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Constraints on Arctic Atmospheric Chlorine Production through Measurements and Simulations of Cl_2 and ClO

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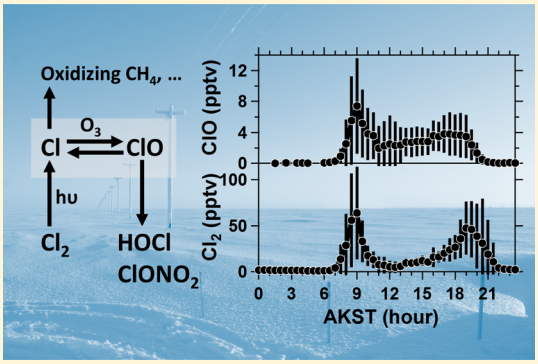
Supporting Information

ABSTRACT: During springtime, unique halogen chemistry involving chlorine and bromine atoms controls the prevalence of volatile organic compounds, ozone, and mercury in the Arctic lower troposphere. In situ measurements of the chlorine monoxide radical, ClO, and its precursor, Cl_2, along with BrO and Br_2, were conducted using chemical ionization mass spectrometry (CIMS) during the Bromine, Ozone, and Mercury Experiment (BROMEX) near Barrow, Alaska, in March 2012. To our knowledge, these data represent the first ClO measurements made using CIMS. A maximum daytime ClO concentration of 28 ppt was observed following an early morning peak of 75 ppt of Cl_2. A zero-dimensional photochemistry model was constrained to Cl_2 observations and used to simulate ClO during a 7-day period of the field campaign. The model simulates ClO within the measurement uncertainty, and the model results highlight the importance of chlorine chemistry participation in bromine radical cycling, as well as the dependence of halogen chemistry on NO_x levels. The ClO measurements and simulations are consistent with Cl_2 being the dominant Cl atom source in the Arctic boundary layer. Simulated Cl atom concentrations, up to ~1 × 10^6 molecules cm^{-3}, highlight the importance of chlorine chemistry in the degradation of volatile organic compounds, including the greenhouse gas methane.



INTRODUCTION

Over the past several decades, observations have shown that halogen chemistry impacts the Arctic boundary layer oxidation capacity, as exhibited by the rapid removal of small hydrocarbons, along with depletion of surface layer ozone and mercury.[1,2] During spring, episodic ozone depletion events (ODEs) exhibit decreases in surface layer tropospheric ozone (O_3) from background mole ratios of ~40 ppb to less than 5 ppb due to reaction with bromine atoms.[3,4] Although chlorine is not the primary sink for ozone during ODEs, it indirectly contributes via the regeneration of bromine atoms through reactions R1−R5, and through production of HO_2 through reaction with hydrocarbons, contributing to the "bromine explosion" cycle of ozone loss.[5] Chlorine atoms can be produced via reactions R1, R5, and R6, and are destroyed by reaction with hydrocarbons, or reaction with O_3 (R2) to produce ClO. ClO can then significantly increase the rate of ozone depletion by converting BrO to bromine atoms or BrCl via reactions R3 and R4, respectively.

$$Cl_2 + h\nu \rightarrow 2Cl \quad \text{(R1)}$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad \text{(R2)}$$

$$ClO + BrO \rightarrow Br + OClO \quad \text{(R3)}$$

$$ClO + BrO \rightarrow BrCl + O_2 \quad \text{(R4)}$$

$$ClO + BrO \rightarrow Br + Cl + O_2 \quad \text{(R5)}$$

$$BrCl + h\nu \rightarrow Br + Cl \quad \text{(R6)}$$

While it has been known that chlorine atom chemistry is active in the Arctic,[2,6−9] and despite one set of observations of high Cl_2 concentrations (maximum of 400 ppt) during the springtime,[10] it has not been possible to directly measure the chlorine atom concentration, due in part to the low concentrations. Rather, Cl atoms have been inferred or calculated from measurements of volatile organic compounds.[2,6,8,11,12] Despite Cl having a greater reaction rate constant with O_3 compared to that for Br, both yield similar halogen monoxide levels (5−35 ppt) due to the relatively lower (by 100−1000×) concentration of available Cl atoms compared with Br.[13] Daytime Cl atom maximum concentrations are

