.440	Oldali	2009]
DOMINO	El Arenosillo,	November &	0.080	Rural	[M. Sörgel1,
DOMINO	Spain	December, 2008	0.080	Kurai	2011]
PMTACS-NY	NY US	July–August,	0.660	Suburban	[Ren et al.,
TWIACD-WI	111,00	2001	0.000	Suburban	2003]
MCMA-2006	New Mexico, US	14 - 31 March,	1.030	Urban	[Dusanter et al.,
11011112000	,	2006			2009]
LOOP/PIPAPO	Milan. Italy	May - June,	0.530	0.530 Suburban	[Alicke et al.,
		1998			2002]
	Kathamandu,	January -			
Kathmandu	Nepal	February,	1.050	Urban	[Yu et al., 2009]
	1	2003			
BERLIOZ	Pabstthum,	July–August,	0.200	Rural	[Alicke et al.,
	Germany	1998			2003]
Guangzhou	Guangzhou,	10-24 July,	3.060	Urban	[Qin et al.,
	China	2006			2009]
PRIDE-PRD 2004	Xinken,	13 October - 2	1.050	Suburban	[Su et al.,

 Table 2-1 Ambient HONO levels in recent studies.

	China	November, 2004			2008a]
PRIDE-PRD 2006	Back Garden, China	June 2006	0.600	Rural	[ <i>Li et al.</i> , 2012]
Tung Chung 2011	Tung Chung, Hong Kong	August and November 2011	0.800	Suburban	[Z Xu et al., 2015]
Intensive Campaign 2012	Hok Tsui, Hong Kong	22 August – 20 December, 2012	0.130	Remote	[ <i>Zha et al.</i> , 2014] (This study)



**Figure 2-2** HONO diurnal pattern in Guangzhou, China (adapted from *Qin et al.* [2009]).

### **2.2 Sources of HONO**

### 2.2.1 Direct Emission Source

Direct emission from vehicle exhausts can strongly influence HONO concentrations in the polluted urban areas [*Kirchstetter et al.*, 1996]. The HONO/NO<sub>x</sub> ratio is generally used for characterizing the direct HONO emission and for estimating the contribution to HONO concentration from vehicles. *Kessler and Platt* [1984] firstly measured the HONO and NO<sub>x</sub> in gasoline vehicle engine exhausts, and they found that the yield of HONO was highly depending on the

amount of excess oxygen. They also observed that HONO/NO<sub>x</sub> ratios were quite different under different engine loading, ratios of  $\ge 1 \times 10^{-4}$  and  $1.5 \times 10^{-3}$  were determined at high and low loadings, respectively. In the first tunnel measurement of HONO, *Kirchstetter et al.* [1996] showed an average HONO/NO<sub>x</sub> ratio of 2.9 ×  $10^{-3}$  based on the measurement data of a gasoline vehicle fleet. A recent tunnel study conducted by *Kurtenbach et al.* [2001] concluded that the estimated HONO/NO<sub>x</sub> ratios were not only depending on the engine loading, but also significantly influenced by the composition of the sampled vehicle fleet. HONO/NO<sub>x</sub> ratios varying from  $2.9 \times 10^{-3}$  to  $2.3 \times 10^{-2}$  were determined in these studies [*Gutzwiller et al.*, 2002; *Kirchstetter et al.*, 1996; *Kurtenbach et al.*, 2001].

Su et al. [2011] proposed another direct emission source of HONO based on the measurement of soil samples. The nitrite ions  $(NO_2^-)$ , which were released by fertilizers, could be a large direct source of HONO in the low pH conditions. The emitted gas-phase HONO was formed via following reaction:

$$NO_2^{-}(aqueous) + H^{+}(aqueous) \leftrightarrow HNO_2(aqueous) \leftrightarrow HONO(gas)$$
 (R2.1)

The authors suggested that the human agricultural and land-use activities could strongly affect the troposphere oxidizing capacity. Moreover, *Oswald et al.* [2013] reported that high concentrations of HONO could be released by ammonia-oxidizing bacteria, suggesting that HONO emission from nonacidic soils could also be an important direct HONO source.

### 2.2.2 Homogeneous Sources

The gas-phase reaction (R2.2) between OH and NO is considered to be the most important homogeneous formation pathway of HONO. Field measurement results indicate that the reaction plays a more significant role in urban areas, where OH and NO concentrations are much higher than those observed in rural areas [*Alicke et al.*, 2002; *Alicke et al.*, 2003].

$$OH + NO \xrightarrow{M} HONO$$
 (R2.2)

Reaction (R2.2) is used to be considered as a reaction only occurring during daytime, since OH concentration is typically close to zero at night [*Kleffmann*, 2007]. However, *Lu et al.* [2012] argued that this reaction may also contribute to nocturnal HONO production in urban areas where high level of nighttime OH was produced under the glare of street lights and neon lights.

Several new homogeneous daytime HONO sources have been proposed according to results of field measurements and laboratory experiments. *Li et al.* [2008] suggested that reaction between photolytically excited NO<sub>2</sub> and H<sub>2</sub>O could be a potential homogeneous source for both HONO and OH,

$$NO_2 + hv(\lambda > 420nm) \rightarrow NO_2^*$$
 (R2.3)

Similar result was reported in another field study by *Wentzell et al.* [2010], however, the importance of this source was recently questioned by *Li et al.* [2012]. The production rates of this source were found to be too small to explain observed HONO [*Amedro et al.*, 2011; *Sorgel et al.*, 2011b; *Wong et al.*, 2011].

Nucleation of gas-phase NH<sub>3</sub>, H<sub>2</sub>O and NO<sub>2</sub> is thought to be another homogeneous HONO source which is based on the theoretical calculation results by *Zhang and Tao* [2010].

$$NH_3(gas) + H_2O(gas) + NO_2(gas) \rightarrow HONO(gas) + HNO_3(solid)$$
 (R2.5)

Lab studies also found that photolysis of ortho-nitrophenols might be a strong HONO source in polluted urban environments during daytime [*Bejan et al.*, 2006], but *Li et al.* [2012] also pointed out that the importance of these recently proposed photolytic sources to atmospheric HONO still requires further validation by field observation results.

There are also some proposed homogeneous HONO sources that were used in previous model simulations [*Ramazan et al.*, 2004; *Zhang et al.*, 2012a].

$$NO + NO_2 + H_2O \rightarrow 2HONO$$
 (R2.6)

$$HNO_3 + hv \rightarrow HONO + O({}^3P)$$
 (R2.7)

These homogeneous reactions are generally omitted in recent studies, as they either have low source strength or lack of support from field measurements [*Kleffmann*, 2007].

### 2.2.3 Heterogeneous Sources

Compared to homogeneous HONO production, heterogeneous reaction on different surfaces are more likely to be the explanation of the measured high HONO levels in suburban or rural areas [*Li et al.*, 2010; *Su et al.*, 2008a]. *Harris et al.* [1982] first suggested that if direct HONO emission is not the dominant source, heterogeneous reactions (R2.8) should be the most probable pathway for nocturnal HONO production.

$$2NO_2 + H_2O(adsorbed) \xrightarrow{surface} HONO + HNO_3$$
(R2.8)

It is believed that reaction (R2.8) could occur on a wide range of surfaces, including surfaces of buildings, structures, vegetation, glasses, rocks and soils [*Finlayson-Pitts et al.*, 2003]. This reaction is also found to be first order in NO<sub>2</sub>, however, results of laboratory studies indicate that its exact HONO production rate is hard to determine, as surface water content and surface area density may also have large effects on this reaction [*Febo and Perrino*, 1991; *Finlayson-Pitts et al.*,

2003; Jenkin et al., 1988; Pitts et al., 1985; Pitts et al., 1984; Sakamaki et al., 1983; Svensson et al., 1987]. The HONO formation rates of this reaction have been estimated in various locations during the nighttime, ranging from  $0.43 - 0.49 \times 10^{-2}$ h<sup>-1</sup> in urban areas and  $0.80 - 1.80 \times 10^{-2}$  h<sup>-1</sup> in rural areas [*Acker et al.*, 2005; *Alicke et al.*, 2002; *Alicke et al.*, 2003; *Kleffmann et al.*, 2003; *Lammel*, 1999; *Su et al.*, 2008b; *Wentzell et al.*, 2010].

Some other heterogeneous HONO sources have been proposed.

$$NO + NO_2 + H_2O \xrightarrow{surface} 2HONO$$
 (R2.9)

Different from the homogeneous reaction (R2.6), HONO production through the heterogeneous reaction (R2.9) was thought to be an important nocturnal HONO source in urban areas and widely adopted in modeling studies [*Calvert et al.*, 1994] However, a later laboratory study challenged that no significant enhancement in reaction rate was observed when high concentration of NO was added into the NO<sub>2</sub>-H<sub>2</sub>O mixture [*Gerecke et al.*, 1998].

