

# High levels of nitryl chloride in the polluted subtropical marine boundary layer

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The cycling of halogen compounds in the lower atmosphere is poorly understood. It is known that halogens such as chlorine, bromine and iodine are converted from halides, which are relatively inert, to reactive radicals. These reactive radicals can affect ozone production and destruction, aerosol formation and the lifetimes of important trace gases such as methane, mercury and naturally occurring sulphur compounds. However, the processes by which halides are converted to reactive halogens are uncertain. Here, we report atmospheric measurements of nitryl chloride, an active halogen, along the southeast coastline of the United States and near Houston, Texas. We show that the main source of nitryl chloride is the night-time reaction of dinitrogen pentoxide with chloride-containing aerosol. The levels observed are much greater than earlier estimates based on numerical models and are sufficiently large to affect oxidant photochemistry in areas where nitrogen oxides and aerosol chloride sources coexist, such as urban areas and ship engine exhaust plumes.

Chemically active halogens (free radicals such as Cl, Br atoms or ClO, BrO and IO) are important trace reactants of the lower atmosphere<sup>1</sup>. They are involved in processes such as oxidant chemistry in the mid-latitudes<sup>2,3</sup>, conversion of marine sulphur emissions to non-sea-salt sulphate aerosol<sup>4</sup> and destruction of ozone in the polar springtime boundary layer<sup>5</sup>. Despite extensive evidence of halogen chemistry in the troposphere<sup>6–9</sup>, the detailed chemical processes by which inert halides (for example, chloride) are converted to the reactive atomic or radical forms (for example, Cl atoms) are still quite uncertain<sup>5,9,10</sup>. Here, we report the first observations of nitryl chloride (ClNO<sub>2</sub>), a potentially important source of active halogens in the troposphere. These measurements show this compound to be quite abundant, more than 1 p.p.b.v. (parts per 10<sup>9</sup> by volume), in the subtropical marine boundary layer (MBL) partly owing to NO<sub>x</sub> (= NO + NO<sub>2</sub>) emissions.

Laboratory studies have shown that ClNO<sub>2</sub> is produced efficiently from the heterogeneous reaction of dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) on sea salt<sup>11–15</sup> and to some extent in dilute chloride solutions<sup>12</sup>. The importance of these processes in the atmosphere has been uncertain because of a lack of direct observations of the relevant species. We present evidence to show that ClNO<sub>2</sub> is produced in high yield at night from the reaction of N<sub>2</sub>O<sub>5</sub> on all chloride-containing aerosol particles. The observed ClNO<sub>2</sub> mixing ratios were larger than predicted by current inventories and models<sup>16,17</sup>, even one that explicitly considers ClNO<sub>2</sub> in polluted

continental outflow<sup>18</sup>. ClNO<sub>2</sub> was found to accumulate at night and be photolysed after sunrise to produce chlorine atoms, at a time when other oxidants and radicals (for example, OH, NO<sub>3</sub>) were scarce, very likely leading to enhanced oxidation of volatile organic compounds (VOCs) and acceleration of photochemical ozone production. The implications of these observations for regional air quality are greatest for near-coastal urban areas, where NO<sub>x</sub>, O<sub>3</sub>, sea salt and aerosol sources coexist.

ClNO<sub>2</sub> was measured in ambient air using chemical ionization mass spectrometry (using I<sup>−</sup> as a reagent ion), simultaneously with N<sub>2</sub>O<sub>5</sub> (by cavity ring-down spectroscopy) and aerosol size distribution and composition. These measurements were conducted on the National Oceanic and Atmospheric Administration (NOAA) research vessel Ronald H. Brown during an air quality and climate study in the Gulf of Mexico, with particular emphasis on Houston, Texas, during the summer of 2006. Detailed descriptions of instrumental methods are given below and in the Supplementary Information. The data show that (1) ClNO<sub>2</sub> is predominantly a night-time species, (2) mixing ratios of ClNO<sub>2</sub> are large and correlate strongly with those of N<sub>2</sub>O<sub>5</sub>, (3) ClNO<sub>2</sub> is sufficiently long-lived at night to constitute a large photolabile Cl and NO<sub>x</sub> reservoir at sunrise and (4) the corresponding Cl production is sufficient to affect regional photochemistry, as indicated by numerical modelling.

