

High levels of molecular chlorine in the Arctic atmosphere

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Chlorine radicals can function as a strong atmospheric oxidant^{1–3}, particularly in polar regions, where levels of hydroxyl radicals are low. In the atmosphere, chlorine radicals expedite the degradation of methane^{4–6} and tropospheric ozone^{4,7}, and the oxidation of mercury to more toxic forms³. Here we present direct measurements of molecular chlorine levels in the Arctic marine boundary layer in Barrow, Alaska, collected in the spring of 2009 over a six-week period using chemical ionization mass spectrometry. We report high levels of molecular chlorine, of up to 400 pptv. Concentrations peaked in the early morning and late afternoon, and fell to near-zero levels at night. Average daytime molecular chlorine levels were correlated with ozone concentrations, suggesting that sunlight and ozone are required for molecular chlorine formation. Using a time-dependent box model, we estimate that the chlorine radicals produced from the photolysis of molecular chlorine oxidized more methane than hydroxyl radicals, on average, and enhanced the abundance of short-lived peroxy radicals. Elevated hydroperoxyl radical levels, in turn, promoted the formation of hypobromous acid, which catalyses mercury oxidation and the breakdown of tropospheric ozone. We therefore suggest that molecular chlorine exerts a significant effect on the atmospheric chemistry of the Arctic.

Although chlorine radicals are strong atmospheric oxidants^{8,9}, direct measurements of Cl atoms and chlorine monoxide (ClO) are challenging and limited owing to their low abundance in the atmosphere^{7,10}, especially at low altitudes. Consequently, significant efforts have been put into detecting chlorine radical precursors, which can photolyse to form Cl atoms. For example, high levels of nitryl chloride (ClNO₂; up to ~1 ppbv at night) at mid latitude^{11,12}, Cl₂ (up to 35 pptv at night) and hypochlorous acid (HOCl; up to 173 pptv during the day) in the Atlantic marine boundary layer⁶, and Cl₂ (up to ~150 pptv at night) in polluted coastal areas^{13,14} have been observed. Chlorine atoms can be an especially important atmospheric oxidant in the polar boundary layer, where hydroxyl radical concentrations (the dominant atmospheric oxidant in most locations) are usually low¹⁵. However, despite evidence for chlorine

chemistry^{5,16,17}, no direct observations of Cl₂ have been made in the polar marine boundary layer.

Here we report the first observations of high levels of Cl₂ with a diurnal profile in the polar boundary layer at Barrow, Alaska (71° 19' N, 156° 39' W) in spring 2009 by chemical ionization mass spectrometry (CIMS) during the Ocean–Atmosphere–Sea Ice–Snowpack (OASIS-Barrow) campaign¹⁸. We frequently observed high levels of Cl₂ greater than 100 pptv, reaching up to 400 pptv (Fig. 1a, red), the highest value ever detected in any location. The observed Cl₂ was at a maximum in the early morning and late afternoon with a daytime (6:00–8:00) mean mixing ratio of 20 pptv, whereas no significant concentrations (<0.8 pptv) were observed at night (0:00–4:00). Both the diurnal pattern and magnitude of the observed Cl₂ were unanticipated, because Cl₂ photolyses rapidly (lifetime = ~10 min) during the day and was expected to have lower concentrations in the daytime and a maximum at night, similar to those observed in Barrow for molecular bromine¹⁹ (Br₂). We rigorously validated the fidelity of our measurements (Methods) and the Cl₂ measurements reflect ambient concentrations and were not an instrument or local environmental artefact.

