

Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry

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Abstract Nitryl chloride (ClNO₂) is a product of nocturnal halogen activation of nitrogen oxides and has potential to impact atmospheric photochemistry. Here we report the first observation result of ClNO₂ in an Asian environment. The measurements were made with a thermal decomposition chemical ionization mass spectrometer at a coastal site in southern China during late summer of 2012. A clear diurnal pattern of ClNO₂ was observed with nighttime 1-min average mixing ratio up to 1997 pptv, which is among the highest values ever reported in the world. The elevated ClNO₂ mixing ratios were observed in plumes from Hong Kong and the Pearl River Delta region compared to the lower levels in maritime air. Calculations suggest that the production of chlorine atom from photolysis of ClNO₂ in the early morning exceeds the production of hydroxyl radical via ozone photolysis by several factors. Therefore, ClNO₂ plays an important role in jump-starting the atmospheric photochemistry in polluted marine boundary layer of southern China.

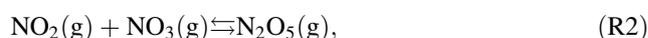
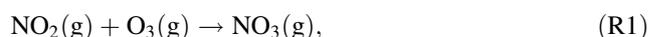
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Release of nitrogen oxides (NO_x = NO + NO₂) from anthropogenic activities has changed significantly the chemistry of atmosphere [1]. During daytime, nitrogen oxides undergo complicated photochemical evolution forming ozone (O₃), nitric acid (HNO₃), and various organic nitrates; this part of chemistry has been extensively addressed since 1980s [2]. At night, reactions of NO₂ with O₃ (R1, R2) lead to the formation of dinitrogen pentoxide (N₂O₅), a key intermediate for heterogeneous reaction on aerosols to form nitrate (NO₃⁻), and if chloride is available, nitryl chloride (ClNO₂; R3) [3, 4]. ClNO₂ is a potentially important player in atmospheric chemistry since it acts as a radical reservoir at night but may be subject to photolysis in the morning liberating reactive chlorine atom (Cl; R4). The Cl atom is a key oxidant in the atmosphere that may initiate the daytime photochemical cycle by oxidizing volatile organic compounds (VOCs) and contribute to the secondary pollution [5].



The above nocturnal process was not tested in the real atmospheres until recently, as a result of the advancement of measurement techniques. The first field observation of ClNO₂ took place in 2006 in the US, which found high levels (>1 ppbv) of ambient ClNO₂ along the coast of Texas [6]. Additional studies were then conducted in both polluted marine [7, 8] and inland environments [9–11] to underline the importance of ClNO₂. To date, however, the research was only conducted in North America as well as certain parts of Europe, and the lack of observational data

in other regions raises the question if the presence of ClNO_2 is a universal phenomenon over the globe. Asia is an interesting region (especially China) to study the ClNO_2 chemistry due to its much higher loadings of NO_x and aerosols. To the best of our knowledge, the measurements we reported here appear to be the first evidence to support the availability and impact of ClNO_2 in Asia.

In the present study, ClNO_2 and related parameters including O_3 , NO_2 , and J_{NO_2} were measured at Hok Tsui ($22^\circ 13' \text{N}$, $114^\circ 15' \text{E}$, 60 m a.s.l.) which is located at the southeast tip of Hong Kong Island during 23 August to 1 September 2012. Hok Tsui can serve as an ideal regional background site of southern China (refer to Cheng et al. [12] for the details of the site). ClNO_2 was detected and quantified with a thermal decomposition chemical ionization mass spectrometer (TD-CIMS), a state-of-the-art technique that combines ion–molecule chemistry and mass spectrometry detection and has the potential to measure many highly reactive species in field [13, 14]. Iodide was used as the primary reagent ion and the instrument setup was similar to that described by Slusher et al. [15] (see the supplementary material for the experimental details online).