## NITRYL CHLORIDE OBSERVATIONS

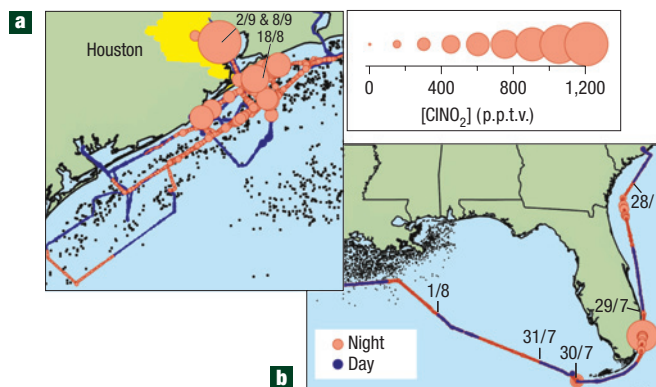
Figure 1b shows the portion of the ship track along the United States southeast coastline and across the Gulf of Mexico, where the air was primarily of remote marine origin. Here, the largest  $\text{NO}_x$  sources were the exhaust plumes of ship engines: all but the most recently emitted of these plumes contained measurable quantities of  $\text{ClNO}_2$ . The  $\text{ClNO}_2$  mixing ratios were surprisingly large, on occasion exceeding 1 p.p.b.v., up to 15% of total reactive nitrogen ( $\text{NO}_y$ ). In contrast,  $\text{ClNO}_2$  mixing ratios in the clean nocturnal MBL were below the 50 p.p.t.v. instrumental detection limit during this campaign. Observations closer to Houston (Fig. 1a) also showed large  $\text{ClNO}_2$  levels at night, in a pattern clustered around  $\text{NO}_x$  sources located in the urban and industrial areas of the Houston ship channel. During the daytime,  $\text{ClNO}_2$  was present in large concentration only during the morning hours (see below): there were indications of much smaller amounts of  $\text{ClNO}_2$  at other times of day under conditions conducive to the formation of daytime  $\text{N}_2\text{O}_5$  (ref. 19). The overall uncertainties for the  $\text{ClNO}_2$  measurements during this campaign are estimated at  $\pm(30\% + 50 \text{ p.p.t.v.})$ .

THE RELATIONSHIP BETWEEN  $\text{N}_2\text{O}_5$  AND  $\text{ClNO}_2$ 

The broad correlation of  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  throughout the six-week campaign strongly indicates that  $\text{N}_2\text{O}_5$  was the source of  $\text{ClNO}_2$ . Figure 2 shows this correlation during two representative periods. In the first, a mixture of  $\text{NO}_x$ -containing ship and oil platform plumes was sampled south of Galveston Bay on 18 August in an air mass also impacted by continental pollution; in the second, nearby urban/industrial emissions were sampled in an inlet off Galveston Bay on 8 September. Timelines for measured total  $\text{NO}_y$ , also in Fig. 2, show many of the same broad features, with  $\text{ClNO}_2$  reaching at most 7% of  $\text{NO}_y$  during these periods. The insets show correlations of measured  $\text{ClNO}_2$  with the calculated uptake rate of  $\text{N}_2\text{O}_5$  on aerosol<sup>20</sup> using a laboratory-derived uptake coefficient,  $\gamma_{\text{N}_2\text{O}_5} = 0.03$  (ref. 21) and measured aerosol surface area. On 8 September, the correlations had similar slopes ( $r^2 = 0.941$ ) throughout the night, indicating similar reaction times because  $\text{NO}_x$  emission sources were nearby; in contrast, the 18 August data, although temporally correlated, exhibited variable slopes from plumes with different transport times to the research vessel.

