

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 atmosphere¹. They are involved in processes such as oxidant chemistry in the mid-latitudes^{2,3}, conversion of marine sulphur emissions to non-sea-salt sulphate aerosol⁴ and destruction of ozone in the polar springtime boundary layer⁵. Despite extensive evidence of halogen chemistry in the troposphere^{6–9}, 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^{5,9,10}. Here, we report the first observations of nitryl chloride (ClNO₂), 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 10⁹ by volume), in the subtropical marine boundary layer (MBL) partly owing to NO_x (= NO + NO₂) emissions.

Laboratory studies have shown that ClNO₂ is produced efficiently from the heterogeneous reaction of dinitrogen pentoxide (N₂O₅) on sea salt^{11–15} and to some extent in dilute chloride solutions¹². 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 ClNO₂ is produced in high yield at night from the reaction of N₂O₅ on all chloride-containing aerosol particles. The observed ClNO₂ mixing ratios were larger than predicted by current inventories and models^{16,17}, even one that explicitly considers ClNO₂ in polluted

continental outflow¹⁸. ClNO₂ 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, NO₃) 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_x, O₃, sea salt and aerosol sources coexist.

ClNO₂ was measured in ambient air using chemical ionization mass spectrometry (using I[−] as a reagent ion), simultaneously with N₂O₅ (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) ClNO₂ is predominantly a night-time species, (2) mixing ratios of ClNO₂ are large and correlate strongly with those of N₂O₅, (3) ClNO₂ is sufficiently long-lived at night to constitute a large photolabile Cl and NO_x 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 NO_x sources were the exhaust plumes of ship engines: all but the most recently emitted of these plumes contained measurable quantities of ClNO_2 . The ClNO_2 mixing ratios were surprisingly large, on occasion exceeding 1 p.p.b.v., up to 15% of total reactive nitrogen (NO_y). In contrast, 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 ClNO_2 levels at night, in a pattern clustered around NO_x sources located in the urban and industrial areas of the Houston ship channel. During the daytime, ClNO_2 was present in large concentration only during the morning hours (see below): there were indications of much smaller amounts of ClNO_2 at other times of day under conditions conducive to the formation of daytime N_2O_5 (ref. 19). The overall uncertainties for the ClNO_2 measurements during this campaign are estimated at $\pm(30\% + 50 \text{ p.p.t.v.})$.

THE RELATIONSHIP BETWEEN N_2O_5 AND ClNO_2

The broad correlation of N_2O_5 and ClNO_2 throughout the six-week campaign strongly indicates that N_2O_5 was the source of ClNO_2 . Figure 2 shows this correlation during two representative periods. In the first, a mixture of 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 NO_y , also in Fig. 2, show many of the same broad features, with ClNO_2 reaching at most 7% of NO_y during these periods. The insets show correlations of measured ClNO_2 with the calculated uptake rate of N_2O_5 on aerosol²⁰ 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 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 ClNO_2 and N_2O_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 NO_2 with O_3 to produce NO_3 and N_2O_5 , heterogeneous reaction of N_2O_5 with aerosol to yield ClNO_2 and loss of NO_3 due to gas-phase reactions (for example, VOC oxidation). The value of k_{het} , the first-order rate coefficient for conversion of N_2O_5 to ClNO_2 , was varied to match the simulated and observed mixing ratios of N_2O_5 and ClNO_2 . The ratio of k_{het} to the total loss rate coefficient of N_2O_5 , calculated from the aerosol surface area density, is a measure of the yield of ClNO_2 from heterogeneous N_2O_5 uptake. The model was applied to plumes in which 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_{het} was from $1 \times 10^{-4} \text{ s}^{-1}$ to $3 \times 10^{-3} \text{ s}^{-1}$, significantly larger than that predicted for N_2O_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 phase²²

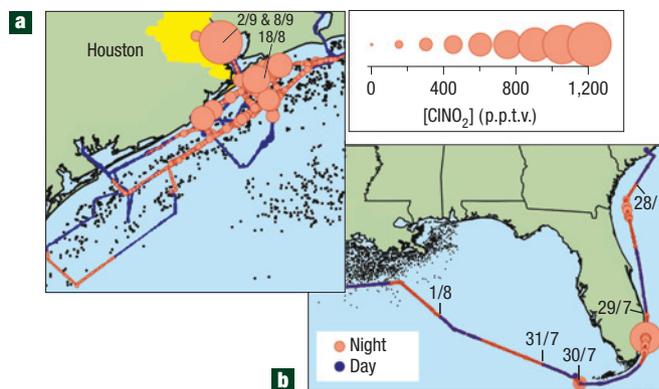
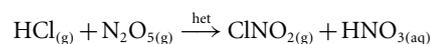