The measurement data are presented in Fig. 1. ClNO_2 was detected throughout the campaign, with a distinct diurnal variation showing nighttime peaks with daytime levels close to the detection limit. This pattern is similar to those observed in the other marine environments [6, 16], and is a result of the fast daytime photolysis of ClNO_2 and nocturnal accumulation of N_2O_5 and hence ClNO_2 . During the campaign, the mean mixing ratio of ClNO_2 was 148 pptv with a large standard deviation of 253 pptv. The maximum

value (1-min average) was 1997 pptv on the night of 23/24 August, which is comparable to the highest ever reported concentration (2.1 ppbv) in the Los Angeles Basin [7] (Table S1 online). This implies active N_2O_5 – ClNO_2 chemistry in the marine boundary layer atmosphere in southern China.

The day-to-day variation of ClNO_2 observed at Hok Tsui was highly related to changes in air masses. During the period of 23–28 August when high nighttime ClNO_2 was measured, the site was significantly influenced by polluted plumes from urban Hong Kong and the Pearl River Delta region as evidenced by the 24-h back trajectories calculated by the HYSPLIT model ([17]; Fig. S3 online). These plumes contained abundant ozone and moderate levels of NO_2 , favoring the production of N_2O_5 , which in turn facilitated the formation of ClNO_2 given the fact that the chloride aerosol is generally adequate in coastal Hong Kong [12]. For example, on the 23/24 August night, approximately 110 ppbv of ozone together with 10 ppbv of NO_2 were observed along with ClNO_2 exceeding 1 ppbv. In contrast, relatively low mixing ratios of ClNO_2 were detected from 29 August to 1 September when the air masses were dominated by the maritime air with low ozone and NO_2 . Obviously, the availability of N_2O_5 precursors (i.e., O_3 and NO_2) should be the limiting factor of the ClNO_2 production at our site.

To assess the potential impact of ClNO_2 on atmospheric photochemistry, the production rate of Cl atom (R_{Cl}) through ClNO_2 photolysis was calculated through an equation (Eq. 1) and compared with the production rate of OH via ozone photolysis which is normally the dominant radical source in nonurban atmospheres. Figure 2 illustrates the production rate of Cl atom as well as the ratio of

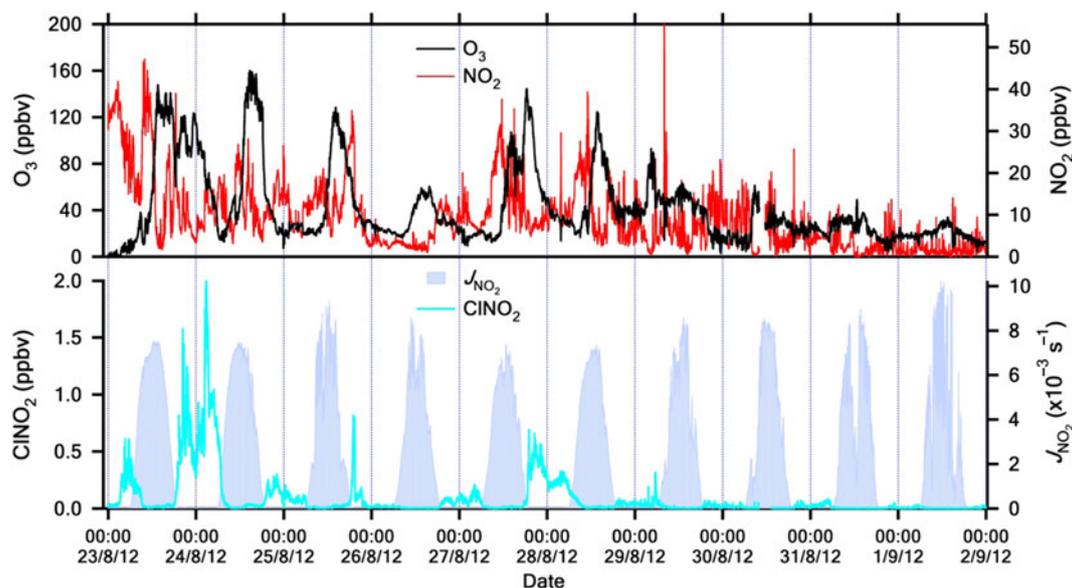


Fig. 1 Time series of ClNO_2 and related parameters observed at Hok Tsui, Hong Kong