Renoxification of nitric acid (HNO<sub>3</sub>) on surfaces is another heterogeneous HONO source, [*Knipping and Dabdub*, 2002], but it is typically neglected in HONO studies because of its slow production rate [*Kleffmann et al.*, 1998].

$$NO + HNO_3 \xrightarrow{surface} HONO + NO_2$$
 (R2.10)

It has been demonstrated that the above heterogeneous reactions (R2.8 to R2.10) can occur during both nighttime and daytime, and nighttime HONO concentrations can be reasonably explained by them [*Vogel et al.*, 2003]. However, considering the fast HONO photolysis in daytime, the source strengths of the existing nocturnal heterogeneous HONO formation pathways are apparently not large enough to maintain the observed daytime HONO level [*Kleffmann*, 2007].

Heterogeneous reduction of NO<sub>2</sub> on soot particles or organic surfaces (R2.11) may be another source of HONO in urban areas. Laboratory experiments show that its conversion efficiency is enhanced under conditions of high soot loadings and NO<sub>2</sub> concentrations [*Ammann et al.*, 2005; *Ammann et al.*, 1998; *Aubin and Abbatt*, 2007; *Kleffmann et al.*, 1999].

$$NO_2 + HC_{red} \xrightarrow{surface} HC_{ox} + HONO$$
 (R2.11)

This redox HONO formation pathway is found to be photo-enhanced in recent laboratory studies [*George et al.*, 2005; *Stemmler et al.*, 2006]. Further investigation suggests that the production rate of this reaction is first order to  $NO_2$ in low  $NO_2$  condition. When  $NO_2$  concentration increased to a certain level, the dominant factor will change to the intensity of light. Compared to the reaction rate of heterogeneous reaction (R2.8), the production rate of this photo-enhanced reaction can be 1-2 orders of magnitude faster [*George et al.*, 2005]. The photolytic conversion of adsorbed HNO<sub>3</sub> and nitrate (NO<sub>3</sub><sup>-</sup>) to gas-phase HONO on wet surface under sunlight is also considered as a major source in low-NO<sub>x</sub> environments [*Zhou et al.*, 2003].

$$HNO_{3} / NO_{3}^{-}(adsorbed) + hv \xrightarrow{surface} HONO / NO_{2}^{-} + O(^{3}P)$$
(R2.12)

The production rate of reaction (R2.12), which is determined in both laboratory and field experiments, is orders of magnitude higher than photolysis of HNO<sub>3</sub> in gas-phase and liquid-phase [*Rohrer et al.*, 2005; *Zhou et al.*, 2003]. Result of a recent field HONO flux study in a rural forest canopy by *Zhou et al.* [2011] also showed that photolysis of adsorbed HNO<sub>3</sub> was a significant daytime HONO source in low-NO<sub>x</sub> environment.

### **2.3 HONO Loss Pathways**

Compared to complex sources, the loss mechanism of HONO is much simpler [*Li et al.*, 2012]. Photolysis of HONO via reaction (R1.1) is typically the most effective loss pathway. Besides the photolysis process, atmospheric HONO can be also removed by reacting with OH:

$$HONO + OH \rightarrow NO_2 + H_2O$$
 (R2.13)

Additionally, HONO can be removed through some other reactions, including

reaction with itself and heterogeneous reaction with HNO<sub>3</sub> [Stutz et al., 2004]:

$$HONO + HONO \rightarrow NO_2 + NO + H_2O$$
 (R2.14)

$$HONO(adsorbed) + HNO_3(adsorbed) \rightarrow 2NO_2(gas) + H_2O(adsorbed)$$
 (R2.15)

Results of laboratory study demonstrated that, when HONO levels were very high (in ppmv level), reactions of (R2.14) and (R2.15) could play important roles in HONO loss processes [*Syomin and Finlayson-Pitts*, 2003]. However, these reactions are too slow under most atmospheric conditions, due to its low concentrations of HONO (pptv - ppbv). Therefore, only reaction (R1.1), reaction (R2.14), and deposition process are considered when determining daytime HONO loss. The calculated lifetime of HONO is about 20min in the most daytime conditions [*Su et al.*, 2008a; *Wentzell et al.*, 2010].

In contrast, HONO at night is mainly removed through physical processes [*Su et al.*, 2008b]. With a lower height of nocturnal boundary layer (typically < 300m), dry deposition of HONO becomes a very important loss pathway during nighttime. A dry deposition velocity of 2 cm/s was firstly determined in *Harrison et al.* [1996], equivalent to a HONO deposition rate of 0.02/boundary layer height (in meter) (s<sup>-1</sup>).

A recent study also suggested that vertical dilution could be an important physical loss pathway for daytime HONO when strong vertical convection occurred. By simulating the daytime HONO gradient using a 1-D model, vertical transport was suggested to be a more significant loss pathway of HONO in the lower boundary layer [*Wong et al.*, 2013]. However, this conclusion is not yet confirmed by any flux measurement, and homogeneous gradients of daytime HONO have been observed in some other flux measurements [*Kleffmann*, 2007; *Trick*, 2004; *Zhang et al.*, 2009].

### **Chapter 3 HONO Measurement Techniques**

Different analytical instruments have been developed and deployed for precisely quantifying atmospheric HONO since three decades ago [*Febo et al.*, 1993; *Kanda and Taira*, 1990; *Platt et al.*, 1980; *Simon and Dasgupta*, 1995; *Sjodin and Ferm*, 1985; *Vecera and Dasgupta*, 1991; *Wu et al.*, 2014].

The differential optical absorption spectroscopy (DOAS) system, which was developed based on the principle of absorption spectroscopy, was the first instrument to measure ambient HONO [Perner and Platt, 1979]. Several other HONO instruments have also been developed based on the same principle, including cavity attenuated phase-shift spectroscopy (CAPS) system [Kebabian et al., 2005], Fourier transform infrared (FTIR) system [Verma et al., 2008] and incoherent broad-band cavity enhanced spectroscopy (IBBCEAS) system [Wu et al., 2014]. These instruments are characterized by their high sensitivity and selectivity, and therefore they are commonly used in the measurements that require high time resolution and accuracy. However, due to their fragile core components (e.g., cavity mirrors and spectrometer) and tedious maintenance procedures, deployments of absorption spectroscopy instruments in field have been rather limited. The other widely used technique for HONO measurement is wet-chemical technique. Wet denuder is one of the frequently used wet-chemical technique for HONO measurement [Acker and Moller, 2007; Acker et al., 2001; Su et al., 2008b]. Instruments based on wet-chemical technique are known for their reliability and easy maintenance. However, their poor time resolutions make them more suitable for long-term measurements. Moreover, the large chemical interference from scrubbing solution makes them hard to precisely determine HONO concentrations in low HONO environments [*Su et al.*, 2008b].

The long path absorption photometer (LOPAP), which is developed by *Kleffmann et al.* [2002], is an instrument that combines the advantages of both wet chemical technique and absorption spectroscopy technique. Therefore, it has the characteristics of both wet-chemical technique (compact, easy maintenance and high reliability) and absorption spectroscopy (sensitive, selective and high time resolution).

In this chapter, the theory of absorption spectroscopy is described, and principles of several commonly used absorption spectroscopy instruments for HONO measurement are reviewed, including the LOPAP (instrument used in the present study).

### 3.1 Theory of Absorption Spectroscopy

Absorption spectroscopy is defined as the spectroscopic technique that measures the absorption of light when it passes through a certain material [*Platt and Stutz*, 2008]. Figure 3-1 presents a beam of light of single wavelength  $\lambda$  passes through an absorption cell, the intensity of light is reduced by two processes: (1) light
absorption by substances within the absorption cell, (2) scattering process.



Figure 3-1 Single-wavelength light passes through absorbing cell (adapted from *Platt and Stutz* [2008]).

However, if only absorption process is considered, the variation of light intensity can be easily given by Lambert-Beer's law:

$$-dI(\lambda) = \sigma(\lambda)c(l)I(\lambda)dl = \alpha(\lambda)I(\lambda)dl$$
(E3.1)

Hence,

$$-\frac{dI(\lambda)}{I(\lambda)} = \alpha(\lambda)dl$$
(E3.2)

Where  $\sigma(\lambda)$  corresponds to absorption cross-section at wavelength of  $\lambda$ , which is a characteristic property of a particular substance, and it is usually estimated in laboratory experiments. c(l) is the concentration of the substances, and  $\alpha(\lambda)$  is defined as the absorption coefficient of the substance at the wavelength of  $\lambda$ .  $I(\lambda)$ is intensity of the emergent light, and dl is the path length of the light. When boundary conditions (length of the absorption cavity, L) in Figure 3-1 is added into consideration, following equation can be obtained:

$$\int_{I_0(\lambda)}^{I(\lambda)} = \int_0^L \alpha(\lambda) dl$$
(E3.3)

Following relationship can be established based on equation (E3.3):

$$I(\lambda) = I_0(\lambda) \exp(\alpha(\lambda)L)$$
(E3.4)

For most of the air pollutants, the absorption coefficient is much smaller than 1  $(\alpha(\lambda) \ll 1)$ , therefore (E3.4) can be simplified to:

$$I(\lambda) = I_0(\lambda) \exp(\alpha(\lambda)L) \approx I_0(\lambda)(1 - \alpha(\lambda)L)$$
(E3.5)

Hence, a rough estimation of absorption coefficient can be gained:

$$\alpha(\lambda) \approx \frac{I_0(\lambda) - I(\lambda)}{I_0(\lambda)} \cdot \frac{1}{L} = \frac{\delta I(\lambda)}{I_0(\lambda)} \cdot \frac{1}{L}$$
(E3.6)

where  $\delta I$  corresponds to  $I_0 - I(\lambda)$ . The minimum  $\alpha(\lambda)$  can be obtained with following formula:

$$\alpha_{\min}(\lambda) = \frac{1}{L} \left( \frac{\delta I(\lambda)}{I_0(\lambda)} \right)_{\min}$$
(E3.7)

Examination of the equation (E3.7) suggests that the optimum detection limits for

instruments using absorption spectroscopy theory can be obtained by reducing the system noise  $(\delta I(\lambda) / I_0(\lambda))$  and increasing the total path length of the light L.