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estimated to be quite low (0.4×10^4–4.0×10^5 molecules cm^{-3})[2,8,11,12] because of the greater sink strength due to its relatively high (compared to that for Br atoms) reactivity toward small hydrocarbons, including methane.[8] This high reactivity allows chlorine to greatly impact the atmosphere's oxidation capacity and radical production through oxidation of methane and subsequent formaldehyde and HO_2 formation.[14] Simultaneous measurements of ClO and Cl_2 can then be used to test the extent to which reaction R1 is the dominant Cl atom source, if the ClO radical sinks are known. As chlorine atoms have a significant impact on the oxidation capacity of the boundary layer, it is important to understand their sources and sinks.

While numerous observations of BrO in the Arctic exist,[15] only two studies thus far have reported detection of ClO, via long-path differential optical absorption spectroscopy (LP-DOAS)[16] and chemical reaction gas chromatography with an electron capture detector.[2,5] Tuckermann et al.[16] observed ClO up to 40 ppt during spring 1995 and 1996 in Svalbard, Norway. In the Amundsen Gulf (Northwest Territories, Canada) during spring 2008, Pöhler et al.[17] attempted ambient ClO measurements, but they were unable to detect ClO above the high limit of detection (125 ppt). During March 2009 near Barrow, Alaska, Stephens et al.[2,5] observed ClO up to 8 ppt. These concentrations are comparable to levels observed for BrO in the Arctic boundary layer.[1,18]

In this study, atmospheric Br_2, Cl_2, BrO, and ClO were simultaneously quantified with high time resolution using chemical ionization mass spectrometry (CIMS) during the Bromine, Mercury, and Ozone Experiment (BROMEX) near Barrow, Alaska, in March 2012.[19,20] This data set provides an excellent opportunity to test our understanding of chlorine atom sources and sinks in the Arctic and their impacts on related radical chemistry, through analysis and zero-dimensional (0-D) modeling, which we present and discuss here.

EXPERIMENTAL SECTION

CIMS Measurements. Br_2, Cl_2, BrO, and ClO measurements were conducted near Barrow, Alaska, from March 21–28, 2012, at a measurement site ~5 km inland (71°16.500 N, 156°38.426 W), located southeast of the town of Barrow, using CIMS, as described by Liao et al.[21] and Pratt et al.[22] Briefly, air was sampled at ~300 liters per minute (lpm) through a 33 cm long inlet comprised of a stainless steel ring torus attached to a 4.6 cm i.d. aluminum pipe extending 9 cm out of the sampling building wall. First, 7.4 lpm of this flow was sampled into a 30 °C heated 25 cm, 0.65 cm i.d. PFA path, part of a custom three-way valve[21] for calibration and background measurements, with 2.0 lpm of the total flow entering the CIMS flow reactor. $I\cdot(H_2O)_n^-$ reagent ions were produced by passing 1.7 lpm of 5 ppm of CH_3I in N_2 through a ^{210}Po ionizer with water addition in N_2 (0.12 lpm) from a room-temperature (~20 °C) 1 L bubbler to the flow reactor, which was held at a constant pressure of 13 Torr. The water addition ensured that the atmospheric water vapor would not affect the CIMS sensitivity. Background measurements were performed every 15 min by passing the air flow through a glass wool scrubber, which has been shown previously to remove halogen species at >95% efficiency.[21,23]