Ozone (O₃) and sunlight were almost certainly required to form the observed Cl₂ at Barrow. No significant Cl₂ (Fig. 1, red) was observed when O₃ (Fig. 1, blue) was depleted below 1 ppbv (Fig. 1). Average daytime Cl₂ mixing ratios were well correlated with O₃ (Fig. 1, right inset). At night, Cl₂ dropped to below 1 pptv (Fig. 1, red and Fig. 2, red) and was significantly less correlated with O₃ (Fig. 1, left inset). Previous laboratory experiments²⁰ and model simulations²¹ found that Cl₂ can form from the photolysis of ozone in aqueous sea-salt particles. However, the ultraviolet radiation flux, ozone concentrations, and sea salt particle surface areas in these experiments²⁰ and simulations²¹ were much higher than those common in the Arctic environment. Recent studies also found that Br₂ can be produced photochemically in saline snowpacks in the Arctic and the production is enhanced by O₃ (ref. 22), and that molecular iodine formed from reaction of iodide and O₃ can account for most of the observed iodine oxide over the tropical Atlantic Ocean²³. On the basis of these observations, Cl₂ may be

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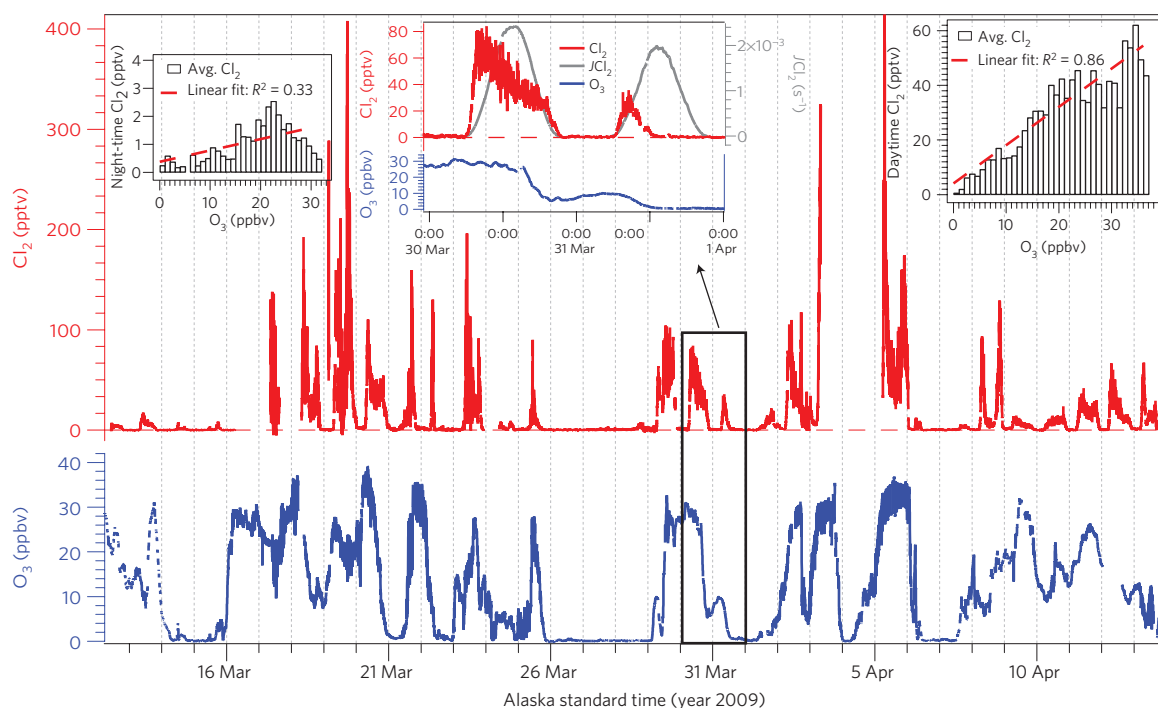


Figure 1 | Observed Cl_2 and O_3 . Observed Cl_2 and O_3 plotted versus time. The vertical grid indicates midnight (0:00) in Alaska Standard Time. Middle inset: Cl_2 and O_3 mixing ratios and Cl_2 photolysis rate ($J\text{Cl}_2$) on 30 and 31 March 2009. Right inset: The correlation between average daytime Cl_2 (9:00–18:00) and O_3 ($R^2 = 0.86$). Left inset: The correlation between average night-time Cl_2 (2:00–4:00) and O_3 ($R^2 = 0.33$).