An approximation of concentration of the substance (c(l)) can be derived from (E3.8):

$$c(l) = \frac{\alpha(\lambda)}{\sigma(\lambda)} = \frac{\delta I(\lambda)}{\sigma(\lambda) I_0(\lambda)} \cdot \frac{1}{L}$$
(E3.8)

#### **3.2 Principle of LOPAP**

The long path absorption photometer (LOPAP) (Figure 3-2) is an in situ measuring device with which HONO is sampled in an external sampling unit chemically and is quantitatively measured using absorption spectroscopy theory in long path absorption cells after conversion into an azo dye.



Figure 3-2 LOPAP instrument with an external sampling unit and notebook for data collecting and processing (adapted from LOPAP operators manual).

# 3.2.1 Wet-chemical Technique in LOPAP: External Sampling Unit

The external sampling unit is separated from the measurement part of the LOPAP instrument and is used to sample atmospheric HONO. As shown in Figure 3-3, the sampling unit has two stripping coils in series to eliminate possible interferences that were often observed in other wet-chemical detectors. Ambient HONO is sampled with following steps: (1) HONO and other possible substances are sampled in the first coil with an HONO absorption efficiency of > 99.9%. Compared to the full uptake of HONO, only small uptake are expected for the other

chemical compounds in this coil; (2) In the second coil, remaining compounds that may cause interferences are sampled again. By calculating the difference between the first and second coil, concentration of the sampled HONO can be determined.



Figure 3-3 Schematic of the external sampling unit (adapted from LOPAP operators manual).

To avoid the interference in the sampling line (i.e. HONO produced on the humid surface of the sampling line), no sampling line was used in the sampling unit. Additionally, to ensure a constant HONO sampling efficiency, the sampling system is connected to a thermostatic water bath. A "debubbler" is used to separate air from the liquid solution.

Gas-phase HONO is sampled by reacting with reagent solution R1, which is 0.06 M sulfanilamide in 1M HCl solution; this solution is then mixed with reagent solution R2 (0.8 mM n(1-naphthyl)-ethylenediamine-dihydrochloride) to form the final azo dye for measurement in the absorption cell.

### 3.2.2 Absorption Spectroscopy Theory in LOPAP: Absorption Photometer

To achieve ideal measurement sensitivity and selectivity, theory of absorption spectroscopy is used to quantify the sampled HONO concentrations in the LOPAP instrument. It is noted that different from the DOAS system, a special Teflon tubing (Teflon AF2400), which is characterized by its low refractive index, is used as the long path absorption cell, so light can be transferred in complete reflection.

The azo dye solutions of both coils are continuously pumped into the absorption cells and a visible light is injected into the Teflon tubing system., The absorption spectra is measured by a spectrometer (Figure 3-4), and the HONO concentration can be retrieved according to formula (E3.8).



Figure 3-4 Schematic setup of the LOPAP instrument (adapted from LOPAP operators manual)

#### **Chapter 4 Knowledge Gap and Research Objectives**

Literature review in chapter 2 shows that HONO field measurements have been made in a wide range of locations, but little attention has been paid to the HONO in the marine boundary layer (MBL) environment. Characteristics of HONO, such as its ambient level and diurnal pattern are not clearly understood as a result of the nearly absence of "marine" HONO measurements. Up to now, production of HONO in the MBL is neglected in most of the current model studies, since the sea is typically considered as a sink of HONO due to the alkaline nature of deep sea water. Recently, *Donaldson and George* [2012] offered a contradictory view that the sea surface might be a potential HONO source, as HONO could be formed in the non-alkaline (pH  $\approx$  7) sea surface micro layer (SML).

The aim of this study is to investigate HONO in the MBL environment following specific objectives: (1) Determine the characteristics of HONO at the coastal site of Southern China; (2) Examine the nighttime/daytime HONO formation in this MBL environment; (3) Understand the role of HONO in the photochemistry.

#### **Chapter 5 Experiment**

#### 5.1 Description of Hok Tsui Study Site

Field measurement was made at the Hok Tsui supersite (22°13'N, 114°15'E), which is located in a remote coastal area of Hong Kong [*Wang et al.*, 2009a]. The site is situated in the southeast part of Hong Kong Island, approximately 10 km from the urban area of Hong Kong Island and 50 km from the highly populated and industrialized Pearl River Delta (PRD) region.



Figure 5-1 Map showing the location and surrounding environment of the Hok Tsui study site. (Waglan Island is where the Hong Kong Observatory operates a surface weather station whose wind data from are used in the present study.) There were no strong emission sources within the surrounding area, except for the occasionally observed ship emissions from the international shipping lane, which is about 6 km south of the site. As shown in the lower part of Figure 5-1, the site is located on a 60 m (a.s.l.) high cliff, and the open area from northeast to west (~ 240°) of the site is covered with sea surface. The field campaign was made from August 17 to December 19, 2012.

#### 5.2 Instrumentation

#### **5.2.1 HONO**

Real-time HONO was measured using a LOPAP, whose principle has been described in detail in chapter 3. This instrument had been validated with the DOAS technique in both smog chamber and ambient atmosphere [*Kleffmann et al.*, 2006]. The sampling unit of LOPAP was mounted at a height of 3 m a.g.l. to reduce the disturbance from vertical transport. The detection limit of our HONO measurement was 1 - 2 pptv with a time resolution of 4 min. During the field campaign, the baseline of the instrument was checked twice automatically and additional 2 - 3 times manually every day by sampling synthetic air from the cylinder. The calibration of sensitivity and measurement span was performed every three days by sampling 0.01  $\mu$ g/m<sup>3</sup> and 0.04  $\mu$ g/m<sup>3</sup> NO<sub>2</sub><sup>-</sup> standard solutions. A sampling efficiency of 99.95% of the instrument was determined with a HONO source generator (QUMA, Model QS-03) before the field observations.

#### **5.2.2 Other Parameters**

NO and NO<sub>2</sub> were measured with a chemiluminescence analyzer (Thermo Environmental Instruments (TEI), Model 42i) equipped with a photolytic converter for converfsion of NO<sub>2</sub> to NO (Blue Light Converter, Droplet Measurement Technologies) [*Z. Xu et al.*, 2013]. During the field study, the conversion efficiency was calibrated every three days and was found to be stable at around 30%. The detection limit was estimated as 50 pptv for NO and NO<sub>2</sub> at a time resolution of 1 min. NO<sub>y</sub> was measured with a MoO/chemiluminescence analyzer (Advanced Pollution Instrumentation (API), Model 200EU), ozone (O<sub>3</sub>) was measured by a commercial UV photometric analyzer (TEI Model 49i), and carbon monoxide (CO) by a non-dispersive infrared analyzer (Advanced Pollution Instrumentation, Model 300EU) [*Wang et al.*, 2009a].

Temperature and relative humidity (RH) were measured by a commercial probe (M.R.Young, Model 41382VC/VF, USA). NO<sub>2</sub> photolysis frequency ( $J_{NO2}$ ) was measured two parallel optical actinometers facing in opposite directions (Metcon, Germany). Wind speed and direction were monitored with a 2-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.

#### **Chapter 6 Results and Discussion**

#### **6.1 Overall Results**

Figures 6-1 to 6-4 show the time series of trace gases and meteorological parameters observed at Hok Tsui during the intensive campaign. Table 6-1 summarizes the statistics of the hourly concentrations of the measured species. Overall inspection of the data reveals that the ambient levels of all trace gases were relatively low, reflecting the regional background nature of the site. Meanwhile, high pollution events with significantly enhanced levels of pollutants were also observed under favorable conditions. Eight ozone episode days (here defined as the day with the peak hourly O<sub>3</sub> concentration exceeding 100 ppbv) were observed throughout the campaign, mainly occurred in August - October (i.e., August 23, 24, 25, 27, 28, September 16, and October 2, 11). The maximum hourly ozone was recorded at 149 ppbv on August 24. The average concentrations of HONO during the campaign were 0.160 ppbv. The maximum concentrations of HONO reached 1.150 ppbv on episode days. During these episodes, intense solar radiation (as indicated by the high J<sub>NO2</sub> values) and weak winds were usually concurrently observed.