Using hydrated I^- ($I\cdot(H_2O)_n^-$) as the reagent ion, Br_2 was quantified at m/z 287 ($I^{79}Br^{81}Br^-$) and 289 ($I^{81}Br^{81}Br^-$), Cl_2 at m/z 197 ($I^{35}Cl^{37}Cl^-$) and 199 ($I^{37}Cl^{37}Cl^-$), BrO at m/z 222 ($I^{79}BrO^-$) and 224 ($I^{81}BrO^-$), and ClO at m/z 178 ($I^{35}ClO^-$) and 180 ($I^{37}ClO^-$). Br_2 and Cl_2 calibrations were performed every 2 h by adding Br_2 and Cl_2, from separate permeation sources, each in a 21 mL min^{-1} N_2 flow, to the ambient sample air flow. A relative sensitivity of 0.47 for BrO (mass 224) relative to Br_2 (mass 287) was used for calibration.[21] The instrument sensitivity of ClO (mass 178) relative to Cl_2 (mass 197) was determined experimentally, as described below, to be 0.26 ± 0.11. The ratio of $I^{35}ClO^-$ (mass 178) to $I^{37}ClO^-$ (mass 180) confirmed that the detected species each contained one chlorine atom (Figure S1). For a measurement cycle of 10.6 s, masses 287 ($I^{79}Br^{81}Br^-$), 197 ($I^{35}Cl^{37}Cl^-$), 224 ($I^{81}BrO^-$), and 178 ($I^{35}ClO^-$) were monitored for 0.5 s each, with a 5% duty cycle for each mass. The 3σ limits of detection for Br_2 (mass 287), Cl_2 (mass 197), BrO (mass 224), and ClO (mass 178) were calculated to be 3.8, 1.4, 1.6, and 2.6 ppt, respectively, on average, for a 2.8 s integration period (corresponding to 1 min of CIMS measurements). Since the variance in the background is likely due to counting statistics,[21] the limits of detection for 1 h averaging are estimated at 0.5, 0.2, 0.3, and 0.3 ppt for Br_2, Cl_2, BrO, and ClO, respectively. The uncertainties in the reported Br_2, Cl_2, BrO, and ClO concentrations were calculated to be (21% + 0.5 ppt), (25% + 0.2 ppt), (30% + 0.3 ppt), and (55% + 0.3 ppt), respectively.

To calibrate for ClO, various calculated concentrations of ClO (50–100 ppb) were photochemically produced in the laboratory. The flow tube was housed in a wooden photolysis box which contained six UV bulbs (UVA 340, Q-labs). ClO was produced in a quartz flow tube (122 cm × 6 cm) by the photolysis of Cl_2 in the presence of excess O_3 (90 ppb) and ~5 ppb of NO_2. The UV lights were controlled by using a switch on the outside of the box to provide control of Cl_2 photolysis, which was also monitored by CIMS measurement of Cl_2 exiting the flow tube. The steady-state ClO concentrations ($[ClO]_{ss}$) in the flow tube were calculated by $[ClO]_{ss} = 2J_{Cl_2}[Cl_2]_{ss}/(k_{ClO\text{-}NO_2}[NO_2])$, where J_{Cl_2} represents the photolysis rate for Cl_2 within the flow tube, $[Cl_2]_{ss}$ is the steady-state Cl_2 mole ratio, $[NO_2]$ is the NO_2 mole ratio, and the reaction rate constant for ClO with NO_2 ($k_{ClO\text{-}NO_2}$) used was 2.4×10^{-12} cm^3 $molecules^{-1}$ s^{-1}.[24] The Cl_2 photolysis rate was determined to be 0.008(±0.002) s^{-1}. With a residence time of ~12 s within the flowtube, reaction R7 was the dominant ClO sink.

$$ClO + NO_2 \rightarrow ClONO_2 \quad (R7)$$

NO_2 was quantified using a NO-NO_2-NO_x analyzer (Thermo Environmental Instruments, Inc.). In the presence of O_3 and by employing a short residence time, NO was below the instrument limit of detection of 0.5 ppb. For each ClO calibration point, the CIMS sensitivity for Cl_2 was also determined. An average relative sensitivity of 0.26 ± 0.11 was determined for ClO relative to Cl_2.

Auxiliary Measurements. Solar radiation data were obtained from the NOAA/ESRL/GMD Barrow Observatory (http://www.esrl.noaa.gov/gmd/obop/brw/). The NOAA Barrow Observatory is located 5 km north of the CIMS measurement site, with only tundra between the sites. Wind direction was measured at the CIMS measurement site and found to be in agreement with that measured at the NOAA Barrow Observatory (not shown). Ozone was measured through the CIMS sampling inlet using a calibrated 2B Technologies model 205 dual-beam O_3 monitor. A map showing the locations of the sampling sites, as well as the town of Barrow, can be found in ref 20.