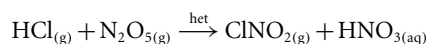
The relationship between  $\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$  was assessed quantitatively for individual plumes by numerical integration of their respective formation and loss processes (see the Supplementary Information), including gas-phase reactions of  $\text{NO}_2$  with  $\text{O}_3$  to produce  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ , heterogeneous reaction of  $\text{N}_2\text{O}_5$  with aerosol to yield  $\text{ClNO}_2$  and loss of  $\text{NO}_3$  due to gas-phase reactions (for example, VOC oxidation). The value of  $k_{\text{het}}$ , the first-order rate coefficient for conversion of  $\text{N}_2\text{O}_5$  to  $\text{ClNO}_2$ , was varied to match the simulated and observed mixing ratios of  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$ . The ratio of  $k_{\text{het}}$  to the total loss rate coefficient of  $\text{N}_2\text{O}_5$ , calculated from the aerosol surface area density, is a measure of the yield of  $\text{ClNO}_2$  from heterogeneous  $\text{N}_2\text{O}_5$  uptake. The model was applied to plumes in which  $\text{NO}_x$  sources could be clearly identified or were sufficiently isolated (for example, ship plumes against a clean background), so that the nocturnal transport time could be estimated.

The range of estimated  $k_{\text{het}}$  was from  $1 \times 10^{-4} \text{ s}^{-1}$  to  $3 \times 10^{-3} \text{ s}^{-1}$ , significantly larger than that predicted for  $\text{N}_2\text{O}_5$  uptake on sea-salt aerosol, which is primarily supermicrometre in size, implying that a substantial fraction of the reaction occurred on submicrometre aerosol. Chemical analyses of submicrometre aerosol showed chloride concentrations in the range 0–1 M, with a median of 0.05 M, consistent with  $\text{HCl}_{(\text{g})}$  partitioning to the aerosol phase<sup>22</sup>



**Figure 1** Maps of the study area. **a, b**, Maps of the study area showing a detailed view of the focused study area in the vicinity of Houston, Texas (shown in yellow) (**a**) and the ship track along the United States southeast coastline and across the Gulf of Mexico (**b**). Measured  $\text{ClNO}_2$  (5 min average) is plotted along the track scaled by size. The colour coding differentiates night time (red) from daytime (blue). Black dots along the Texas–Louisiana coast are oil and natural gas platforms. The locations of measurements shown in Figs 2 and 3 (18 August, 2 September and 8 September) are indicated.