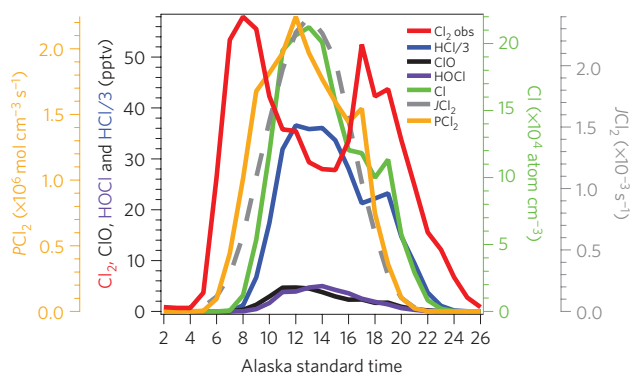


Figure 2 | Average diurnal profiles of chlorine species. Observed average diurnal profiles of Cl_2 (red), Cl_2 photolysis rate ($J\text{Cl}_2$; dashed grey), estimated average Cl_2 production rate ($\text{PCl}_2 = J\text{Cl}_2 \times \text{Cl}_2$; orange), and model-predicted average diurnal profiles of HCl (blue), ClO (black), HOCl (purple) and Cl atoms (green). The average diurnal profiles are plotted for the days when the average daytime (6:00–20:00) Cl_2 levels were higher than 15 pptv.

photochemically formed with O_3 on the saline snowpack or ice surfaces but further studies are needed to explore the detailed Cl_2 formation mechanisms.

The observed diurnal pattern of Cl_2 provides information about its source, sink and potential geographical impact. Figure 2 shows the average diurnal profile of Cl_2 (red) for the days when average daytime Cl_2 levels were above 15 pptv. The corresponding noontime production rate of the Cl_2 was estimated to be $2.0 \times 10^6 \text{ mol cm}^{-3} \text{ s}^{-1}$ on average (Fig. 2, orange), and had a diurnal profile similar to the photolysis rate of Cl_2 (Fig. 2, dashed grey). The average Cl_2 diurnal profile had a local minimum at solar noon. This is consistent with a maximum noontime chlorine photolysis rate and photochemically activated emission from a surface source (snow or ice) that is diluted into the boundary

layer, as demonstrated by one-dimensional model predictions of nitrogen oxide (NO) profiles from snow emissions at Summit, Greenland²⁴. The loss of Cl_2 after sunset leading to insignificant night-time levels (Fig. 2, red) is also consistent with a non-photochemical loss of Cl_2 such as deposition to the snowpack. The short daytime photochemical lifetime of Cl_2 and lack of Cl_2 at night indicate that Cl_2 may not be efficiently transported, and that the geographical impact of the chlorine cannot be estimated from measurement at one site.

Two potential sources of the observed Cl_2 are aerosol^{20,21} and snow or ice chloride^{22,25}. Cl_2 levels were not correlated with aerosol properties such as particle surface area ($R = 0.057$) and volume ($R = -0.004$). The average surface snow chloride of 6.6 ppmv measured during the same campaign (corresponding to $1.85 \times 10^{-2} \text{ mol m}^{-2}$ that can be emitted from the upper 10 cm of snow) could supply more than enough chlorine (1.5×10^8 pptv, to an estimated effective mixing height for Cl_2 of 2.5 m; ref. 26) and indicated that surface snow or ice was probably the main source of the observed Cl_2 .