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Model Description. The 0-D model described by Custard et al.[25] was used to investigate the observations obtained during this study. A full list of included reactions is provided in ref 25. Briefly, the model contains an explicit photochemical mechanism for ozone, halogen and HO_x radicals, nitrogen oxides, and hydrocarbon-mediated reactions.[25] For this study, Cl_2, Br_2, and O_3 were constrained to observations obtained during March 21−28, 2012, at the field site. Time-varying photolysis rates were calculated by scaling previously determined photolysis rates to the observed solar radiation for the simulated time period.[26] CH_3COCH_3 and CH_3CHO influence the oxidation capacity of the boundary layer via interaction with atmospheric halogens, mainly bromine;[27,28] therefore, in the model, both CH_3COCH_3 and CH_3CHO were constrained to previously measured diurnal cycles of these species,[29] as in the simulations by Custard et al.[25] NO_x was defined in the base model simulation to represent a background clean air diurnal cycle, with a minimum of 14 ppt at 18:00 AKST (Alaska Standard Time) and a maximum of 32 ppt at 12:00 AKST,[25] as wind direction measurements (25−130°) indicated that sampled air masses were from the Beaufort Sea and were not in contact with the town of Barrow prior to arrival at the sampling site. As simultaneous NO_x measurements were not available during BROMEX, model sensitivity tests were conducted by varying the magnitude of the NO_x diurnal cycle to evaluate the effect NO_x would have on the ClO chemistry. NO_x was constrained within the model for two different scenarios covering varying NO_x levels based on previous observations from Barrow, Alaska.[25,30] A polluted NO_x scenario had a diurnal cycle from 378 to 168 ppt, while the background NO_x scenario cycled from 32 to 14 ppt. The elevated NO_x sensitivity tests are particularly important for March 25−28, 2012, when wind directions often were from 100 to 130°, for which Barrow has previously been shown to be occasionally influenced by elevated NO_y, up to 14 ppb, due to transport from the Prudhoe Bay oilfields.[31]

RESULTS AND DISCUSSION

ClO Observations. Observed O_3, Cl_2, and ClO molar ratios during a seven-day period of BROMEX (March 21−27, 2012) are shown in Figure 1. To our knowledge, these data represent the first set of simultaneous Cl_2 and ClO observations via CIMS. During previous chemical reaction gas chromatography measurements in Barrow in March 2009, Thompson et al.[5] reported ClO concentrations between 5 and 15 ppt, when Cl_2 was 50−100 ppt.[10] We observed daytime ClO concentrations ranging from 5 to 28 ppt, consistent with Thompson et al.[5] and Tuckermann et al.,[16] who observed daytime ClO from their detection limits of 9−20 ppt up to 40 ppt during spring 1995 and 1996 in Ny-Ålesund, Svalbard. In Figure 2, we present the average diurnal profile for Cl_2 and ClO. Similar to previous observations in Barrow by Liao et al.,[10] Cl_2 showed two mid-day maxima, with near-zero levels at night. The early morning (9:00 am AKST) peak in Cl_2 likely results from the initialization of snowpack Cl_2 production at sunrise, as predicted by laboratory studies showing photochemical Cl_2 production from artificial snow.[32] As early morning Cl_2 is produced, it photolyzes to yield chlorine atoms (R1), which produce ClO in the presence of O_3 (R2), such that the ClO diurnal cycle is similar in shape to that for Cl_2 when ClO formation is not limited by O_3. The diurnal profile of Cl_2 is complex, as it depends on O_3 and radiation,[10] as well as on the diurnal profiles of gas-phase photolysis, snowpack photochemistry, vertical mixing, and both gas- and condensed-phase reactions.

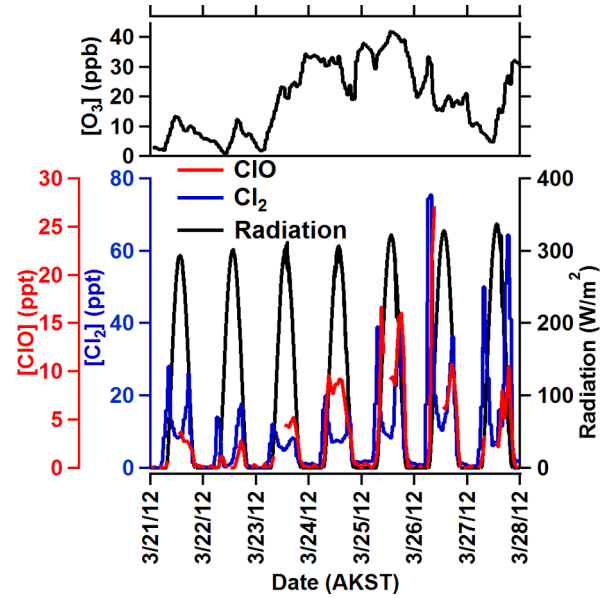

Figure 1. O_3, Cl_2, and ClO concentrations, as well as radiation, measured near Barrow, Alaska, during BROMEX.