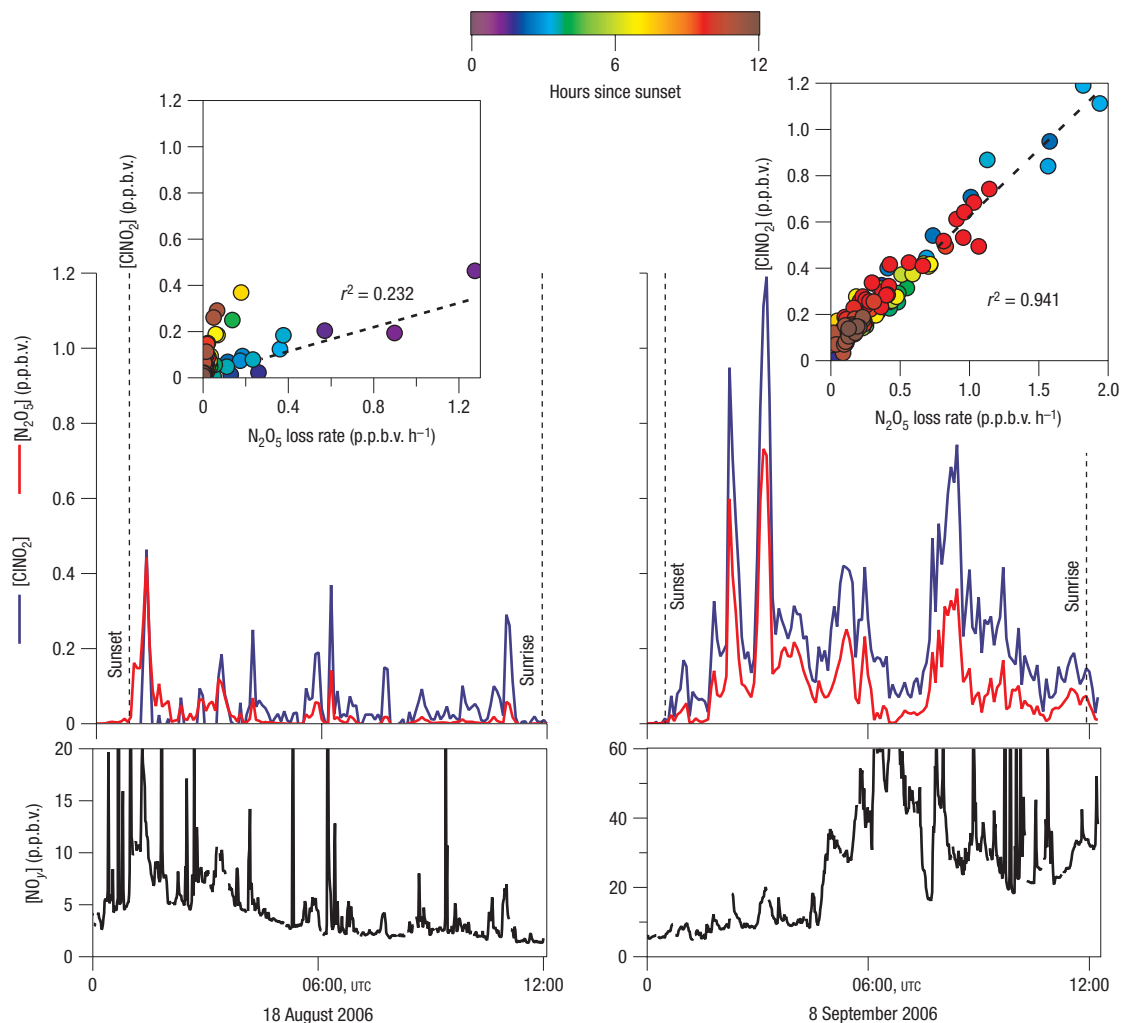
and a minor contribution from submicrometre sea salt. Although measured submicrometre chloride mass loadings were insufficient to produce observed  $\text{ClNO}_2$ , there was sufficient measured gas-phase chloride (mainly  $\text{HCl}$ ) to replenish aerosol-phase  $\text{Cl}^-$  and support continuous heterogeneous  $\text{ClNO}_2$  production. Laboratory studies have shown 25% yields of  $\text{ClNO}_2$  on solutions with  $[\text{Cl}^-]$  as low as approximately 0.1 M, consistent with  $\text{Cl}^-$  being an efficient scavenger of the  $\text{NO}_2^+$  ion proposed as an intermediate in the first step of  $\text{N}_2\text{O}_5$  surface reaction<sup>12</sup>. In our study,  $\text{ClNO}_2$  was observed in the presence of  $\text{N}_2\text{O}_5$  and submicrometre  $\text{Cl}^-$  molarities as low as 0.02 M. The net effect of these gas-particle processes can be summarized by the following reaction.



