



Molecular halogens before and during ozone depletion events in the Arctic at polar sunrise: concentrations and sources

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Abstract

The molecular halogens Br₂, BrCl and Cl₂ were monitored from 9 February to 13 March 2000 as part of the ALERT 2000 campaign to investigate the causes of ozone depletion at polar sunrise. The measurements were performed over the transition period from winter to spring in the high Arctic, at Alert, on northern Ellesmere Island in Nunavut, Canada. The measurement campaign for these species covered the period from 24-h darkness, at the beginning of the campaign, to several hours of direct sunlight per day at the end of the campaign. The halogen measurements were made by atmospheric pressure ionization tandem mass spectrometry, using multiple isotopes for each species, and reporting a 20-s average for each species every 2 min. Bromine was observed above the 0.2 ppt detection limit throughout the campaign at mixing ratios up to 27 ppt. BrCl was not observed above its 2 ppt detection limit until mid-way through the campaign, but was present almost continuously thereafter, and reached levels of 35 ppt. Molecular chlorine was not observed above its 2 ppt detection limit. During periods of ozone depletion, there was a very strong inverse relationship between O₃ and Br₂, and a moderately strong inverse relationship between O₃ and BrCl. The slopes of linear regressions of Br₂ and BrCl vs. O₃ indicate ≈ 1 ppb decrease in O₃ mixing ratio for every ppt of either of the molecular halogens. In some cases, O₃ depletion events seemed to be triggered by bursts of the halogen species initiated by photochemical processes, even in very weak “twilight”. In other cases, ozone depletion observed at Alert appeared to result from transport of O₃-depleted, halogen-enriched air from other locations. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the mid-1980s, the first reports appeared that in the Arctic during late winter and spring, surface boundary layer air showed sudden, and quite dramatic, losses of ozone (Bottenheim et al., 1986; Oltmans and Komhyr, 1986). Soon after it was discovered that these ozone depletion episodes coincided with a noticeable increase in filterable bromine (the sum of all bromine-containing compounds that could be collected on cellulose-based

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filters) and that a strong, negative, linear correlation existed between this bromine and ozone (Barrie et al., 1988). It is now generally accepted that the ozone depletion involves a chain reaction process whereby the bromine atom (Br) is the reactant, and the resultant bromine oxide molecule (BrO) is recycled into Br. Efforts have been undertaken to confirm the bromine chemistry by identification and quantification of the individual bromine compounds that might be involved. Ozone depletion episodes appear only in late winter and spring, and it has been surmised that some form of photochemical process is involved in the Br atom production process. Initial attention was focused on bromoform (CHBr₃) as the potential source of Br atoms (Bottenheim et al., 1990; Yokouchi et al., 1994). Reactions of gases with bromide in sea salt were also suggested as a potential source of photochemically active bromine compounds (Finlayson-Pitts et al., 1990). Subsequent reports (Moortgat et al., 1993) do not support bromoform as the bromine source and attention is now focused on sea salt. However, until recently, the specific gas-phase halogens involved have not been identified. Impey et al. (1997, 1999) devised and employed an elegant method to determine the abundance of “photolyzable” bromine, presumably either molecular bromine (Br₂) or hypobromous acid (HOBr). In addition to the non-specific measurements of bromine, there is additional evidence for the role of gas-phase bromine in ozone destruction in the Arctic troposphere in the form of BrO measurements. Such measurements have been made at ground level in the Arctic during springtime using differential optical absorption spectrometry (DOAS) (Hausmann and Platt, 1994; Kreher et al., 1997; Platt and Hausmann, 1994; Tuckermann et al., 1997). Column BrO over Arctic regions has also been measured from satellites (Chance, 1998; Richter et al., 1998; Wagner and Platt, 1998) and high altitude aircraft (McElroy et al., 1999) and there is evidence that much of it is in the troposphere.

While the data supporting bromine chemistry in the troposphere is strongest in the Arctic at polar sunrise, there is increasing evidence that bromine may also play a role in the chemistry of the marine boundary layer and around alkaline dry lakes in mid-latitudes (Dickerson et al., 1999; Hebestreit et al., 1999; Nagao et al., 1999).

Bromine chemistry in the Arctic at polar sunrise may also impact mid-latitudes directly. For example, Bi-galski et al. (1997) report increased bromine concentrations in particles collected near the northern part of Lake Huron, Canada in March in air masses that originated in the Arctic.