The 4-month measurement period covered three seasons, i.e., late summer, autumn, and early winter. To facilitate analysis of the 'seasonal' variation, the entire study period was divided into 4 'monthly' periods, which were August 17 – September 16, September 17 – October 16, October 17 – November 16 and November 17 –

December 20, 2012. Table 6-2 presents the statistics of major trace gases for the four different periods. CO and NO<sub>y</sub> clearly showed an ascending trend from late summer to early winter. This can be attributed to the increasing transport of regional pollution from eastern China to Hong Kong driven by the winter Asian monsoon. O<sub>3</sub> showed higher levels in the autumn season (the  $2^{nd}$  and  $3^{rd}$  periods) compared to those in late summer and early winter, which is in line with the findings of previous studies [*Wang et al.*, 2009a]. HONO showed a significantly higher level in the 1<sup>st</sup> period (late summer), with comparable levels observed in the latter three periods.



Figure 6-1 Time series of trace gases and meteorological parameters measured at Hok Tsui during August 17 – September 16, 2012 (HONO measurement started on August 22, 2012).



**Figure 6-2** Time series of trace gases and meteorological parameters measured at Hok Tsui during September 17 – October 16, 2012.



**Figure 6-3** Time series of trace gases and meteorological parameters measured at Hok Tsui during October 17 – November 16, 2012.



**Figure 6-4** Time series of trace gases and meteorological parameters measured at Hok Tsui during November 17 – December 20, 2012.

Species	Mean	Maximum	Minimum	SD	Ν	
<b>O</b> 3	45	149	1	24	2934	
CO	308	1185	29	164	2932	
NO	0.7	40.4	0.0	2.2	2863	
NO <sub>2</sub>	5.0	54.4	0.0	5.2	2863	
NOy <sup>a</sup>	6.5	66.4	1.1	5.3	1906	
HONO <sup>b</sup>	0.160	1.150	0	0.15	2587	

Table 6-1 Statistics on hourly data of trace gases measured at Hok Tsui.

<sup>a</sup>The NO<sub>y</sub> measurements started on October 1, 2012.

<sup>b</sup>The HONO measurements started on August 22, 2012.

	Aug. 17-Sep. 16			Sep. 17-Oct. 16		Oct. 17-Nov. 16		Nov. 17-Dec. 20				
Species	Mean	SD	N	Mean	SD	N	Mean	SD	N	Mean	SD	N
<b>O</b> 3	31	25	742	66	21	720	53	16	672	32	15	800
CO	165	112	742	284	92	720	342	138	672	432	166	798
NO	1.3	3.0	742	0.3	0.7	720	0.3	0.7	637	0.8	2.9	764
NO <sub>2</sub>	6.1	6.0	742	3.0	3.5	720	4.3	4.3	637	6.6	5.5	764
NOy <sup>a</sup>				4.8	2.3	374	5.8	4.3	733	8.0	6.5	799
HONO <sup>b</sup>	0.23	0.24	597	0.14	0.09	629	0.13	0.12	576	0.14	0.12	785

Table 6-2 Statistics on hourly data of trace gases for four 'monthly' periods.

<sup>a</sup>The NO<sub>y</sub> measurements started on October 1, 2012.

<sup>b</sup>The HONO measurements started on August 22, 2012.

Figure 6-5 shows the average diurnal variations of trace gases and meteorological parameters during the campaign. O<sub>3</sub> showed a typical diurnal pattern characteristic of rural locations, with the concentrations increasing from early morning (07:00 local time (LT)) to late afternoon (15:00 LT). The diurnal difference was about 23 ppbv, indicative of ozone production during daytime. NO, NO<sub>2</sub> and NO<sub>y</sub> showed a similar diurnal profile with double peaks in the early morning (07:00 – 09:00 LT) and in the evening (20:00 – 21:00 LT). HONO exhibited an interesting diurnal pattern at Hok Tsui. After the sunset, the HONO concentrations increased steadily until the next morning (06:00 LT), suggesting nighttime production and accumulation, then decreased a little after sunrise due to the fast photolysis, but increased again and kept at relatively high levels till the late afternoon (14:00 LT),

implying strong daytime source(s) to compensate the photolysis. Similar daytime HONO production processes have been recently observed in some other areas, however, the mechanism is still under discussion [*Villena et al.*, 2011; *Wentzell et al.*, 2010; *Zhang et al.*, 2012b].



Figure 6-5 Average diurnal profiles of major trace gases and meteorological parameters measured at Hok Tsui.

Figure 6-6 shows the averaged diurnal patterns without ozone episodes, which is representative of "background" condition in the MBL environment. Compared to the averaged diurnal profiles shown in Figure 6-5, background diurnal pattern in Figure 6-6 shows a similar profile but lower concentrations in all measured pollutants: the lowest HONO mixing level decreases from 0.13 ppbv (entire

campaign) to 0.11 ppbv (background) at 17:00 LT, and the peak value dropped from 0.19 ppbv to 0.15 ppbv at 10:00 LT, concentrations of other trace gas pollutants are also slightly lower. We will further discuss in later part of this chapter about the nighttime and daytime production of HONO in the marine atmosphere of Hong Kong.

Non-episode



Figure 6-6 Average diurnal profiles of major trace gases and meteorological parameters during non-episode days at Hok Tsui.

#### **6.2 Nocturnal HONO Formation**

In this section, we identify cases with air coming from different origins (sea-coming and land-coming) to investigate the conversion of  $NO_2$  to HONO on both land and sea surfaces, which may help to improve the current understanding of HONO sources in MBL.

#### 6.2.1 HONO/NO<sub>2</sub> Ratios

With the assumption that the heterogeneous reactions are the first order in NO<sub>2</sub> on all surfaces, the normalized HONO/NO<sub>2</sub> ratio is usually used as an indicator of the extent of NO<sub>2</sub> to HONO conversion. Results of previous studies suggested that the value of HONO/NO<sub>2</sub> ratios increased with the larger contribution from heterogeneous HONO formation. The HONO/NO<sub>2</sub> ratios of less than 0.01 are usually related to fuel combustion processes, ratios of 0.01 - 0.1 are related to the surface reactions under low humidity conditions, and ratios of higher than 0.1 are commonly observed in high humidity environments [*Stutz et al.*, 2004]. In this study, the nocturnal HONO/NO<sub>2</sub> ratios frequently exceeded 0.1 (see Figure 6-7), which should indicate the strong influence from the humid MBL environment condition.



Figure 6-7 HONO/NO<sub>2</sub> vs Time on the night of November 21, 2012

The scattering plot of nocturnal hourly (18:00 - 06:00 LT) HONO and NO<sub>2</sub> concentrations for the entire campaign are used to indicate the contribution from different sources. As shown in Figure 6-8, a weak correlation ( $\mathbb{R}^2 \approx 0.4$ ) between HONO and NO<sub>2</sub> is obtained, this is similar to the poor relationship observed in another MBL study [*Wojtal et al.*, 2011], and in contrast to the good correlations that were obtained in urban area [*Sorgel et al.*, 2011a; *Zhou et al.*, 2002]. The regression ratio of the lower boundary is 0.0083, which is quite close to the widely used emission ratio (0.0080) determined in a tunnel study [*K Kurtenbach et al.*, 2001], and a similar lower regression ratio (0.0084) in another nocturnal MBL study [*Wojtal et al.*, 2011], indicating direct emission (oil combustion processes) had a very minor contribution to the HONO at Hok Tsui. Ship plumes were occasionally observed during the campaign, an averaged HONO/NO<sub>2</sub> ratio

of 0.0076 is estimated in these plumes, which is very close to the emission ratios determined in the above studies. The upper boundary for the HONO/NO<sub>2</sub> ratio is 0.196, larger than most of the observed ratios in previous studies in different sites in Europe, North America and Asia [*Harrison and Kitto*, 1994; *Lammel and Cape*, 1996; *Qin et al.*, 2006; *Stutz et al.*, 2002; *Su et al.*, 2008b], but smaller than the observed ratio of 0.30 in the urban area of Nepal [*Yu et al.*, 2009]. The large HONO-NO<sub>2</sub> ratios at Hok Tsui suggest that surface heterogeneous reaction played a significant role in this place.



Figure 6-8 Relationship between nocturnal HONO and NO<sub>2</sub>.

#### 6.2.2 Calculation of NO<sub>2</sub>-to-HONO Conversion Rates

In this section, the conversion rates of NO<sub>2</sub>-to-HONO ( $C_{HONO}$ ) are estimated based on the observation of linear increase of HONO/NO<sub>2</sub> ratios with time.

The C<sub>HONO</sub> is commonly used as a metric of the strength of HONO production by reaction (R2.8) [*Alicke et al.*, 2002; *Alicke et al.*, 2003; *Su et al.*, 2008b; *Wentzell et al.*, 2010], and it was firstly determined in [*Alicke et al.*, 2002] (Figure 6-9) with the following equation:

$$C_{HONO} = \frac{[HONO]_{(t_2)} - [HONO]_{(t_1)}}{(t_2 - t_1)[\overline{NO_2}]}$$
(E6.1)

In the equation (E6.1), HONO formation rate is scaled with mean NO<sub>2</sub> concentration during the time interval of  $(t_2-t_1)$ , *Alicke et al.* [2003] demonstrated that this procedure could reduce to a large extent the influence of the formation of NO<sub>2</sub> and vertical mixing processes, as most of the HONO and NO<sub>2</sub> are emitted near the surface. However, some other physical processes like diffusion, deposition and air-mass change which may also have large impacts to the calculated conversion, are not taken into consideration in this equation. Though it is impossible to completely rule out the impact from the physical processes, their impacts can be partly reduced by using a more sophisticated scaling procedure. *Su et al.* [2008b] suggested the following method:

$$C_{HONO}^{X} = \frac{\left(\frac{[HONO]_{(t_{2})}}{[X]_{t_{2}}} - \frac{[HONO]_{(t_{1})}}{[X]_{t_{1}}}\right)\overline{[X]}}{\frac{1}{2}(t_{2} - t_{1})\left(\frac{[NO_{2}]_{(t_{2})}}{[X]_{t_{2}}} + \frac{[NO_{2}]_{(t_{1})}}{[X]_{t_{1}}}\right)}$$
(E6.2)



Figure 6-9 First estimation of C<sub>HONO</sub> (adapted from *Alicke et al.* [2002]).