The simulation–measurement comparison implies not just a larger than anticipated source for  $\text{ClNO}_2$ , but also a long lifetime for  $\text{ClNO}_2$  ( $>30 \text{ h}$ ) in the nocturnal MBL. The latter is expected, because the most likely nocturnal  $\text{ClNO}_2$ -loss pathway is heterogeneous uptake, and Henry's law constant ( $4.6 \times 10^{-2} \text{ M per atm for water}$ )<sup>15</sup> and uptake coefficients ( $\gamma < 5 \times 10^{-6}$  over water and  $\text{Cl}^-$ -containing solutions)<sup>21</sup> are small. Reactions of  $\text{ClNO}_2$  with gas-phase species have not been extensively studied, but those that are known, such as reaction with  $\text{NO}$  ( $k = 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) (ref. 23), are slow. Indeed, the lifetime of  $\text{ClNO}_2$  may be such that it will be widespread in polluted regions of the nocturnal MBL. The detection limit of our measurement (50 p.p.t.v.) did not permit us to explore this further.

THE EFFECT OF  $\text{ClNO}_2$  ON ATMOSPHERIC CHEMISTRY

Efficient  $\text{ClNO}_2$  production has two important consequences for air quality in coastal regions. First,  $\text{ClNO}_2$  acts as a nocturnal reservoir for  $\text{NO}_x$ , regenerating  $\text{NO}_2$  on photolysis at sunrise. In environments where  $\text{ClNO}_2$  yields are appreciable (such as the 10–65% found in this study), overnight conversion of  $\text{NO}_x$  to  $\text{HNO}_3$  ( $\text{NO}_x$  loss) would be considerably reduced<sup>24</sup>. Second,  $\text{ClNO}_2$  produces reactive chlorine atoms that can significantly enhance



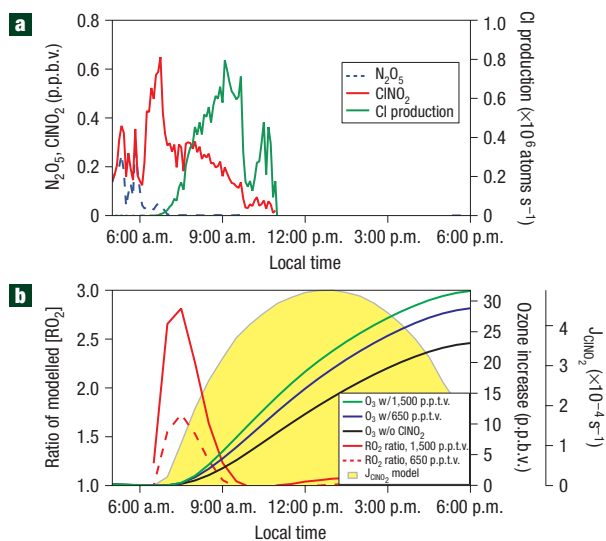
**Figure 2** Measurements of  $\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$  on two different nights. Time series of  $\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$  on the nights of 18 August and 8 September. The bottom panels show total reactive nitrogen ( $\text{NO}_x$ ). The insets show the correlation between  $\text{ClNO}_2$  and the heterogeneous uptake rate of  $\text{N}_2\text{O}_5$  (see text), colour coded according to sampling time since sunset. The nearly constant ratio of  $\text{ClNO}_2$  over  $\text{N}_2\text{O}_5$  loss rate observed on 8 September ( $r^2 = 0.941$ ) suggests that  $\text{ClNO}_2$  is dominated by rapid production.

VOC oxidation rates, particularly in a VOC-rich area such as Houston, at a time of day when other common oxidants (for example,  $\text{NO}_3$ , OH) are scarce<sup>25</sup>.