Figure 1 Maps of the study area. **a, b**, Maps of the study area showing a detailed view of the focused study area in the vicinity of Houston, Texas (shown in yellow) (**a**) and the ship track along the United States southeast coastline and across the Gulf of Mexico (**b**). Measured ClNO_2 (5 min 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 ClNO_2 , there was sufficient measured gas-phase chloride (mainly HCl) to replenish aerosol-phase Cl^- and support continuous heterogeneous ClNO_2 production. Laboratory studies have shown 25% yields of ClNO_2 on solutions with $[\text{Cl}^-]$ as low as approximately 0.1 M, consistent with Cl^- being an efficient scavenger of the NO_2^+ ion proposed as an intermediate in the first step of N_2O_5 surface reaction¹². In our study, ClNO_2 was observed in the presence of N_2O_5 and submicrometre 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 ClNO_2 , but also a long lifetime for ClNO_2 ($>30 \text{ h}$) in the nocturnal MBL. The latter is expected, because the most likely nocturnal ClNO_2 -loss pathway is heterogeneous uptake, and Henry's law constant ($4.6 \times 10^{-2} \text{ M per atm for water}$)¹⁵ and uptake coefficients ($\gamma < 5 \times 10^{-6}$ over water and Cl^- -containing solutions)²¹ are small. Reactions of ClNO_2 with gas-phase species have not been extensively studied, but those that are known, such as reaction with NO ($k = 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (ref. 23), are slow. Indeed, the lifetime of 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 ClNO_2 ON ATMOSPHERIC CHEMISTRY

Efficient ClNO_2 production has two important consequences for air quality in coastal regions. First, ClNO_2 acts as a nocturnal reservoir for NO_x , regenerating NO_2 on photolysis at sunrise. In environments where ClNO_2 yields are appreciable (such as the 10–65% found in this study), overnight conversion of NO_x to HNO_3 (NO_x loss) would be considerably reduced²⁴. Second, ClNO_2 produces reactive chlorine atoms that can significantly enhance