In the equation (E6.2), X is a measured pollutant such as CO, SO<sub>2</sub>, black carbon (BC) and NO<sub>2</sub> which can be used as the "scaling species". According to a comparison of the calculation results using different scaling species, there is no much difference between the obtained C<sub>HONOS</sub> [*Su et al.*, 2008b]. NO<sub>2</sub> is commonly used for the scaling process (E6.3) [*Wentzell et al.*, 2010].

$$C_{HONO} = \frac{\frac{[HONO]_{(t_2)}}{[NO_2]_{(t_2)}} - \frac{[HONO]_{(t_1)}}{[NO_2]_{(t_1)}}}{(t_2 - t_1)}$$
(E6.3)



Figure 6-10 Calculation of  $C_{HONO}$  with equation (E6.3) (adapted from *Wentzell et al.* [2010]).

In the present study, a slightly modified approach was adopted. Considering almost linear increase of HONO concentrations and HONO/NO<sub>2</sub> ratios with time in our identified cases, we performed the least linear regression analysis for the HONO/NO<sub>2</sub> ratios against time (e.g., Figure 6-11), and  $C_{HONO}$  is determined as the regression slope. A comparison of this approach with that using equation (E6.3) show a difference of the calculated  $C_{HONO}$  of less than 10%.



**Figure 6-11** Calculation of C<sub>HONO</sub> using linear regression method on the night of October 20, 2012.

## 6.2.3 Nocturnal C<sub>HONO</sub> in Land-origin and Sea-origin Air Masses

To investigate the HONO formation mechanism in the terrestrial and MBL environments, nocturnal  $C_{HONO}$  ratios are determined and compared in the selected land-coming (representativeness of HONO heterogeneous production on land surface) and sea-coming air masses (representativeness of HONO heterogeneous production on sea surface). Representative air masses were chosen with the following criteria: (1) Only air masses showing steadily increase in HONO concentrations and relatively constant levels of other measured pollutants (O<sub>3</sub>, CO NO and NO<sub>2</sub>) were selected to ensure the HONO formation was mainly

due to the contribution from chemical conversion not physical processes [Su et al., 2008b; Wentzell et al., 2010]; (2) 6-h 3-D back trajectories were computed using the latest version of the HYSPLIT model (version 4.9) [Draxier and Hess, 1998] (driven by the final (FNL) archive meteorology data) to distinguish the air masses passing over land or ocean within the nocturnal boundary layer. The starting altitude of model was set to 50 m above ground level to reduce the impact from topography, and the starting time was the middle time of the respective case; (3) on-site winds were examined to identify different air masses: the cases with continuing (> 3 h) surface winds from the open area covered by sea surface (NE-West, clockwise) were considered as the "sea cases", whereas those with winds from the other directions (West-NE) were considered as the "land cases" (See Figure 5-1). It is worth noting that the land-originated air masses may have inevitably spent some time (< 1 h) over the sea surface during transport. With these procedures, three land cases and three sea cases were selected, and the C<sub>HONO</sub> for each case was calculated and further investigated. The three cases in each type were observed in different periods which were apart for at least 2 weeks, and they should be representative of the HONO production on the land and sea surface around the study site.

Figure 6-12 illustrates a typical land case on the night of September 13-14, 2012. In this case, the surface winds kept blowing from the NNE, and the wind speeds were very fast, ranging from 8 m/s to 10 m/s. The concentrations of NO<sub>2</sub> were stable at  $\sim$ 2 ppbv from 00:30 LT to 03:30 LT, in the meanwhile, HONO mixing ratios increased steadily from 0.069 ppbv to  $\sim$ 0.108 ppbv, and the HONO/NO<sub>2</sub>

ratios continually increased from 0.03 to 0.07.



Figure 6-12 Land surface case encountered on the night of September 13-14, 2012 (Missing data points were due to instruments' auto calibrations).

The 6-h back trajectory shown in Figure 6-13 illustrates that the air masses had spent most of the time moving over land surface and traveled a small distance above sea surface before reaching the measurement site. It is worth noting that the urban center of Hong Kong is to the northwest direction of the study site, hence the air masses observed in this case should not be strongly influenced by strong urban emissions. A C<sub>HONO</sub> of  $1.30 \times 10^{-2}$  h<sup>-1</sup> (R<sup>2</sup> = 0.80) for the selected case is calculated by the modified regression method.



Figure 6-13 6-h 3-D back trajectory for the night of September 13-14, 2012.

The second land case was identified on the night of September 28-29 (see Figure 6-14) and had lasted for 5.5 hours. The HONO/NO<sub>2</sub> rose from 0.02 to 0.09, which was attributed to the increase of HONO mixing ratios (from 0.110 ppbv to 0.360 ppbv) and the slightly decrease of NO<sub>2</sub> concentrations (from 6 ppbv to 4 ppbv). Except for the small period of time at the beginning of this case (before 22:00 LT), the wind directions and wind speeds during the remaining time were quite similar with the last land case.



Figure 6-14 Land surface case encountered on the night of September 28-29, 2012 (Missing data points were due to instruments' auto calibrations).

Compared to the trajectory shown in Figure 6-13 (NNE), the air masses (shown in Figure 6-14) in this case came straight from the north and closer to the urban area of PRD region. This should be the reason why the observed NO<sub>2</sub> levels in this case were much higher than those in the other cases. The C<sub>HONO</sub> determined in this land case was  $1.20 \times 10^{-2}$  h<sup>-1</sup> (R<sup>2</sup> = 0.84).



Figure 6-15 6-h 3-D back-trajectory for the night of September 28-29, 2012.

The third land case (shown in Figure 6-16) was observed on the night of November 4-5, 2012, the averaged wind speed was much smaller (~5 m/s) than the previous two cases (~9 m/s). The HONO concentration ascended from 0.015 ppbv to 0.177 ppbv, with several small spikes observed before 01:00 LT. It is noted that these spikes, which showed the similar rapid variations with NO<sub>2</sub> mixing ratios, should be due to the fast transport of ship emission plumes to the site. The averaged NO<sub>2</sub> mixing ratio was ~2.6 ppbv, and the HONO/NO<sub>2</sub> ratios also increased from 0.01 to 0.06. The calculated C<sub>HONO</sub> was  $1.21 \times 10^{-2}$  h<sup>-1</sup> (R<sup>2</sup> = 0.77).



Figure 6-16 Land surface case encountered on the night of November 4-5, 2012 (Missing data points were due to instruments' auto calibrations).

The C<sub>HONO</sub> values determined in the selected three land cases  $(1.30 \times 10^{-2} \text{ h}^{-1}, 1.20 \times 10^{-2} \text{ h}^{-1}$  and  $1.21 \times 10^{-2} \text{ h}^{-1}$ ) are comparable with each other and the ratios reported by previous studies  $(0.88 - 1.80 \times 10^{-2} \text{ h}^{-1})$  in other rural areas [*Acker et al.*, 2005; *Alicke et al.*, 2002; *Alicke et al.*, 2003; *Su et al.*, 2008b; *Wentzell et al.*, 2010], suggesting the same nocturnal HONO source mechanism in the land-coming air masses measured at Hok Tsui and in other nocturnal HONO source studies in the terrestrial environment.

Figure 6-17 shows the time series of HONO and other related parameters observed

on the night of November 20-21, 2012, which is one selected case of the sea-origin air masses. The mixing ratios of HONO were ~0.150 ppbv at 03:00 LT and slightly increased to approximately 0.230 ppbv in the following three hours. From 03:00 to 06:00 LT, the concentrations of NO<sub>2</sub> were relatively stable (~2.5 ppbv, except for several ship emission plumes) while the levels of HONO rose rapidly from 0.150 ppbv to 0.230 ppbv.



Figure 6-17 Sea surface case encountered on the night of November 20-21, 2012 (Missing data points were due to instruments' auto calibrations).

During this case, the surface winds were continually blowing from the SW at a slow wind speed of  $\sim$ 2-3 m/s from sunset (18:00 LT) to the next morning (06:00 LT),

which were significantly different from the strong SE winds revealed from the 6-h back trajectory (see Figure 6-19). An examination of the on-site winds was made using the data from Waglan Island station. This island is 5 km southeast of Hok Tsui and more representative of regional winds. Figure 6-18 shows regional wind direction and wind speed that observed in Waglan Island during the case, which are in accordance with the back trajectory. Therefore, the reduced wind speeds and shifted wind directions at Hok Tsui should be due to the variation of topographical conditions near the study site.