The effect of  $\text{ClNO}_2$  as a Cl atom source is shown in Fig. 3a for the morning of 2 September 2006. In this case,  $\text{ClNO}_2$  remained into the mid- to late-morning hours, long after  $\text{N}_2\text{O}_5$  had been destroyed by thermal decomposition and photochemical degradation of  $\text{NO}_3$ . The resulting Cl source, calculated from the observed  $\text{ClNO}_2$  and measured photolysis rates, approached  $1 \times 10^6 \text{ atoms cm}^{-3} \text{ s}^{-1}$ . This Cl source can be compared to other photolytic oxidant sources present in this early-morning air mass: OH from  $\text{O}_3$ , OH from HONO and  $\text{HO}_2$  from HCHO, listed in Table 1. The  $\text{O}_3$  and HCHO sources were calculated from measured concentrations and photolysis rates. The HONO source was estimated from measured  $\text{NO}_2$  assuming a 5% HONO/ $\text{NO}_2$  ratio consistent with observations during the TexAQ5 2000 study at the LaPorte site<sup>26</sup>, 5 km from our site. Estimated OH from HONO,  $8 \times 10^6 \text{ mol cm}^{-3} \text{ s}^{-1}$ , is consistent with calculations from observed HONO at another continental site<sup>27</sup>, although it is not clear that HONO in a marine environment will be as large. The Cl atom source from  $\text{ClNO}_2$  is modest relative to the other oxidants; however, Cl is more reactive than OH, and will more

efficiently produce radicals from oxidation of less-reactive VOCs, such as alkanes. Table 1 shows both the absolute radical production rates and production rates weighted by the ratio of reaction rate coefficients for Cl and OH with propane (an abundant alkane). By this measure, Cl is the dominant oxidant.

The precise consequences of  $\text{ClNO}_2$  chemistry to marine and coastal  $\text{O}_3$  production depend on the VOC and  $\text{NO}_x$  levels within a given air mass. Figure 3b gives an example calculation using the master chemical mechanism (see the Supplementary Information) with added photolysis of  $\text{ClNO}_2$  and Cl-VOC chemistry. The model case used has been described previously<sup>28</sup> and is typical of a polluted air mass after one-day transport in the MBL. Addition of 650 p.p.t.v. of  $\text{ClNO}_2$  (consistent with some of the highest observed levels on 2 September) and 1,500 p.p.t.v. of  $\text{ClNO}_2$  (slightly higher than the high values we observed in this study) resulted in early increases in photochemical activity as measured by faster  $\text{O}_3$  production and larger midday  $\text{O}_3$ . These increases in ozone of 6 and 9 p.p.b.v., respectively, above that present at sunrise, were driven by both  $\text{NO}_x$  and Cl release. The latter is illustrated from the morning peak in total peroxy radical concentration  $\text{RO}_2$  ( $\text{RO}_2 = \text{hydroperoxy} + \text{organic peroxy radicals}$ ) of factors of 1.7 and 2.8.



**Figure 3** Production of Cl atoms from ClNO<sub>2</sub> photolysis. **a**, Measured mixing ratios of ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> and the Cl atom production rate resulting from the photolysis of ClNO<sub>2</sub> on 2 September 2006, while the ship was stationary in an inlet off Galveston Bay. **b**, Master chemical mechanism results for a representative modestly polluted marine air mass, to which 650 and 1,500 p.p.t.v. of ClNO<sub>2</sub> have been added. Note that **b** is not intended as a model for the specific conditions in **a**, but rather to provide a general representation of the effect of ClNO<sub>2</sub> chemistry.

A thorough understanding of the effects of ClNO<sub>2</sub> on regional photochemistry requires three-dimensional regional models. However, recent studies of other potential Cl sources in urban airsheds corroborate the predicted enhancement in photochemical ozone from our model. Knipping and Dabdub<sup>3</sup> considered the production of Cl species from sea salt with a primary focus on the production of Cl<sub>2</sub> from OH chemistry, and estimated that near-shore Cl sources impact greater Los Angeles with up to 12 p.p.b.v. of extra photochemical O<sub>3</sub>. Increased O<sub>3</sub> production has also been attributed to industrial and domestic sources of photolabile Cl (for example, Cl<sub>2</sub> or HOCl) in the Houston area<sup>2</sup>, and control strategies have been proposed<sup>29</sup>. Our results imply that control of all Cl sources would require control of marine and coastal NO<sub>x</sub> sources because ClNO<sub>2</sub> may be appreciable in comparison with directly emitted Cl sources.