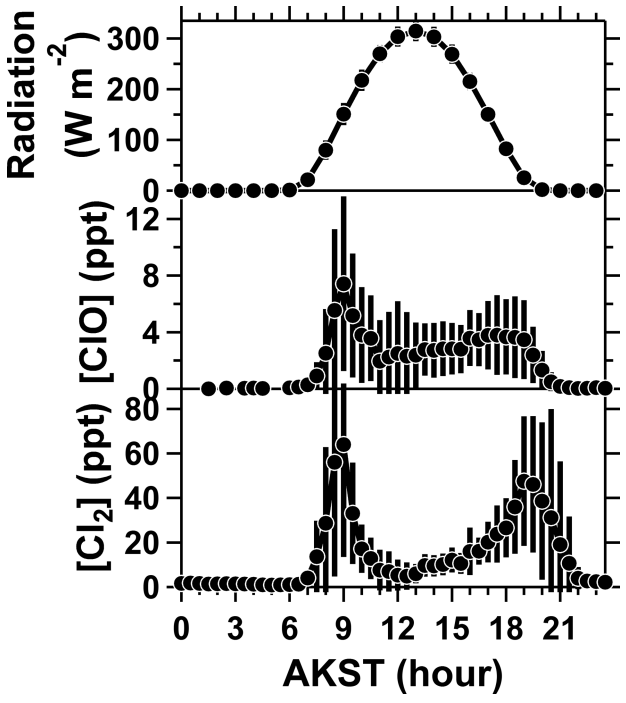

Figure 2. Measured diurnal average concentrations of Cl_2 and ClO from March 21−28, 2012. Error bars show standard deviations.

The five-day period of March 23−27, during which Cl_2 showed daytime maxima of ∼20−75 ppt, was characterized by the highest observed ClO concentrations, as expected since ClO production occurs via chlorine atom reaction with O_3, and O_3 was relatively high, at ∼20−40 ppb (Figure 1). When O_3 was partially depleted (<10 ppb) on March 21 and 22, the lowest daytime ClO values were measured at less than 5 ppt. On those days, Cl_2 was also lower, at 15−25 ppt, consistent with the previous radiation-dependent observation of Cl_2, which also showed a positive correlation with O_3.[10] The highest

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ClO concentration (28 ppt) was recorded on March 26, when a morning Cl_2 peak of 75 ppt was observed. Elevated morning concentrations of Cl_2 generally coincided with larger ClO concentrations, as observed on March 25 and 26. Active local-scale halogen-mediated destruction of ozone was occurring from March 25−27, as shown by the decreasing O_3 concentrations and presence of elevated Br_2 and BrO concentrations (Figure S2).

The March 25−26 trend of elevated morning Cl_2 concentrations leading to higher ClO was not observed on March 27, when only 12 ppt of ClO was produced following a 50 ppt Cl_2 peak. The observed ClO concentrations can be examined through the ClO steady-state equation (eq 1), which equates the sources and sinks of ClO:

$$[\mathrm{ClO}]_{ss} = \left\{2J_{\mathrm{Cl}_2}[\mathrm{Cl}_2]\Big/\left(2k_{\mathrm{ClO}}[\mathrm{ClO}] + k_{\mathrm{ClO\text{-}NO}_2}[\mathrm{NO}_2] + k_{\mathrm{ClO\text{-}NO}}[\mathrm{NO}] + k_{\mathrm{ClO\text{-}OH}}[\mathrm{OH}] + k_{\mathrm{ClO\text{-}HO}_2}[\mathrm{HO}_2] + J_{\mathrm{ClO}} + k_{\mathrm{ClO\text{-}CH_3OO}}[\mathrm{CH_3OO}] + k_{\mathrm{ClO\text{-}CH_3COOO}}[\mathrm{CH_3COOO}] + k_{\mathrm{ClO\text{-}BrO}}[\mathrm{BrO}]\right)\right\} \times \left\{k_{\mathrm{Cl-O_3}}[\mathrm{Cl}][\mathrm{O_3}]\Big/\sum[\mathrm{Cl\ sinks}]\right\} \quad (1)$$