During studies of the first specific measurements of tropospheric Cl₂ in marine air on the coast of Long Island (Spicer et al., 1998), a small signal due to Br₂ was also observed and tended to track the Cl₂ signal. However, the signals attributed to Br₂ were sufficiently

close to the detection limit at that time of ~6 ppt that the data were not reported. Such levels of Br₂ are similar to those predicted in the modeling studies of Dickerson et al. (1999) for the marine boundary layer. In this paper we report and discuss measurements of Br₂ and BrCl in the boundary layer at Alert, Nunavut, Canada, as part of the Polar Sunrise Experiment: ALERT 2000.

2. Experimental

2.1. Description and discussion of APCI/MS/MS

A triple quadrupole mass spectrometer (Perkin-Elmer/Sciex API-365) equipped with an atmospheric pressure chemical ionization (APCI) source operating in negative ion mode, was used to quantitatively determine Br₂, Cl₂, BrCl, and (occasionally) other selected species during the field campaign. This technique has been described elsewhere (Spicer et al., 1998; Foster et al., 2001). Ambient air is drawn through the APCI source by a sampling pump. Reactive molecules in the ambient air stream are ionized by a corona discharge, and the reactant ions ionize trace gases in the air sample via ion–molecule reactions. The ions are electrostatically accelerated into the mass spectrometer through a 200 μm orifice. The mass spectrometer consists of two mass filters (Q1 and Q3) in series separated by a collision cell (Q2). All of the ions are focused into Q1 using a radio frequency quadrupole (Q0) and several electrostatic lenses. The parent ions of interest are separated from other ions in Q1. The parent ions of interest are then focused into Q2. The collision cell contains nitrogen to augment the fragmentation of the parent ions into structurally characteristic ions of lesser mass—daughter ions. The daughter ions are focused into Q3 where they are separated by mass and detected by an electron multiplier. This entire process, from the time of ionization to the time of detection, takes only a few milliseconds. The instrument can be programmed to pass only one selected ion mass through Q1, fragment that ion in Q2 and scan the fragment ion masses in Q3 to provide a daughter ion spectrum characteristic of the parent chemical. This mode is useful for identifying unknown species and for confirming identities. The instrument can also be operated as a continuous, multiple species monitor. In this mode, Q3 does not scan, but rather is set to pass only a preselected daughter ion mass that is characteristic of the target chemical. Because of the high speed of the system, Q3 can be switched to pass several characteristic daughter ions in sequence, providing an additional level of selectivity. For example, there are two major bromine isotopes of nearly equal abundance at 79 and 81 amu. Therefore, parent Br₂ ions are observed at 158, 160, and 162 amu, and parent/daughter combinations of 158/79, 160/79,

Table 1
Ions used for quantitative measurement of molecular halogens during ALERT 2000

Compound	Parent/daughter ion pairs monitored
Br ₂	158/79 and 160/79
Cl ₂	70/35 and 72/35
BrCl	114/35 and 116/37

160/81, and 162/81 may be monitored. Rapid switching of Q1 and Q3 settings allows multiple parent/daughter ion combinations for numerous target chemicals to be scanned in seconds. Table 1 shows the parent/daughter ion pairs, which were monitored for each halogen compound.

Sample air was obtained through ≈ 9 m of 0.64-cm OD PFA Teflon tubing. The sample line was heated to 21°C. The sample inlet was 1.5 m above the snow surface, ≈ 7.6 m from the SW corner of the FTX building. The inlet was shielded to prevent snow from entering the sample line. The sample air was drawn continuously through an electronic 3-way Teflon valve connected to a timer, so the sample could be automatically diverted through a denuder every few hours to quantify the instrument background signal. The residence time in the sample line was < 1 s. Laboratory tests showed the following line losses for this configuration: Cl₂, 10% and Br₂, 4%. The data have been corrected for these losses.

Two permeation ovens (Metronics Model 340) were used for calibrations. A Br₂ permeation tube and a Cl₂ permeation wafer (both from VICI Metronics) were used to generate calibration standards via standard addition. The emissions from the permeation devices were transferred to the inlet of the mass spectrometer using a low flow of clean air, where they were diluted into the sample air flow. The emission rate of the Br₂ tube was confirmed by collection in dilute NaHCO₃ followed by ion chromatography analysis. The Cl₂ wafer emission rate was verified by comparing the mass spectrometer signal for the wafer with the signal from a higher emission rate certified Cl₂ permeation tube (VICI Metronics). The comparisons were carried out within the linear range of the mass spectrometer.