#### GLOBAL ASPECTS AND OVERALL SIGNIFICANCE OF NITRYL CHLORIDE

ClNO<sub>2</sub> chemistry can have global, in addition to regional, impacts. Just over half of the global population lives within 200 km of a coastline<sup>30</sup>, where urban and industrial NO<sub>x</sub> and aerosol pollution combines with sea-salt aerosol, leading to enhanced photochemical O<sub>3</sub> production. A simple and admittedly rough estimate of the global ClNO<sub>2</sub> source can be made from the N<sub>2</sub>O<sub>5</sub> to ClNO<sub>2</sub> conversion efficiencies determined in this study and global NO<sub>x</sub> emission data<sup>31</sup>. Considering only NO<sub>x</sub> sources within 50 km of a coastline and marine vessel sources, and further assuming that on average half of that NO<sub>x</sub> is converted to NO<sub>y</sub> through conversion to and reaction of N<sub>2</sub>O<sub>5</sub> (ref. 32), then N<sub>2</sub>O<sub>5</sub> to ClNO<sub>2</sub> conversion efficiencies similar to those inferred from these observations (5% for coastal urban and 15% for ship emissions) result in an estimate of 3.2 Tg yr<sup>-1</sup> as Cl. This is much larger than the global ClNO<sub>2</sub> estimate of 0.06 Tg Cl yr<sup>-1</sup> from Erickson *et al.*<sup>16</sup>, but is about 8% of the total Cl atom source inferred from the <sup>13</sup>C/<sup>12</sup>C kinetic isotope effect of Cl reaction with methane<sup>8</sup>. The ozone production

**Table 1** The effect of ClNO<sub>2</sub> as a radical source on 2 September 2006.

Radical source	Maximum rate (molecules cm <sup>-3</sup> s <sup>-1</sup> )	Effective radical source from propane (p.p.b.v.)*
Cl	0.8 × 10 <sup>6</sup>	28 <sup>†</sup>
OH from O <sub>3</sub>	1.1 × 10 <sup>7</sup>	1.6
OH from HONO	8 × 10 <sup>6</sup>	3.6
HO <sub>2</sub> from HCHO <sup>‡</sup>	6.3 × 10 <sup>6</sup>	0.94

\*Integrated from sunrise to 1100 local time.

<sup>†</sup> Estimated by multiplying the integrated source by the ratio of the rate constant of the Cl atom to that for OH.

<sup>‡</sup> Assumed to make OH radicals on reaction with NO (present after sunrise).

that results from this Cl source will have consequences for global climate forcing and tropospheric chemistry. The resulting halogen release may also have an impact on the abundances of non-sea-salt sulphate generated from dimethyl sulphate.

These first observations of ambient ClNO<sub>2</sub> demonstrate its efficient production from heterogeneous uptake of N<sub>2</sub>O<sub>5</sub> on aerosol particles, linking odd-nitrogen and halogen cycles in polluted coastal environments and ship plumes. ClNO<sub>2</sub> was significant (>1 p.p.b.v.), amounting to as much as 15% of NO<sub>y</sub>, implying that its production takes place not only on sea salt, but also on chloride-containing particles of continental origin. Photolysis of ClNO<sub>2</sub> results in NO<sub>x</sub> regeneration and chlorine atom production during morning hours, at times when other radical species, for example, NO<sub>3</sub> and OH, are at their lowest abundance. This Cl atom source initiates and accelerates daytime oxidant production in near-coastal environments where NO<sub>x</sub>, O<sub>3</sub> and sea-salt sources coexist.