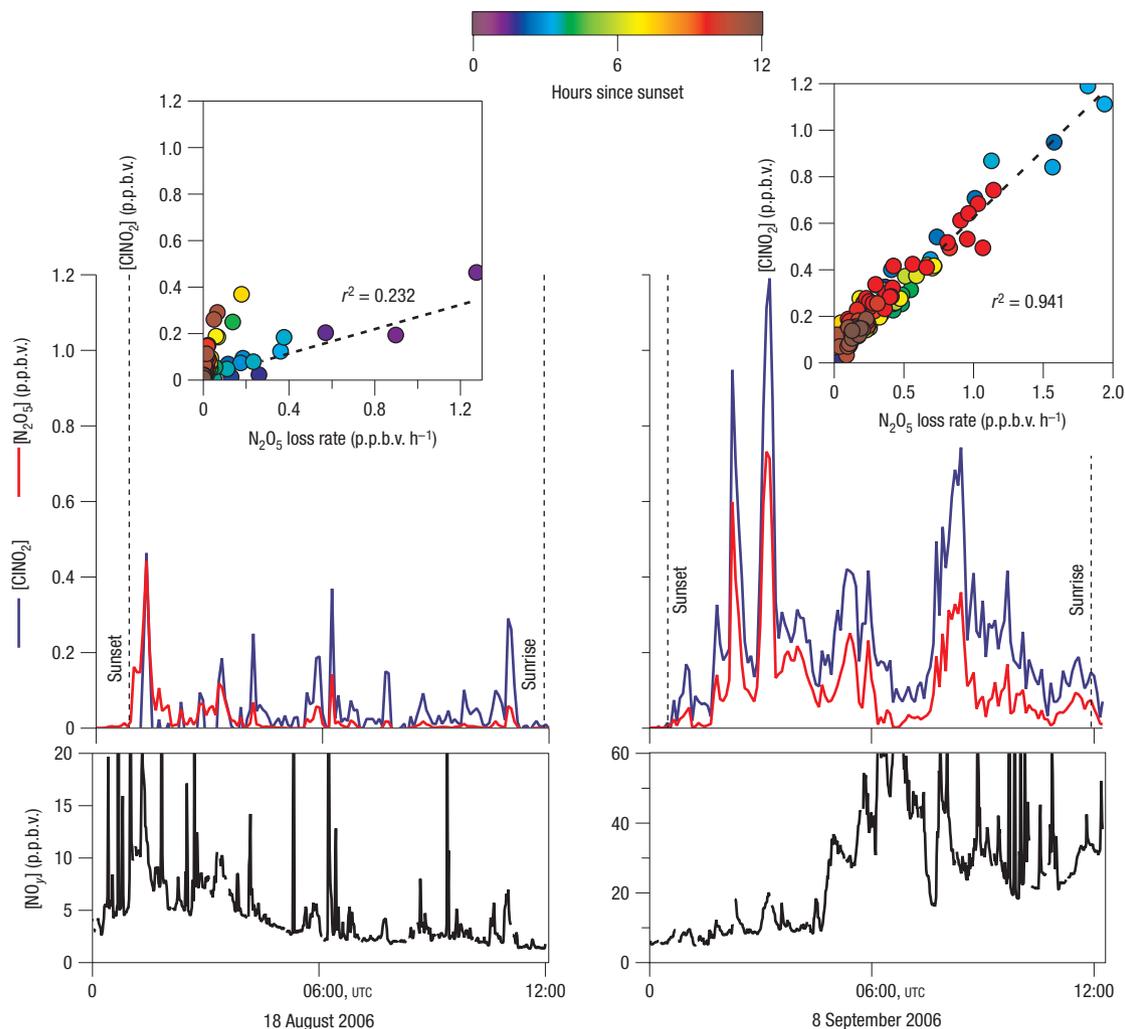


Figure 2 Measurements of ClNO_2 and N_2O_5 on two different nights. Time series of ClNO_2 and N_2O_5 on the nights of 18 August and 8 September. The bottom panels show total reactive nitrogen (NO_x). The insets show the correlation between ClNO_2 and the heterogeneous uptake rate of N_2O_5 (see text), colour coded according to sampling time since sunset. The nearly constant ratio of ClNO_2 over N_2O_5 loss rate observed on 8 September ($r^2 = 0.941$) suggests that 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, NO_3 , OH) are scarce²⁵.

The effect of ClNO_2 as a Cl atom source is shown in Fig. 3a for the morning of 2 September 2006. In this case, ClNO_2 remained into the mid- to late-morning hours, long after N_2O_5 had been destroyed by thermal decomposition and photochemical degradation of NO_3 . The resulting Cl source, calculated from the observed 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 O_3 , OH from HONO and HO_2 from HCHO, listed in Table 1. The O_3 and HCHO sources were calculated from measured concentrations and photolysis rates. The HONO source was estimated from measured NO_2 assuming a 5% HONO/ NO_2 ratio consistent with observations during the TexAQs 2000 study at the LaPorte site²⁶, 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 site²⁷, although it is not clear that HONO in a marine environment will be as large. The Cl atom source from 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 ClNO_2 chemistry to marine and coastal O_3 production depend on the VOC and 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 ClNO_2 and Cl-VOC chemistry. The model case used has been described previously²⁸ and is typical of a polluted air mass after one-day transport in the MBL. Addition of 650 p.p.t.v. of ClNO_2 (consistent with some of the highest observed levels on 2 September) and 1,500 p.p.t.v. of ClNO_2 (slightly higher than the high values we observed in this study) resulted in early increases in photochemical activity as measured by faster O_3 production and larger midday O_3 . These increases in ozone of 6 and 9 p.p.b.v., respectively, above that present at sunrise, were driven by both NO_x and Cl release. The latter is illustrated from the morning peak in total peroxy radical concentration RO_2 ($\text{RO}_2 = \text{hydroperoxy} + \text{organic peroxy radicals}$) of factors of 1.7 and 2.8.

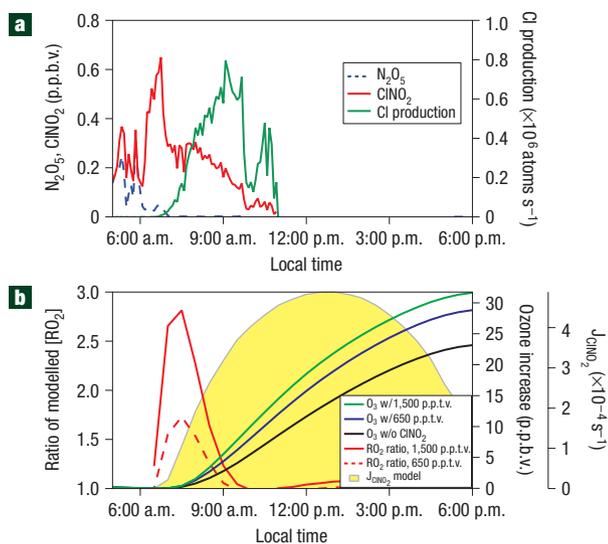


Figure 3 Production of Cl atoms from ClNO_2 photolysis. **a**, Measured mixing ratios of ClNO_2 and N_2O_5 and the Cl atom production rate resulting from the photolysis of ClNO_2 on 2 September 2006, while the ship was stationary in an inlet off Galveston Bay. **b**, Master chemical mechanism results for a representative modestly polluted marine air mass, to which 650 and 1,500 p.p.t.v. of ClNO_2 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_2 chemistry.