Figure 6-18 On-site wind at Wagland Island on the night of November 20-21, 2012 (Figure downloaded from HKO website).

Figure 6-17 also shows the time series of the HONO/NO<sub>2</sub> ratio. The ratio was ~0.06 at 03:00 LT, and increased to ~0.2 when HONO reached its peak level before sunrise (~06:00 LT). A C<sub>HONO</sub> of  $3.6 \times 10^{-2}$  h<sup>-1</sup> (R<sup>2</sup> = 0.81) was then estimated from

the linear regression method. As shown in Figure 6-19, air masses in the selected sea case had spent all the time moving over sea surface, and the estimated  $C_{HONO}$  may reveal the source strength of heterogeneous HONO production on sea surface.



Figure 6-19 6-h 3-D back-trajectory for the night of November 20-21, 2012.

The second selected sea case was observed when the southwesterly winds prevailed. Figure 6-20 and 6-21 show the measurement data and 6-h back trajectory for the case that encountered on the night of October 19-20, 2012. In the beginning of this case, meteorological condition was not very stable, and wind directions were shifting between NW and SW. The small peak of NO<sub>2</sub> (~3.5 ppbv) measured at 02:30 LT did not show much impact on HONO levels, as meanwhile the HONO mixing ratios even slightly decreased from 0.040 ppbv to 0.020 ppbv. From 03:30 LT, the meteorological condition became stable with the southwesterly winds prevailing till sunrise (06:00 LT).



Figure 6-20 Sea surface case encountered on the night of October 19-20, 2012 (Missing data points were due to instruments' auto calibrations).

While the NO<sub>2</sub> mixing ratios remained almost constant (~1.5 ppbv), the HONO levels increased from 0.030 ppbv to 0.130 ppbv. As a result, the HONO/NO<sub>2</sub> ratios dramatically increased from 0.02 to 0.15 (see Figure 6-20). The calculated C<sub>HONO</sub>, which was  $3.2 \times 10^{-2}$  h<sup>-1</sup> (R<sup>2</sup> = 0.81), was in accordance with the rate calculated in

the aforementioned case.



Figure 6-21 6-h 3-D back-trajectory for the night of October 19-20, 2012.

The third case (shown in Figure 6-22 and 6-23) was encountered on the night of September 21-22, 2012. The HONO concentrations were quite stable (~0.110 ppbv) before 01:40 LT. However, the HONO/NO<sub>2</sub> ratios increased from 0.04 to 0.12 during that period, which should be due to the decrease of the NO<sub>2</sub> concentration (from 2.2 ppbv to 1.5 ppbv). After that the HONO concentrations kept leveling up from 0.090 ppbv to 0.200 ppbv, and then reached the highest HONO/NO<sub>2</sub> ratio of 0.18 in this case. The meteorological parameters which could have influence on the

HONO level (on-site wind, regional wind and RH) also showed little difference from the previously two cases.



Figure 6-22 Sea surface case encountered on the night of September 21-22, 2012 (Missing data points were due to instruments' auto calibrations).

Examination of the back trajectories indicated the air masses in both land and sea cases were moving within the nocturnal boundary layer. However, smaller scale vertical movements of the air masses could not be precisely simulated by the back trajectory model. Due to the poor resolution of the ARL data (190 km  $\times$  190 km), it is hard to know how close the air masses were moving upon sea or ground surface.


Figure 6-23 6-h 3-D back-trajectory for the night of September 21-22, 2012.

Our results revealed that the C<sub>HONO</sub> ratios (shown in Table 6-3) in air masses moving upon the sea are much larger (~3 times) than those in the air masses passing over the land. Result of a T-test (P-value < 0.01) indicated that the difference between C<sub>HONO</sub> ratios on sea and land is statistically significant. This result is also in accordance with the C<sub>HONO</sub> ( $3.2 \times 10^{-2}$  h<sup>-1</sup>) derived from the latest study in the MBL environment [*Wojtal et al.*, 2011]. In addition, the difference in C<sub>HONO</sub> between land and sea could be even larger, since air masses in the land cases had traveled a small distance upon sea surface before arriving the study site. For the land case, it is widely accepted that the major nocturnal HONO source in terrestrial environment is the heterogeneous reaction on the ground surface, but the dominant HONO source in the MBL environment is still unclear. It could be the same reaction stoichiometry occurs in the sea surface micro layer (SML, first 100-1000  $\mu$ m water layer of the sea surface, pH  $\approx$  7) but has stronger source strength, or there may be other potential sources like some unknown reactions between organic compounds within SML or micro meteorology. More measurements of HONO and further understanding of boundary layer dynamics in the MBL environment are definitely required, and contribution from sea to the HONO concentrations in the coastal regions should not be neglected in the future researches.

The obtained results also have an important implication for HONO simulation in both global and regional chemical transport models. Some of the current models that accommodate HONO formation mechanism do not separately consider the land and sea surfaces in the simulations [*Elshorbany et al.*, 2012], and the others do not consider the HONO production on the sea at all [*Goncalves et al.*, 2012; *Sarwar et al.*, 2008; *Zhang et al.*, 2012a]. This is mostly due to the absence of the field HONO measurement in the MBL. If this finding is confirmed and applicable to different coastal regions, modelers may need to configure different parameterization schemes for HONO formation on land and sea.

Surface type	Date	Сноло (10 <sup>-2</sup> h <sup>-1</sup> )	Duration (hour)	Wind direction	Mean NO2 conc. (ppbv)	HONO/NO <sub>2</sub> increment (10 <sup>-2</sup> )
Land	September 13-14	1.30	3.0	NNE	1.79±0.34	4.6
	September 28-29	1.20	5.5	NNE	5.13±0.53	7.2
	November 4-5	1.21	4.8	NNE	2.60±1.13	5.4
Sea	September 21-22	3.36	3.0	SW	1.65±0.42	9.9
	October 19-20	3.17	3.3	SW	1.31±0.48	10.8
	November 20-21	3.29	2.8	SW	2.34±1.80	9.3

 Table 6-3 Summary of the selected "sea" and "land" cases

## **6.3 Daytime HONO Formation**

### 6.3.1 Photostationary State (PSS) Calculation

As mentioned in chapter 4, the formation mechanism of daytime HONO is not well understood and remains an area of intensive research. Except for direct emission sources, homogeneous reaction (R2.2) and heterogeneous reaction (R2.8) are considered as two important daytime sources of HONO. However, the source strengths of these two reactions are not sufficient to sustain the measured daytime HONO levels. To investigate the exact daytime HONO production mechanism, the widely used photostationary state calculation (PSS) is adopted in this study [*Acker*  et al., 2006; Alicke et al., 2002; Kleffmann et al., 2005; Michoud et al., 2014; Zhou et al., 2003], and the equation is shown as follows:

$$\frac{d[HONO]}{dt} = (P_{\text{hom}o} + P_{\text{hetero}} + P_{\text{emission}} + P_{\text{unknown}}) - (L_{\text{photolysis}} + L_{OH+HONO})$$
(E6.4)

In this equation,  $\frac{d[HONO]}{dt}$  denotes the variation of the measured HONO levels,  $P_{homo}$  is the source strength of the homogeneous reaction (R2.2),  $P_{emission}$  denotes the contribution from the direct HONO emission, and  $P_{unknown}$  is the total production rate of extra daytime HONO source(s) which cannot be explained by the previous three terms.  $L_{photolysis}$  is the daytime loss from HONO photolysis (R1.1), and  $L_{OH+HONO}$  is the loss rate from (R2.14).

It is generally believed that during the daytime when the photolysis rate of HONO ( $J_{HONO}$ ) exceeds  $1.0 \times 10^{-3}$  s<sup>-1</sup>, the lifetime of HONO is in the range of 10 - 20 min [*Kleffmann et al.*, 2005]. In this study,  $\frac{d[HONO]}{dt}$  is calculated every 5 min which is due to the limitation of the time resolution ( $\approx 4.5$  min) of the LOPAP instrument. According to the early discussions in this work, contribution from the direct HONO sources,  $P_{emission}$ , can be neglected in our study. In the loss terms, dry deposition loss of HONO is neglected, as the dry deposition velocity of HONO is  $\sim 2$  cm/s, which is way to small compared to the rates of the other two loss terms (photolysis and reaction with OH) in equation (E6.4) [*Harrison et al.*, 1996]. Additionally, contribution from horizontal transport of HONO is also neglected in the daytime

HONO study due to its short lifetime.

The source strength of the unknown daytime HONO source,  $P_{unknown}$ , can be calculated with the following equation:

$$P_{unknown} \approx \frac{d[HONO]}{dt} + L_{photolysis} + L_{OH+HONO} - P_{hom\,o} - P_{hetero}$$
(E6.5)

When J<sub>HONO</sub> exceeds  $1.0 \times 10^{-3} \text{ s}^{-1}$ ,  $\frac{d[HONO]}{dt}$  is close to 0, equation (E6.5) can

be simplified to:

$$P_{unknown} \approx L_{photolysis} + L_{OH+HONO} - P_{homo} - P_{hetero}$$
(E6.6)

Hence, HONO levels in photostationary state can be obtained by equation (E6.7):

$$HONO_{PSS} \approx \frac{k_{\text{hom}o}[\text{NO}][\text{OH}] + C_{HONO}[\text{NO}_2]}{J_{HONO} + k_{OH+NO}[\text{OH}]}$$
(E6.7)

In this equation,  $k_{homo}$  and  $k_{OH+NO}$  are the reaction rates of (R2.2) and (R2.14); C<sub>HONO</sub> is the nocturnal NO<sub>2</sub>-to-HONO conversion rate which is determined in the early section in this chapter. The NO and NO<sub>2</sub> concentrations are the observed values, and the concentrations of OH and HONO photolysis rate (J<sub>HONO</sub>) are simulated.