#### METHODS

Nitryl chloride measurements were made with a chemical ionization mass spectrometer (CIMS) using iodide (I<sup>-</sup>) as a reagent ion. The instrument is similar to that described by Slusher *et al.*<sup>33</sup>, and the ion chemistry pertinent to ClNO<sub>2</sub> is discussed by McNeill *et al.*<sup>34</sup>. The ion {I·ClNO<sub>2</sub>}<sup>-</sup> at mass 207.9 was chosen for this measurement because it was deemed most specific and had a very low background in the CIMS system. The CIMS instrument was set to scan 10 ions for 0.5 s each, including the reagent ion, and complete mass scans were carried out approximately every few days. Zero levels were determined for 2 min every hour by online thermal decomposition of ambient air on a stainless-steel surface at 200 °C. The instrument was calibrated post-campaign using three independent methods: conversion of a known amount of N<sub>2</sub>O<sub>5</sub> on a NaCl slurry surface, and measurement of the output of a synthetic ClNO<sub>2</sub> source by NO<sub>y</sub> and by ultraviolet absorption spectroscopy. The three methods yielded an average response factor that had a relative standard deviation of ±18%. The response factor is a function of reagent ion number density, so the measured reagent ion counts were used to calculate a response factor as a function of time for the entire campaign. The overall uncertainty was ±(30% + 50 p.p.t.v.) for the ClNO<sub>2</sub> measurement for 5 min integrated data.

N<sub>2</sub>O<sub>5</sub>, NO<sub>3</sub> and NO<sub>2</sub> were measured by a multichannel cavity ring-down spectrometer<sup>35,36</sup>. NO<sub>3</sub> was measured by absorption at 662 nm and N<sub>2</sub>O<sub>5</sub> was measured as NO<sub>3</sub> after thermal conversion. NO<sub>2</sub> was measured by absorption at 532 nm in two cells that followed the NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> ring-down cells. Zeroing of the NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> channels was accomplished through the addition of nitric oxide (NO) to the inlet and NO<sub>2</sub> was zeroed by overflowing the absorption cell with clean 'zero' air. The transmission efficiency of the inlets was examined routinely by addition of a synthetic sample of N<sub>2</sub>O<sub>5</sub>, and by determination of the NO<sub>2</sub> formed when NO is added in the zero mode. The accuracy of the N<sub>2</sub>O<sub>5</sub> measurement was ±(25% + 0.1 \* [NO<sub>3</sub>] + 0.5 p.p.t.v.), and the (1 s) measurement precision was ±0.5 p.p.t.v.

The aerosol surface area was derived from the number size distributions measured with two differential mobility analysers (submicrometre fraction) and with an aerodynamic particle sizer (supermicrometre fraction) at a relative humidity of 55%–60% with 5 min time resolution and was corrected for changes in size due to water loss or uptake when the ambient relative humidity was different to the measurement relative humidity. Aerosol composition



reported here was measured by ion chromatography of impactor samples<sup>37</sup>. The nitrogen oxide species, NO, NO<sub>2</sub> and total NO<sub>y</sub> and O<sub>3</sub> were measured using the methods described by Williams *et al.*<sup>38</sup>. The photolysis rate of ClNO<sub>2</sub> (*j*(ClNO<sub>2</sub>)) was calculated from a parameterization of photolysis rates of NO<sub>2</sub>, and O<sub>3</sub> (*j*(NO<sub>2</sub>), and *j*(O<sub>3</sub>)) measured by filter radiometry<sup>39</sup>.

Total gaseous chloride was measured by the mist-chamber ion chromatographic method described by Scheuer *et al.*<sup>40</sup> and Dibb *et al.*<sup>41</sup>. The Cl<sup>-</sup> ion concentration was measured every 5 min. Although not measured as such, gaseous chloride is presumed to be in the form of HCl. The collection of other volatile chlorine species, for example ClNO<sub>2</sub> or Cl<sub>2</sub>, is not expected due to their low solubility and slow hydrolysis in neutral pH water.

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