Numerous multipoint calibrations performed in the laboratory before and after the field campaign confirmed the wide linear range of the instrument. The response factor for BrCl was found to be similar to that for Cl₂ in laboratory tests. Calibrations for Br₂ and Cl₂ were performed at least once each day of monitoring. The precision of the calibrations was $\pm 10\%$ for a given set of instrument conditions. The ambient measurements have been adjusted for daily changes in instrument sensitivity. The background or zero signal for the halogens was determined every 4–6 h by automatically

passing the sample air through an annular denuder coated with potassium carbonate. Laboratory tests demonstrated quantitative removal of Br₂, Cl₂, and BrCl by the denuder.

For this campaign, the signal for each ion pair was integrated for 20 s. Detection limits were estimated from the standard deviation of the signal for zero air (denuder in flow path) and the molecule's response factor. For S/N of 3, the detection limits were 0.2 ppt for Br₂ and 2 ppt for Cl₂ and BrCl. Laboratory tests showed no effect of humidity on the response factors for these species.

3. Results and discussion

Measurement of the molecular halogen species mixing ratios was carried out during the period from 9 February 2000 (DOY 40) to 13 March 2000 (DOY 73) from the FTX building (82°27.28'N, 62°29.69'W) at Alert, Nunavut, Canada. Maps showing the location of Alert and the geography of Northern Ellesmere Island may be found in Worthy et al. (1994). The mass spectrometer was occasionally employed to measure other chemicals in the positive ion mode, but the majority of this period was devoted to monitoring Br₂, Cl₂, and BrCl. The field campaign (9 February–13 March) took place during the transition from winter to spring at Alert. During the early part of the campaign, our measurements were made in 24 h/day darkness. Twilight gradually developed around noon local time, until the first direct sunlight on 3 March. At the end of our study period, Alert experienced ≈ 6 h of direct sunlight each day. Characterization of the meteorology, air quality, snow physics and snow chemistry during this period may be found in other articles in this issue.

As noted earlier, the tandem mass spectrometer has the ability to confirm the identity of an analyte by taking a daughter ion spectrum of the parent mass of interest. Fig. 1 shows the daughter ion spectrum for mass 160 during ambient monitoring at Alert. The daughter ions at 79 and 81 amu are characteristic of bromine, and the ratio of the peak intensities is consistent with the Br isotope distribution ($\approx 1:1$). A similar daughter ion spectrum for mass 116 (BrCl) is shown in Fig. 2. BrCl at 116 amu can be composed of ⁷⁹Br³⁷Cl and ⁸¹Br³⁵Cl. Because the chlorine atom carries the negative charge, the daughter ion spectrum shows the Cl ions at 35 and 37 amu. The ions are in approximately a 3:1 ratio, consistent with the natural isotope abundance of chlorine.

The isotope ratios provide an additional level of selectivity and quality control. Fig. 3 shows an example of the bromine ion ratio for Br₂ (79 amu/81 amu) and the Br₂ mixing ratio during ambient air monitoring on 9 March 2000 at Alert. The Br₂ mixing ratio varied from

~0.4 ppt during most of the period, to >4 ppt around 1700 GMT (during an ozone depletion episode). Throughout this period, the bromine isotopic ratio remained nearly constant at ≈ 1 , demonstrating

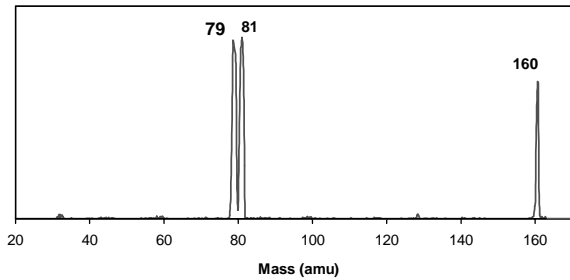


Fig. 1. Daughter ion spectrum of mass 160 (Br_2) during ambient

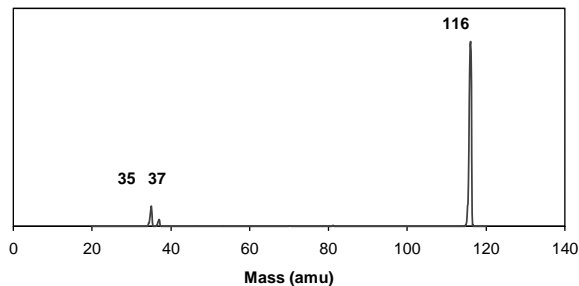


Fig. 2. Daughter ion spectrum of mass 116 (BrCl).

that the masses being monitored are made up of only bromine.