where

$$\sum[\mathrm{Cl\ sinks}] = [\mathrm{Cl}] \times \left(k_{\mathrm{Cl\text{-}HO_2}}[\mathrm{HO_2}] + k_{\mathrm{Cl\text{-}O_3}}[\mathrm{O_3}] + k_{\mathrm{Cl\text{-}MEK}}[\mathrm{MEK}] + k_{\mathrm{Cl\text{-}CH_4}}[\mathrm{CH_4}] + k_{\mathrm{Cl\text{-}C_2H_2}}[\mathrm{C_2H_2}] + k_{\mathrm{Cl\text{-}C_2H_4}}[\mathrm{C_2H_4}] + k_{\mathrm{Cl\text{-}C_2H_6}}[\mathrm{C_2H_6}] + k_{\mathrm{Cl\text{-}C_3H_6}}[\mathrm{C_3H_6}] + k_{\mathrm{Cl\text{-}C_3H_8}}[\mathrm{C_3H_8}] + k_{\mathrm{Cl\text{-}}i\mathrm{C_4H_{10}}}[i\mathrm{C_4H_{10}}] + k_{\mathrm{Cl\text{-}}n\mathrm{C_4H_{10}}}[n\mathrm{C_4H_{10}}] + k_{\mathrm{Cl\text{-}HCHO}}[\mathrm{HCHO}] + k_{\mathrm{Cl\text{-}CH_3CHO}}[\mathrm{CH_3CHO}]\right)$$

$[\mathrm{ClO}]_{ss}$ depends on both the Cl_2 and O_3 concentrations, although several species can also influence the $[\mathrm{ClO}]_{ss}$ by acting as sinks for ClO. Of the ClO sinks shown in eq 1, NO and NO_2 are known to have highly varying ambient concentrations in the Arctic.[25] During Barrow 2009 measurements, the average NO_x during clean air trajectory conditions was 84(+110/−84) ppt, with a peak value of ∼190 ppt.[5] Given the potential for elevated concentrations of NO_x from the Prudhoe Bay oilfields to have impacted the measurement site on March 25−28, based on wind directions of 100−130°,[31] the influence of NO_x on the $[\mathrm{ClO}]_{ss}$ was examined. The $[\mathrm{ClO}]_{ss}$ was calculated throughout each simulation for both estimated clean and polluted NO_x conditions. During clean conditions, the $[\mathrm{ClO}]_{ss}$ was calculated as ∼15 times greater than the $[\mathrm{ClO}]_{ss}$ during slightly polluted conditions (Figure S3). This demonstrates the strong sensitivity of [ClO] to NO_x (R7) and the potential for increasing Arctic development to influence chlorine chemistry and VOC concentrations. These results agree with the findings of Custard et al.,[25] in which elevated levels of NO_x suppressed the atmospheric concentration of halogen monoxides during ODEs.

Model Simulations. To investigate our understanding of the observed halogen chemistry, ClO was simulated using a 0-D model for comparison to the observational data. A time series of the observed and simulated ClO, constrained by observed Cl_2, is shown in Figure 3. For most days, the model simulation

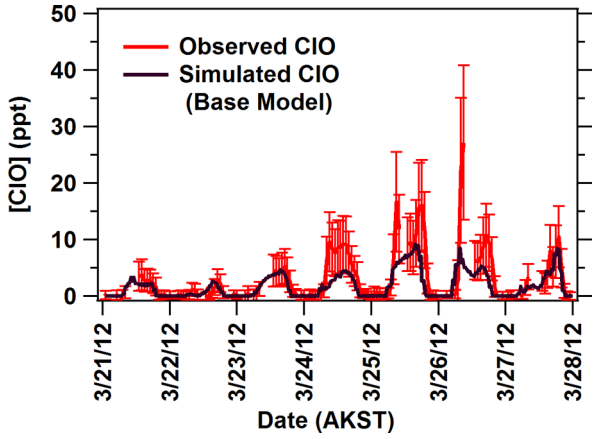

Figure 3. Time series of observed ClO, with measurement uncertainty shown, and simulated ClO concentrations at Barrow, Alaska, from the base model scenario.