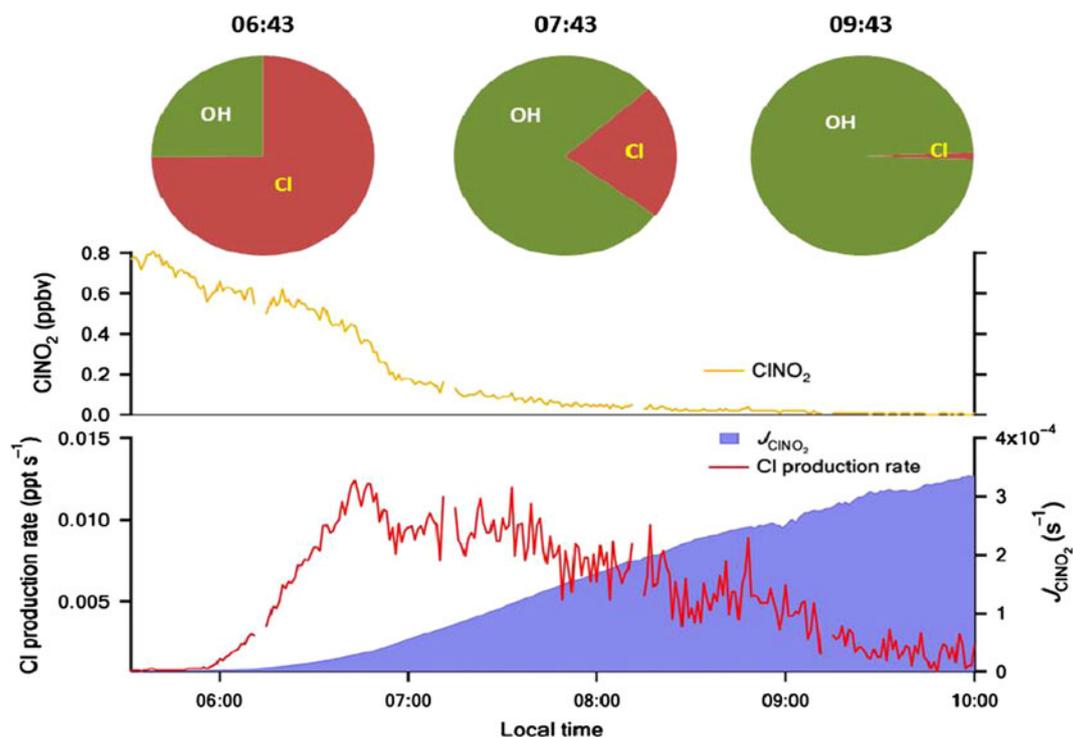


Fig. 2 CINO₂ mixing ratio and production rate of Cl atom from CINO₂ photolysis in the early morning of 24th August 2012. Pie charts represent the ratio of Cl atom production (red) and OH radical production via O₃ photolysis (green) at 06:43, 07:43, and 09:43 local time

Cl atom production to OH production in the early morning of 24 August 2012. After sunrise (i.e., 06:00–07:00, local time), fast photolysis of CINO₂ led to high production of Cl atom (maximum rate = 0.012 ppt s⁻¹) that exceeded the OH production from ozone photolysis by a factor of 3. Consequently, CINO₂ photolysis should be an important radical source in the early morning period, although the ozone photolysis became more and more important later. Cl atom is an important oxidant toward VOCs especially alkanes, with the reaction rates several orders of magnitude faster than OH [18]. This analysis suggests that CINO₂ accumulated over night may play a significant role in imitating the next day's photochemistry.

$$R_{\text{Cl}} = J_{\text{CINO}_2}[\text{CINO}_2]. \quad (1)$$

In conclusion, the presence of high CINO₂ in Asian coastal environment was confirmed by the observations. CINO₂ seems to be an important radical source that jump-starts the atmospheric photochemistry in the early morning. Current air quality models usually miss this process in predicting the formation of secondary pollutants such as ozone and secondary aerosols. Future efforts are needed to determine CINO₂ (and related species) in other polluted coastal and inland regions in Asia, to understand its chemistry and impact, and to improve the related chemical mechanism in the current air quality models.

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