An earlier article (Foster et al., 2001) presented the time series for Br_2 , BrCl and O_3 for the ALERT 2000 campaign, and discussed the relationship between the halogens and ozone in qualitative terms. We have now examined these relationships in more detail. Measurable Br_2 was present throughout the field campaign from 9 February–13 March 2000, demonstrating a dark source for Br_2 . BrCl was not observed above its detection limit of 2 ppt until late February, after which it was nearly always present. The first observation of BrCl occurred several days before direct sunlight at Alert, so BrCl formation in the dark is also likely. However, we cannot rule out a role for radiation from the daily periods of “twilight” at Alert during this late February period. Molecular chlorine was not observed above the 2 ppt detection limit at any time during the campaign. The results reported here for Br_2 and Cl_2 can be compared with the observations of Impey et al. (1997, 1999) using a less-specific measurement method. In the spring of 1995 at Alert, Impey et al. (1997) occasionally observed photolyzable chlorine (assumed to be a combination of Cl_2 and HOCl) above their 9 ppt detection limit in March. We did not observe Cl_2 above our 2 ppt detection limit. The chlorine in BrCl would be measured as photolyzable chlorine using their technique; we estimate that the Impey et al. method exhibits 1.2 times the sensitivity to BrCl as to Cl_2 . Thus the peak photolyzable chlorine reported by Impey et al. (1997) of about 35 ppt around 15 March would correspond to

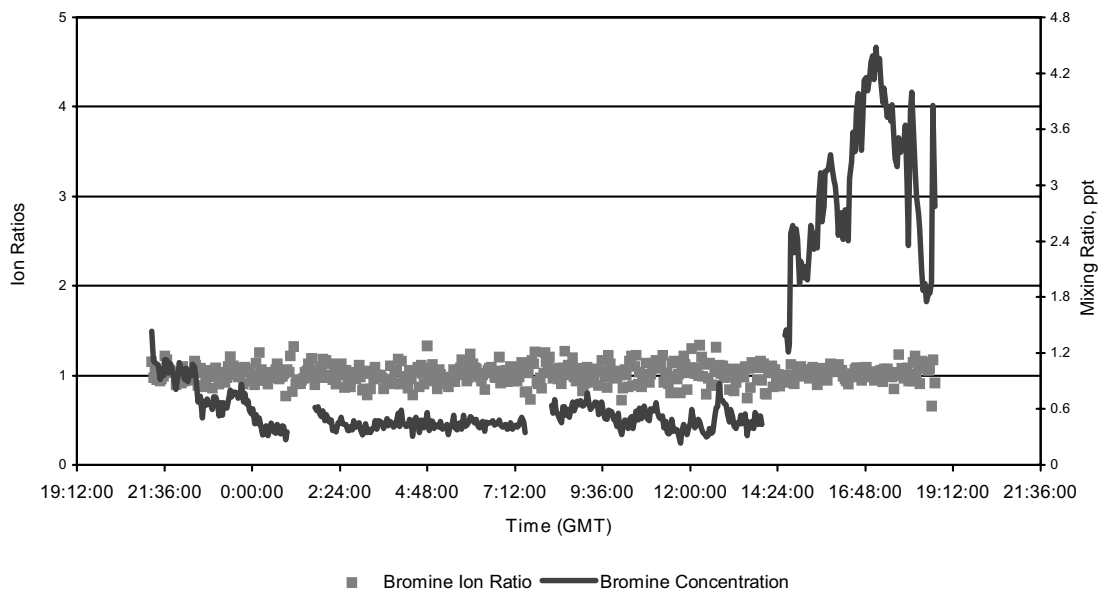


Fig. 3. Br_2 mixing ratio and isotopic ratio during Br_2 monitoring at Alert on 9 March 2000.