of ClO is within the uncertainty of the measurements, although often on the lower side, particularly for March 25−26. As the model is constrained to observed Cl_2, uncertainties in simulations of ClO due to poorly understood heterogeneous Cl_2 recycling pathways on particles and the snowpack are largely avoided. However, as discussed above, NO_x greatly affects the ClO concentration. Simulated ClO under low NO_x (14−32 ppt) and high NO_x (168−378 ppt) conditions are shown in Figure S4, which shows daily maximum ClO of up to ∼9 ppt and up to ∼1 ppt under the low and high NO_x conditions, respectively. Therefore, any possible ClO underestimations in the base model scenario may well be due to NO_x variations, although we cannot rule out the possibility that there may be other more minor reactive chlorine sources, such as BrCl, which has been reported in the Arctic boundary layer.[33,34] In this study we were unable to quantify BrCl due to significant interferences at mass 241 ($I^{79}Br^{35}Cl^-$) and/or mass 243 ($I^{81}Br^{35}Cl^-$; $I^{79}Br^{37}Cl^-$). However, Liao et al.[10] previously conducted simultaneous measurements of BrCl and Cl_2 with maximum BrCl of 14 ppt, compared to maximum Cl_2 of 400 ppt. BrCl photolyzes 6 times faster than Cl_2 (at ∼solar noon).[25] Therefore, we can roughly estimate that $d[\mathrm{Cl}]/dt$ from BrCl is likely <11% of $d[\mathrm{Cl}]/dt$ from Cl_2.

We also recognize that, while not constrained as direct sources in our model, several chlorinated photolabile reservoir species, such as HOCl, $ClNO_2$, and $ClONO_2$, combined could contribute to the total chlorine atom production rate that yielded the measured ClO. We rule out organohalogen compounds because, despite being present in the Arctic boundary layer, their concentrations are very low and have photochemical lifetimes that are much longer than those of the molecular halogens.[35] Although HOCl, $ClNO_2$, and $ClONO_2$ measurements have not yet been reported in the Arctic, $ClNO_2$ and HOCl have been measured at mid-latitude polluted coastal sites at up to 3500 and 170 ppt, respectively.[15] While HOCl can be produced from reaction R8, and $ClNO_2$ from R9,[15]

$$\mathrm{ClO} + \mathrm{HO_2} \rightarrow \mathrm{HOCl} + \mathrm{OH} \quad (R8)$$

$$\mathrm{Cl} + \mathrm{NO_2} \rightarrow \mathrm{ClNO_2} \quad (R9)$$

laboratory studies have shown that $ClNO_2$ is also produced when gas-phase N_2O_5 undergoes reactive uptake on ice/aerosol surfaces containing Cl^-, as shown in reactions R10 and R11.[36−38]

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$$N_2O_5 \rightarrow NO_2^+{}_{(aq)} + NO_3^-{}_{(aq)} \quad (R10)$$

$$NO_2^+{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow ClNO_2 \quad (R11)$$

However, photolysis rates of HOCl and $ClNO_2$ are approximately 15 and 48 times slower than that of Cl_2, respectively.[5] Even if these two compounds were produced at similar rates as Cl_2, the Cl atom production rates from HOCl and $ClNO_2$ would be only 3% and 1% of Cl_2. We are unaware of any previous ambient measurements of $ClONO_2$, which should be produced via R7.[39] $ClONO_2$ is extremely soluble,[40] and hence direct emission from snowpack seems unlikely. Therefore, model underestimation of ClO due to missing sources of HOCl, $ClNO_2$, or $ClONO_2$ is unlikely, unless fast snowpack production of HOCl and $ClNO_2$ exists.