Analysis of the geographical source of Cl_2 suggests that the snow-covered land or ice surface is the source of Cl_2 . We examined 2-day back trajectories of air masses arriving at Barrow using a Lagrangian particle dispersion model²⁷ (FLEXPART) to identify the potential geographical source of Cl_2 precursors. We found that these air masses neither had a distinct direction preference nor exhibited a significant correlation with the locations with multiple-year sea ice on the days during which high levels of Cl_2 were observed (Supplementary Fig. 2). Nevertheless, the FLEXPART simulations show that the mean boundary layer (0–400 m) residence time of air masses within 500 km of Barrow was about 20 times longer when high levels of Cl_2 were observed relative to when low levels were observed. This is consistent with snow and ice surfaces near Barrow being the source of the molecular chlorine.

The observed Cl_2 levels are consistent with the measurements of other chlorine compounds and known chlorine chemistry. We constructed a time-dependent box model to simulate average

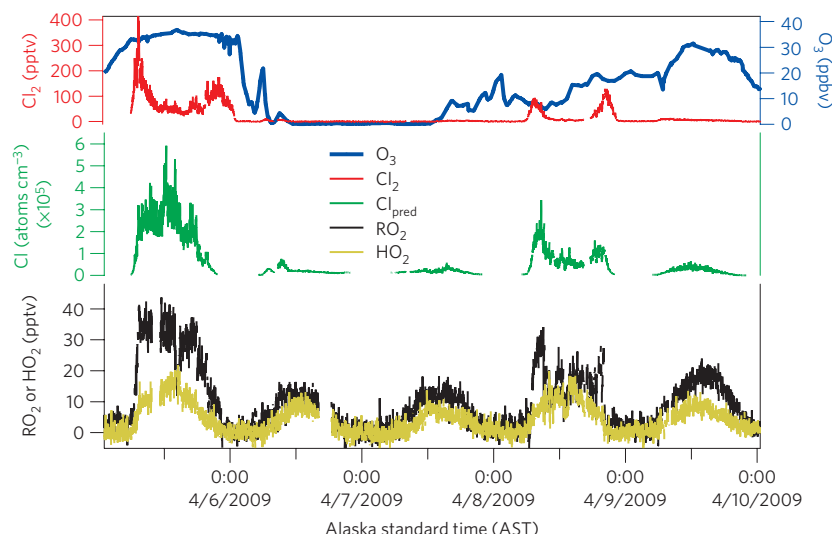


Figure 3 | An example of the impact of Cl₂ on RO₂ and HO₂. Observations of Cl₂, O₃, RO₂ and HO₂, and predicted Cl atom concentrations constrained to the observed Cl₂.

diurnal profiles of Cl, ClO, HOCl and hydrogen chloride (HCl; Fig. 2) based on known chlorine chemistry (Supplementary Table 1) and constrained to Cl₂ observations. The model-predicted Cl, ClO, HOCl and HCl all reached maximum concentrations near noon. At noon, about 2.0×10^5 Cl atoms cm⁻³ on average were predicted. At mid-day, the dominant chlorine species was HCl (~100 pptv on average), and the predicted HCl was consistent with observations (Supplementary Fig. 3). The mixing ratios of HOCl were similar to ClO but a factor of 5 smaller than Cl₂. This is because Cl atoms predominantly react with volatile organic compounds (VOCs) to form HCl, and less efficiently (by a factor of 3) with ozone to form ClO. The predicted ClO levels were within the ranges of ClO measurements in other Arctic regions⁷.