#### **6.3.2 Estimations of OH Concentrations and JHONO**

Since OH was not measured in this study, the OH mixing ratios used in PSS calculation are estimated with the assumptions that OH concentrations reach the peak level at noontime and equal to 0 at sunrise and sunset. A recent OH measurement made by *Lu et al.* [2012] reported noontime peak of  $1.5 - 2.6 \times 10^7$  molec cm<sup>-3</sup> at a suburban site at Backgarden, Guznagzhou. Considering that our measurement site is located in a rural environment which is less polluted, a smaller noontime OH peak value of  $1.0 \times 10^7$  molec cm<sup>-3</sup> is used in this study. The OH concentration during other times of day can be estimated by the following equation:

$$[OH] = [OH]_{peak} \times \cos^3(SZA)$$
(E6.8)

Where  $[OH]_{peak}$  denotes the assumed OH peak of  $1.0 \times 10^7$  molec cm<sup>-3</sup>, and SZA corresponds to the solar zenith angle which can be determined as follows [*Jacobson*, 2005]:

$$\cos(SZA) = \sin\varphi\sin\delta + \cos\varphi\cos\delta\cos h \tag{E6.9}$$

In equation (E6.9), *h* is the hour angle in the local solar time;  $\delta$  is the current declination of the sun; and  $\varphi$  is the local latitude. The  $f(x) = cos^3(x)$  function, whose shape closely matches the diurnal variation of O<sup>1</sup>D production rates, is selected in this study as it is generally believed that the OH concentration scales well with O<sup>1</sup>D production rates [*Rohrer and Berresheim*, 2006].



Figure 6-24 Averaged hourly OH diurnal profile during entire campaign.

In this study,  $J_{HONO}$  is simulated using the observed  $J_{NO2}$  and the approach which was suggested by *Kraus and Hofzumahaus* [1998]:

$$J_{HONO} = 0.189 \times J_{NO_2} + 8.433 \times 10^{-2} \times (J_{NO_2})^2$$
(E6.10)

The estimated OH and  $J_{HONO}$  values are all within the rational ranges and comparable with the previously reported values in the PRD region [*Li et al.*, 2012; *Su et al.*, 2008a].



Figure 6-25 Averaged hourly J<sub>HONO</sub> diurnal profile for the entire campaign.

#### 6.3.3 Roles of the Known HONO Sources

As discussed in the early part of this chapter, the diurnal variation of HONO (shown in Figure 6-5) is quite unique at Hok Tsui. The daytime HONO peak, which appeared shortly after sunrise, showed even higher HONO concentration than the nighttime peak. Though the source strengths of the known daytime HONO sources (homogeneous reaction (R2.2) and heterogeneous reaction (R2.8)) are generally believed not enough to maintain the observed daytime levels, it is of interest to know their relative contributions at Hok Tsui. To ensure that HONO reaches the photostationary state, only datasets that meet the requirement of  $J_{HONO} \ge 1.0 \times 10^{-3}$ s<sup>-1</sup> are selected and used in the calculation.

#### 6.3.3.1 Homogeneous Source

Reaction (R2.2) was thought to play a major role in daytime HONO formation, especially in the heavily polluted environment. With the PSS calculation method, contribution from the homogeneous HONO formation can be estimated and compared with the measured daytime HONO.

$$HONO_{PSS} = \frac{k_{homo}[NO][OH]}{J_{HONO} + K_{OH+NO}[OH]}$$
(E6.11)

By assuming reaction (R2.2) is the dominant daytime HONO source, HONO concentration in a photostationary state,  $HONO_{PSS}$ , can be calculated.



Figure 6-26 Measured HONO concentrations (blue line) and calculated daytime HONO<sub>PSS</sub> (green line) concentrations in the polluted MBL environment (Missing points in HONO<sub>PSS</sub> were due to insufficient  $J_{HONO}$  values).

Figure 6-26 and 6-27 show the measured HONO levels and the calculated daytime HONO concentrations (HONO<sub>PSS</sub>) in the PSS states during selected heavily polluted (August 22 – August 31, shown in Figure 6-26) and overall background (non-episode days, shown in Figure 6-27) periods with only homogeneous source being considered in the calculation. Compared to the non-episode days, the homogeneous reaction clearly played a significant role in daytime HONO formation at Hok Tsui, and it can explain up to ~ 65% of the measured HONO peak when NO levels were quite high (~ 30 ppbv). However, the observed daytime HONO mixing ratios are still higher than the calculated concentrations, which means that the source strength of reaction (R2.2) is not adequate to explain the ambient daytime HONO levels, especially under the low-NO conditions.



Figure 6-27 Measured HONO concentrations (blue line) and calculated daytime HONO<sub>PSS</sub> (green line) concentrations in the overall background MBL environment (Missing points in HONO<sub>PSS</sub> were due to insufficient  $J_{HONO}$  values).

#### 6.3.3.2 Heterogeneous Source

As mentioned above, the estimated HONO level is much lower than observation when only homogeneous reaction of OH and NO is considered as the dominant daytime HONO source. The calculated HONO can be enhanced by including the heterogeneous reaction (R2.8), which is the dominant nocturnal HONO source.

$$[HONO_{PSS}] = \frac{k_{homo}[NO][OH] + C_{HONO}[NO_2]}{J_{HONO} + K_{OH+NO}[OH]}$$
(E6.12)



Figure 6-28 Measured daytime HONO (blue line) and calculated HONO<sub>PSS</sub> (orange line) in the polluted MBL environment (Missing points in HONO<sub>PSS</sub> were due to insufficient J<sub>HONO</sub> values).

Figure 6-28 and 6-29 show the calculated HONO concentrations in comparison with the observed values during the selected episode days and the overall clear days. The HONO<sub>PSS</sub> concentrations are enhanced after adding heterogeneous source into the PSS calculation, the combination of two sources can explain 30% - 75%

daytime HONO levels in some cases. However, during most of the days, it is clear that daytime HONO cannot be sustained with only these two sources.



**Figure 6-29** Measured daytime HONO (blue line) and calculated HONO<sub>PSS</sub> (orange line) in the overall background MBL environment (Missing points in HONO<sub>PSS</sub> were due to insufficient J<sub>HONO</sub> values).

### 6.3.4 Role of the Unknown HONO Source(s)

The above calculation results indicate the existence of other potential daytime HONO source(s), whose source strength(s) are still not clear but can be estimated by the PSS calculation using following equation:

$$P_{Unknown} \approx [\text{HONO}_{obs}] \times (J_{HONO} + k_{OH+NO}[\text{OH}]) - (k_{homo}[\text{NO}][\text{OH}] + C_{HONO}[\text{NO}_2])$$
(E6.13)

Where HONO<sub>obs</sub> denotes the measured HONO values.



Figure 6-30 Averaged diurnal pattern of HONO and averaged production rates for known and unknown sources.

Figure 6-30 shows the averaged production rates for the known sources ((R2.2) and (R2.8),  $P_{known}$ ) and unknown sources ( $P_{Unknown}$ ) together with averaged diurnal HONO and NO<sub>2</sub> mixing ratios. The calculated  $P_{Unknown}$  is 4 - 8 times larger than  $P_{known}$ , and reaches its peak at noontime (12:00 LT) when minimum NO<sub>2</sub> concentration is in its minimum. It is not clear whether this unknown source is related to the NO<sub>2</sub> or other parameters like solar radiation and gas-phase HNO<sub>3</sub>,

thus correlation studies below are conducted to find out the more information about the exact mechanism of the unknown source.

### 6.3.5 Correlation Studies

To further investigate the relationship between the unknown daytime HONO source and other pollutants, and to find out possible formation pathways to explain the large daytime HONO production rates, correlation analyses are carried out. The correlation between  $P_{\text{Unknown}}$  and water content of air (H<sub>2</sub>O) is shown in Figure 6-31, and the very poor correlation indicates that the HONO source is not very sensitive to the water vapor in the atmosphere.



Figure 6-31 Correlation between Punknown and absolute water content.



Figure 6-32 Correlation between P<sub>unknown</sub> and [NO<sub>2</sub>].

Figure 6-32 shows the correlation between the unknown source and NO<sub>2</sub> concentration. As the surface area density (S/V) is nearly a constant for the ground surface during daytime, good correlation between P<sub>unknown</sub> and NO<sub>2</sub> typically indicates a relationship between the unknown source and the heterogeneous reaction on ground surface [*Su et al.*, 2008b]. The correlation is moderate (R = 0.37) and much better than those reported in Xinken, China (R = 0.08) [*Su et al.*, 2008b], Paris, France (R  $\approx$  0) [*Michoud et al.*, 2014] and Harrow, Canada (R = 0.20) [*Wentzell et al.*, 2010]. This result suggests that this unknown source could be partially related to the heterogeneous conversion of NO<sub>2</sub> to HONO on ground/sea surfaces. The correlation between P<sub>unknown</sub> and reaction on aerosol is not examined as no measurement data is available.