For BROMEX, simulated chlorine atom concentrations vary from 0 at night to daytime maxima as high as ~1.4×10^6 molecules cm^{-3}, as shown in Figure 4. These estimated Cl concentrations are much greater than most previous estimates (7.5×10^4–6×10^5 molecules cm^{-3}) for the Arctic boundary layer.[2,10,11] However, previous estimates were derived from measurements of hydrocarbons, e.g., butanes,[8] for which the calculated Cl concentrations are related to the transport path of the relatively long-lived hydrocarbons prior to measurement. Therefore, it is expected that hydrocarbon-based estimates of chlorine atom concentrations are substantially underestimated, since chlorine chemistry appears to primarily occur near the snowpack surface,[9] and given secondary radical production.[41] The maximum chlorine atom concentration derived in this study would significantly decrease the lifetime of methane from ~9 years (global average) to 3.8 years in the Arctic boundary layer, given $k_{Cl+CH_4} = 3.99 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1},[14] for a 24-h average Cl of 2.1×10^5 molecules cm^{-3}. Similarly, under these chlorine-enriched conditions, the lifetime for ethane goes from a local OH-determined lifetime of 151 days (T = 245 K) to about 1 day, given $k_{OH+C_2H_6} = 9.6 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{Cl+C_2H_6} = 5.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.[42] Thus, the Arctic boundary layer is, in springtime, an aggressively oxidizing environment for VOCs, because of the impact of chlorine chemistry.

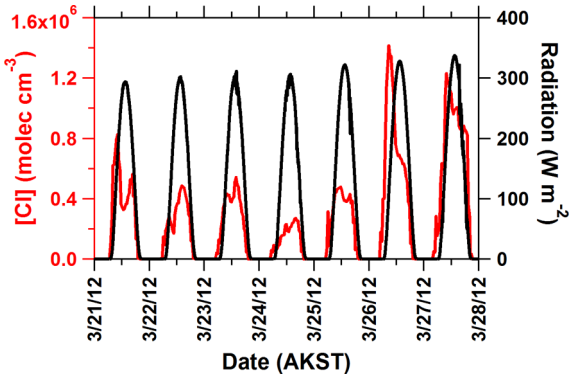

Figure 4. Observed radiation and simulated chlorine atom concentrations for the base model scenario.

In addition to changing the fates of VOCs, chlorine chemistry also indirectly impacts bromine chemistry propagation.[5] The rate of bromine-mediated O_3 depletion can be limited by the rate of conversion of BrO back to Br, via reactions R3–R5.[43,44] To study this impact, we ran the model with and without Cl_2 present and examined BrO, which can be examined by satellite remote sensing.[14] As shown in Figure S5, BrO increases by ~60% in the absence of chlorine chemistry, in part by removing reactions R3–R5. Thus, models and calculations of the rate of O_3 depletion must properly account for chlorine chemistry.

As strong atmospheric oxidants, chlorine atoms are important contributors to the degradation of small hydrocarbons, including methane, particularly in the polar regions, where hydroxyl radical concentrations are low.[18] During March 2012 near Barrow, Alaska, the prevalence of Arctic halogen chemistry was observed through simultaneous, high time resolution measurements of Cl_2 and ClO via CIMS. Modeling suggests that Cl_2, likely from snowpack production, is the primary source of Cl atoms, maximum concentrations for which are comparable to those calculated by Liao et al.,[10] but greater than those estimated previous from hydrocarbon decays. NO_x concentrations play an important role in the determination of ClO and BrO concentrations, such that increasing Arctic development[45] will impact halogen chemistry, as also observed here during days of air mass influence from the Prudhoe Bay oilfields. However, there is much more to be learned about polar chlorine chemistry, given limited measurements reported in the literature thus far. The relative roles of snowpack and aerosol production of molecular halogens are ill-defined, and for chlorine species, gas-phase intermediates have not been measured. Field studies focused on exploring the role of chlorine-containing intermediates (i.e., HOCl, $ClNO_2$, and $ClONO_2$) should be pursued. Vertical profiles of these species and Cl_2, in a combined measurement and modeling study to enable testing of our understanding of the chemistry, could help unravel this challenging problem, which has relevance to the fates of many VOCs, including the greenhouse gas methane.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b03909.

Figure S1, background-subtracted signals for $I^{37}ClO^-$ versus $I^{35}ClO^-$; Figure S2, measured Br_2 and BrO during the studied period; Figure S3, ClO_{ss} calculated under low and high NO_x conditions; Figure S4. modeled ClO under low and high NO_x conditions; and Figure S5, simulated BrO, with and without chlorine chemistry (PDF)

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Notes

The authors declare no competing financial interest.

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