Our discovery of high levels of chlorine in the Arctic boundary layer has significant impacts. Chlorine atoms produced from Cl₂ photolysis significantly increased VOC oxidation. For example, 60% of methane was oxidized by Cl atoms and 40% was oxidized by hydroxyl radicals (OH) measured by CIMS at the Barrow measurement site (1.5 m above the snowpack) and the oxidation rate of CH₃CH₃ by Cl atoms was about 25 times faster than that by OH radicals on average when both OH and Cl₂ measurements were available. The impact of Cl atoms on OH oxidation may be underestimated because OH measurements were usually unavailable during high Cl₂ measurement periods. This is further supported by the observations²⁸ of enhanced levels of short-lived peroxy radicals (RO₂ and HO₂; Fig. 3, black and gold) when high levels of Cl₂ (Fig. 3, red) were detected (for example, on 5 and 8 April 2009 in Fig. 3): the highest mixing ratios of RO₂ and HO₂ were observed during the days when Cl₂ was above 200 pptv; the mixing ratios of RO₂ and HO₂ when high O₃ (Fig. 3, blue) and low Cl₂ levels were observed (for example on 9 April 2009) were lower than those when elevated Cl₂ was observed (for example, on 5 and 8 April 2009); the diurnal patterns of high levels of Cl atoms (Fig. 3, green) were also similar to those of RO₂ and HO₂. Together, these indicate that high levels of Cl₂ at Barrow reacted with VOCs and enhanced levels of RO₂, HO₂, and probably OH (whose measurements were unavailable during most of the periods when high levels of Cl₂ were observed).

Chlorine chemistry can impact ozone and mercury depletion through interaction with bromine and HO_x chemistry. Chlorine oxidation enhances HO₂ levels and increases hypobromous acid (HOBr) formation, which largely determines the efficiency of bromine heterogeneous recycling and is the key to sustaining active

gas-phase bromine species, surface ozone depletion and mercury oxidation²⁹. For example, reaction of ClO with bromine oxide (BrO) contributed 21% (R20 and R23 in Supplementary Table 1) and bromine chemistry contributed 73% (R1 and R2 in Supplementary Table 3S) to ozone depletion during this campaign. Reaction of BrO with HO₂ without reforming O₃ dominated (74%) bromine-catalysed ozone loss at Barrow¹⁹, and the enhanced HO₂ levels due to chlorine chemistry contributed significantly to bromine-catalysed ozone loss (approximately 22% on average). The impact of chlorine chemistry on mercury depletion (for example, through enhanced bromine heterogeneous recycling) may be larger than the direct impact of chlorine reaction with mercury discussed in ref. 29.

Our study provides the first direct evidence of high levels of Cl₂ in the polar marine boundary layer, and reveals their important impacts on atmospheric oxidation capacity at Barrow. Chlorine atoms are often the primary oxidant at Barrow, and chlorine chemistry has a large impact on bromine chemistry. As Cl₂ has a lifetime of ~10 min in the daytime and a few hours at night, high levels of Cl₂ observed at Barrow do not imply high levels of Cl₂ in the entire Arctic. Further direct measurements of Cl₂ and other chlorine species (for example, ClO, HCl and HOCl) at other locations in the Arctic, particularly over the sea ice, are needed to determine whether this phenomenon is widespread. Furthermore, laboratory experiments are needed to explore the formation mechanisms of Cl₂ to help further estimate the trends and the impact of chlorine in the Arctic. Despite these challenges, our study is an important first step in evaluating the impacts of the high levels of molecular chlorine on the Arctic environment.

Methods

Molecular chlorine was measured by a CIMS at Barrow, Alaska in spring 2009 using an inlet approximately 1.5 m above the snow surface. A detailed description of the CIMS methods is provided in ref. 18. Hydrated I⁻ (after 18 March 2009) and SF₆⁻ (before 18 March 2009) were used as reagent ions to detect Cl₂, HCl (before 18 March), BrO and a variety of other halogen species.

We validated our measurements by performing a variety of diagnostic tests of the measurement technique, including regular calibration with a Cl₂ source, instrument background determinations, examination of the isotopic ratio of the detected compounds, and consideration of conversion on inlet surfaces. The instrumental background of Cl₂ and other halogen species was determined by frequently removing ambient halogens from the sampled air flow with a glass wool filter. A Cl₂ permeation tube was used as a calibration standard and its output was added to the inlet every 2 h. The detection limit of the Cl₂ measurements is estimated to be 1.1 pptv (3σ) for 1 min data and the uncertainty of the Cl₂ measurements is <10%. Ratios of signals for the detected masses (ICl³⁵Cl³⁵ at mass