Solar radiation or light intensity is considered as one of the most important parameter in the heterogeneous conversion of NO<sub>2</sub> on surfaces [*Stemmler et al.*,

2006]. The light induced heterogeneous reaction should be proportional to the term of  $[NO_2] \times J_{NO2}$ . The correlation shown in Figure 6-33 is enhanced (R = 0.57) by adding  $J_{NO2}$  into the term, implying that photochemistry plays a significant role in this formation pathway. A higher value of correlation coefficient (R = 0.59) (shown in Figure 6-34) can be determined with the form of  $[NO_2] \times J_{NO2} \times [H_2O]$ , which usually represents the gas-phase reaction (R2.4). However, the very small enhancement and the very poor correlation between P<sub>unknown</sub> and [H<sub>2</sub>O] may suggest the very minor role of [H<sub>2</sub>O] and (R2.4) in the daytime HONO formation.



**Figure 6-33** Correlation between  $P_{unknown}$  and  $[NO_2] \times J_{NO2}$ .



Figure 6-34 Correlation between  $P_{unknown}$  and  $[NO_2] \times J_{NO2} \times [H_2O]$ .

Correlation of other pollutants like gas-phase and accumulated HNO<sub>3</sub> are also analyzed in this study. Gas-phase HNO<sub>3</sub> is estimated by subtracting the NO, NO<sub>2</sub>, peroxyacetyl nitrate (PAN) and HONO from simultaneously measured NO<sub>y</sub> concentrations. According to the calculation method presented by *Li et al.* [2012], the averaged gas-phase HNO<sub>3</sub> concentrations over the prior 24-h period was considered as the accumulated HNO<sub>3</sub>. The very small values of R (0.04 and 0.02, respectively) imply that they are not the likely sources for the daytime HONO.

Results of correlation analyses indicate that the unknown daytime source at Hok Tsui may be the photo-enhanced heterogeneous conversion of  $NO_2$  to HONO on surfaces. Further investigation of the exact HONO daytime formation mechanism is needed.

#### 6.4 Contribution from HONO to OH Radical

HONO has been known to be the dominant source of OH in some areas during the early morning when other OH sources like ozone and formaldehyde (HCHO) are in low levels. However, recent studies found that HONO could play a more significant role through entire day as high daytime HONO concentrations were observed in many studies. To investigate the contribution to OH from HONO at Hok Tsui, the production rates of OH (P<sub>OH</sub>) from ozone and HONO are estimated and compared. OH production rates from ozone photolysis,  $P_{OH}^{O(^{1}D)}$ , can be calculated with the following equation:

$$P_{OH}^{O(^{1}D)} = \frac{2J_{O(^{1}D)} \times [O_{3}] \times k_{H_{2}O} \times [H_{2}O]}{k_{H_{2}O} \times [H_{2}O] + k_{N_{2}} \times [N_{2}] + k_{O_{2}} \times [O_{2}]}$$
(E6.14)

Which is derived from the following reactions:

$$O_3 + hv \rightarrow O(^1D) + O_2(\lambda < 320 \,\mathrm{nm}) \tag{R6.1}$$

$$O(^{1}D) + H_{2}O \rightarrow 2OH \tag{R6.2}$$

Where  $J_{O(^{1}D)}$  is calculated using a parameterization in the Master Chemical Mechanism (MCM v3) [*Saunders et al.*, 2003] and scaled with the observed J<sub>NO2</sub>. OH production rates from HONO photolysis,  $P_{OH}^{HONO}$ , can be determined with the following equation:

$$P_{OH}^{HONO} = J_{HONO} \times [HONO]$$
(E6.15)

Mean production rates during daytime (06:00 – 18:00 LT, only sunny days are included) for episode and non-episode days are estimated. The 12-h averaged OH production rates of HONO photolysis (0.091 pptv/s) and O<sub>3</sub> photolysis (0.099 pptv/s) during non-episode days suggest that they play equally important roles. However, the averaged  $P_{OH}^{HONO}$  (0.320 pptv/s) on episode days is much larger than that the averaged  $P_{OH}^{O(^{1}D)}$  (0.144 pptv/s).

Figure 6-35 shows the daytime patterns of  $P_{OH}^{HONO}$  and  $P_{OH}^{O(^{1}D)}$  in a selected episode day (October 23, 2012). Data of J<sub>NO2</sub> indicated that the day was sunny and clear. O<sub>3</sub> increased shortly after sunrise (06:00 LT) and reached its maximum concentration of ~105 ppbv at noontime (12:30 LT). The peak of HONO mixing ratio (1.100 ppbv) was observed in the early morning, and the averaged HONO level during daytime was also in a very high level (~0.450 ppbv). As shown in this figure,  $P_{OH}^{HONO}$  fast increased to the maximum rate (0.793 pptv/s) at 09:50 LT when  $P_{OH}^{O(^{1}D)}$  was ~ 0.087 pptv/s. When  $P_{OH}^{O(^{1}D)}$  reached its peak (0.580 pptv/s) in the afternoon,  $P_{OH}^{HONO}$  also showed a comparable OH production rate (0.500 pptv/s). It was clear that photolysis of HONO was a more significant OH source than ozone photolysis during episode days.



**Figure 6-35** Daytime (06:00-18:00 LT) patterns of J<sub>NO2</sub>, HONO, O<sub>3</sub> and OH production rates (P<sub>OH</sub>) for HONO (green) and O<sub>3</sub> (pink) in the selected episode day (October 23, 2012).

 $P_{OH}^{HONO}$  and  $P_{OH}^{O(^{1}D)}$  are also examined and compared in a selected non-episode case. During the day of November 1, 2012, HONO concentrations did not show strong variation and remained stable at ~0.100 ppbv, and O<sub>3</sub> mixing ratios increased slowly from 47 ppbv (06:00 LT) to 70 ppbv (18:00 LT). As shown in Figure 6-36, a maximum OH production rate of 0.233 pptv/s was obtained at 10:00 LT, indicating that photolysis of HONO was a larger OH source before noon (The largest  $P_{OH}^{O(^{1}D)}$  was ~0.198 pptv/s during that period). Compared to the 12-h averaged  $P_{OH}^{HONO}$  (0.044 pptv/s) and  $P_{OH}^{O(^{1}D)}$  (0.139 pptv/s) determined in a rural site at Pabstthum,

Germany [*Alicke et al.*, 2003], averaged rates of  $P_{OH_net}^{HONO}$  (0.106 pptv/s) at Hok Tsui was much larger and comparable with  $P_{OH}^{O(^{1}D)}$  (0.125 pptv/s), implying that HONO apparently plays a more important role at Hok Tsui.



**Figure 6-36** Daytime (06:00-18:00 LT) patterns of J<sub>NO2</sub>, HONO, O<sub>3</sub> and net OH production rates (P<sub>OH\_net</sub>) for HONO (green) and O<sub>3</sub> (pink) in the selected non-episode day (November 1, 2012).

# **Chapter 7 Conclusions**

This research investigated HONO formation mechanisms during nighttime and daytime in a marine boundary layer (MBL) environment and the possible role of HONO in photochemistry.

The main finding are summarized as below:

- Average mixing ratios of HONO showed a nocturnal HONO peak (0.155 ppbv) and another even higher daytime peak (0.160 ppbv) suggesting strong daytime HONO source(s) around Hok Tsui site.
- (2) Nocturnal cases of sea-coming and land-coming air masses are selected using back trajectories and on-site winds. The NO<sub>2</sub>-to-HONO conversion rates in the sea cases  $(3.17 3.36 \times 10^{-2} h^{-1})$  are almost 3 times of those for .the land cases  $(1.20 1.30 \times 10^{-2} h^{-1})$ . This is the first report of the conversion rates on sea surface.
- (3) The strengths of "known" and "unknown" sources for daytime HONO are estimated using a photostationary state (PSS) assumption. Production rates of the unknown source ( $\leq 0.2$  pptv/s) is found 4-8 times larger than the known sources. Good correlation between the unknown source and the proxy of photo-enhanced heterogeneous NO<sub>2</sub> conversion ([NO<sub>2</sub>] × J<sub>NO2</sub>)

suggest that this reaction may contribute significantly to the daytime HONO levels.

(4) Photolysis of HONO is a stronger source of OH compared to photolysis of ozone and its contribution is not only significant during sunrise, but throughout entire day at Hok Tsui.

This study is one of the few investigations of HONO in the marine boundary layer. The key finding is the apparent large conversion rates of NO<sub>2</sub> on sea surfaces, which has not been reported in previous researches and has not been considered in current photochemical models. If the findings of the study are confirmed and applicable to other regions, researchers may need to reconsider the role of sea surface in nighttime/daytime HONO production, and global and regional chemical transport models may also need to add parametrization scheme for HONO formation on the sea. Further laboratory/field studies are needed to find out the reason(s) for the larger conversion rates on sea surface.

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