A thorough understanding of the effects of ClNO_2 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 Dabdub³ considered the production of Cl species from sea salt with a primary focus on the production of Cl_2 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_3 . Increased O_3 production has also been attributed to industrial and domestic sources of photolabile Cl (for example, Cl_2 or HOCl) in the Houston area², and control strategies have been proposed²⁹. Our results imply that control of all Cl sources would require control of marine and coastal NO_x sources because ClNO_2 may be appreciable in comparison with directly emitted Cl sources.

GLOBAL ASPECTS AND OVERALL SIGNIFICANCE OF NITRYL CHLORIDE

ClNO_2 chemistry can have global, in addition to regional, impacts. Just over half of the global population lives within 200 km of a coastline³⁰, where urban and industrial NO_x and aerosol pollution combines with sea-salt aerosol, leading to enhanced photochemical O_3 production. A simple and admittedly rough estimate of the global ClNO_2 source can be made from the N_2O_5 to ClNO_2 conversion efficiencies determined in this study and global NO_x emission data³¹. Considering only NO_x sources within 50 km of a coastline and marine vessel sources, and further assuming that on average half of that NO_x is converted to NO_y through conversion to and reaction of N_2O_5 (ref. 32), then N_2O_5 to ClNO_2 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^{-1} as Cl. This is much larger than the global ClNO_2 estimate of $0.06 \text{ Tg Cl yr}^{-1}$ from Erickson *et al.*¹⁶, but is about 8% of the total Cl atom source inferred from the $^{13}\text{C}/^{12}\text{C}$ kinetic isotope effect of Cl reaction with methane⁸. The ozone production

Table 1 The effect of ClNO_2 as a radical source on 2 September 2006.

Radical source	Maximum rate (molecules $\text{cm}^{-3} \text{ s}^{-1}$)	Effective radical source from propane (p.p.b.v.)*
Cl	0.8×10^6	28†
OH from O_3	1.1×10^7	1.6
OH from HONO	8×10^6	3.6
HO_2 from HCHO‡	6.3×10^6	0.94

*Integrated from sunrise to 1100 local time.

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

‡ 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_2 demonstrate its efficient production from heterogeneous uptake of N_2O_5 on aerosol particles, linking odd-nitrogen and halogen cycles in polluted coastal environments and ship plumes. ClNO_2 was significant (>1 p.p.b.v.), amounting to as much as 15% of NO_y , implying that its production takes place not only on sea salt, but also on chloride-containing particles of continental origin. Photolysis of ClNO_2 results in NO_x regeneration and chlorine atom production during morning hours, at times when other radical species, for example, NO_3 and OH, are at their lowest abundance. This Cl atom source initiates and accelerates daytime oxidant production in near-coastal environments where NO_x , O_3 and sea-salt sources coexist.

METHODS

Nitryl chloride measurements were made with a chemical ionization mass spectrometer (CIMS) using iodide (I^-) as a reagent ion. The instrument is similar to that described by Slusher *et al.*³³, and the ion chemistry pertinent to ClNO_2 is discussed by McNeill *et al.*³⁴. The ion $\{\text{I}\cdot\text{ClNO}_2\}^-$ 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_2O_5 on a NaCl slurry surface, and measurement of the output of a synthetic ClNO_2 source by NO_y and by ultraviolet absorption spectroscopy. The three methods yielded an average response factor that had a relative standard deviation of $\pm 18\%$. 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 $\pm(30\% + 50 \text{ p.p.t.v.})$ for the ClNO_2 measurement for 5 min integrated data.

N_2O_5 , NO_3 and NO_2 were measured by a multichannel cavity ring-down spectrometer^{35,36}. NO_3 was measured by absorption at 662 nm and N_2O_5 was measured as NO_3 after thermal conversion. NO_2 was measured by absorption at 532 nm in two cells that followed the NO_3 and N_2O_5 ring-down cells. Zeroing of the NO_3 and N_2O_5 channels was accomplished through the addition of nitric oxide (NO) to the inlet and NO_2 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_2O_5 , and by determination of the NO_2 formed when NO is added in the zero mode. The accuracy of the N_2O_5 measurement was $\pm(25\% + 0.1 \cdot [\text{NO}_3] + 0.5 \text{ p.p.t.v.})$, and the (1 s) measurement precision was $\pm 0.5 \text{ p.p.t.v.}$

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 samples³⁷. The nitrogen oxide species, NO, NO₂ and total NO_y and O₃ were measured using the methods described by Williams *et al.*³⁸. The photolysis rate of ClNO₂ (*j*(ClNO₂)) was calculated from a parameterization of photolysis rates of NO₂, and O₃ (*j*(NO₂), and *j*(O₃)) measured by filter radiometry³⁹.

Total gaseous chloride was measured by the mist-chamber ion chromatographic method described by Scheuer *et al.*⁴⁰ and Dibb *et al.*⁴¹. The Cl⁻ 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 ClNO₂ or Cl₂, is not expected due to their low solubility and slow hydrolysis in neutral pH water.

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