197 AMU and $\text{Cl}^{35}\text{Cl}^{37}$ at mass 199 AMU; Supplementary Fig. 1) confirmed that the detected species contained two chlorine atoms. In addition, measurements of HOBr, which is readily converted to Br_2 on inlet surfaces³⁰, and BrO by the same instrument during the campaign¹⁸ demonstrated that the CIMS inlet was compatible with efficient sampling of reactive gases. Furthermore, laboratory experiments suggested that significant interferences in Cl_2 measurements due to conversion of HOCl on the inlet surface are unlikely. We estimate a conservative upper limit of HOCl conversion to Cl_2 on the inlet of 15% based on NaCl-coated test inlets.

The Cl_2 measurements were not a local environment artefact. Barrow is a remote site with little industry with the largest pollution source due to power generation. We found no clear correlation between our Cl_2 measurements and observations of NO ($R^2 = 0.000$; Supplementary Fig. 6), carbon monoxide (CO; $R^2 = 0.006$), and VOCs such as benzene ($R^2 = 0.008$). All of these species were found in significant concentrations when the measurement site was impacted by air from the town of Barrow. Moreover, high levels of Cl_2 were often observed when the wind blew from the Arctic Ocean (Chukchi Sea) and when FLEXPART back trajectories (Supplementary Fig. 2) indicated an Arctic Ocean origin of the air mass. Furthermore, Cl_2 is very unlikely to have a diurnal pattern with a maximum in the daytime and correlate with O_3 if Cl_2 was generated from anthropogenic sources such as fuel combustion or incineration. For these reasons, we have ruled out local pollution as the source of the observed Cl_2 .

O_3 was measured by a chemiluminescence instrument. Photolysis rates (J values) were calculated from the actinic fluxes measured from the NCAR CCD Actinic Flux Spectroradiometer. HO_2 , RO_2 and OH measurements were made by the NCAR CIMS instrument using NO_3^- as a reagent ion²⁸. Total aerosol surface area and volume were calculated from a system consisting of two scanning mobility particle sizers and one optical particle counter.

A time-dependent box model was used to study the impact of the observed Cl_2 on chlorine chemistry. Chlorine species (Cl, ClO, HOCl and HCl) were simulated in the model. The model included chemical reactions R1S–R21S (Supplementary Table 1) and was constrained to observations of Cl_2 , O_3 , NO, NO_2 , CH_2O , RH, OH, HO_2 and actinic fluxes. The input data were average diurnal measurements on a ten-minute time interval. Typical concentrations of the input are shown in Supplementary Table 2. As high levels of NO and NO_2 were due to local pollution, NO and NO_2 measurements were filtered to remove levels higher than 20 pptv. Loss rates of HOCl and HCl to heterogeneous surfaces (k_{HOCl} , k_{HCl} , k_{Cl_2}) were assumed to be the condensation rate to the aerosol surface. As the surface area and reactivity of the snow surface are not well understood, the heterogeneous loss rates may be underestimated.

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Author contributions

H.J.B., P.B.S., F.M.F. and J.J.O. planned and organized the project. J.L., D.J.T. and L.G.H. conducted measurements of halogen species by CIMS at Barrow. J.L. analysed and modelled the data, performed laboratory tests and wrote the manuscript. L.G.H. revised the manuscript. Z.L. and Y.W. calculated FLEXPART back trajectories. C.A.C. and R.S.H. performed HO_2 and RO_2 measurements. P.B.S. and C.R.S. performed ClO_2 measurements. A.J.W. performed O_3 and NO measurements. S.R.H. and K.U. performed photolysis rate measurements. H.J.B. measured chloride concentrations in the snow. E.C.A., D.R. and A.F. performed VOC measurements. R.L.M. performed OH measurements. J.N.S. measured aerosol size distribution. R.M.S. performed ozonesonde measurements. All authors reviewed and commented on the paper.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to L.G.H.

Competing financial interests

The authors declare no competing financial interests.