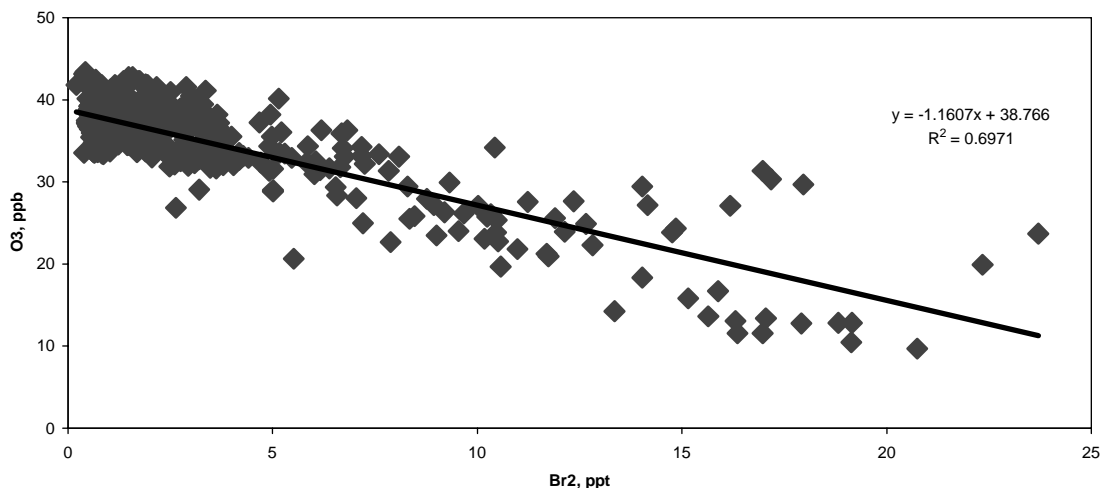


Fig. 4. Relationship between hourly ozone and bromine mixing ratios at Alert for 9 February–13 March 2000.

about 29 ppt calculated as BrCl, consistent with the peak BrCl observed in this study for early March. Impey et al. (1999) tried to separate the contribution for HOBr and Br₂, and reported the highest Br₂ levels during the periods of greatest O₃ depletion, with Br₂ mixing ratios at these times of 15–25 ppt. Our Br₂ measurements during the strongest O₃ depletion episodes agree very well with their observations.

Our previous report (Foster et al., 2001) showed time series for Br₂, BrCl, and O₃, which demonstrated a strong inverse pattern between the halogen compound mixing ratios and the O₃ mixing ratio. In order to quantify these relationships, the Br₂, BrCl, and O₃ data were averaged over the same hourly intervals, and the hourly averages plotted. The relationship between hourly O₃ and hourly Br₂ for the entire campaign is shown in Fig. 4. A strong linear relationship is evident, with an *R*² value of 0.7. This is a very strong correlation for ambient air data measured by two totally independent instruments. The regression equation shows an O₃ intercept of ~39 ppb, which can be interpreted as the “background” O₃ level at Alert during this period in the absence of Br₂ or, the background O₃ excluding O₃ depletion events. The slope suggests a 1.2 ppb decrease in O₃ for every 1 ppt of Br₂. However, this relationship is likely confounded by the simultaneous presence of BrCl and possibly other bromine atom precursors. The regression equation for the O₃/BrCl relationship is

$$O_3 = -0.9[\text{BrCl}] + 38 \quad (1)$$

with *R*² = 0.42. While the slopes and intercepts of the linear regressions of O₃ vs. Br₂ and O₃ vs. BrCl are quite similar, there is much more scatter in the BrCl relationship, and the *R*² is much lower. The cause of this increased variability is unknown. However, it is worth noting that the instrument sensitivity is about ten times

poorer for BrCl than for Br₂, so some increased variability of the BrCl results is not surprising. However, it seems likely that other factors also contribute.

The inverse relationship between ozone on the one hand, and gaseous bromine and BrCl on the other, together with the known chain reaction sequences of halogens that result in O₃ destruction, suggest strongly that these two species contribute to ozone depletion in the Arctic spring. However, many questions about the etiology of O₃ depletion remain unanswered, so the degree to which these processes are affecting the atmosphere at other times and locations is unknown. Does the inverse relationship signify that O₃ depletion was initiated by locally generated gas-phase halogen species, or does it suggest that the halogen species were formed well upwind, perhaps days earlier in areas where sunlight was available to drive the reactions, and that the relationship is simply due to meteorological modulation, as parcels of O₃-depleted air containing residual gas-phase Br₂ and BrCl are transported to the measurement site?

It is clear that Br₂ is produced locally in the snowpack, as shown by elevated levels in snowpack interstitial air at Alert (Foster et al., 2001). Indeed, Br₂ was observed in the air at Alert even in early February in complete darkness. Also, the short-lived BrO radical, which is a known product of the reaction of Br with O₃, was measured at Alert later in the spring, and was observed during O₃ depletion episodes (Hausmann and Platt, 1994; Honninger and Platt, 2002), so some local O₃ destruction must be occurring. Indeed, it was found that some destruction of ozone within the snowpack (dark and light) does occur (Albert et al., 2002). Gas-phase O₃ destruction by Br₂ or BrCl requires visible light for photolysis, and some of the early O₃ depletion episodes occurred before direct sunlight reached Alert

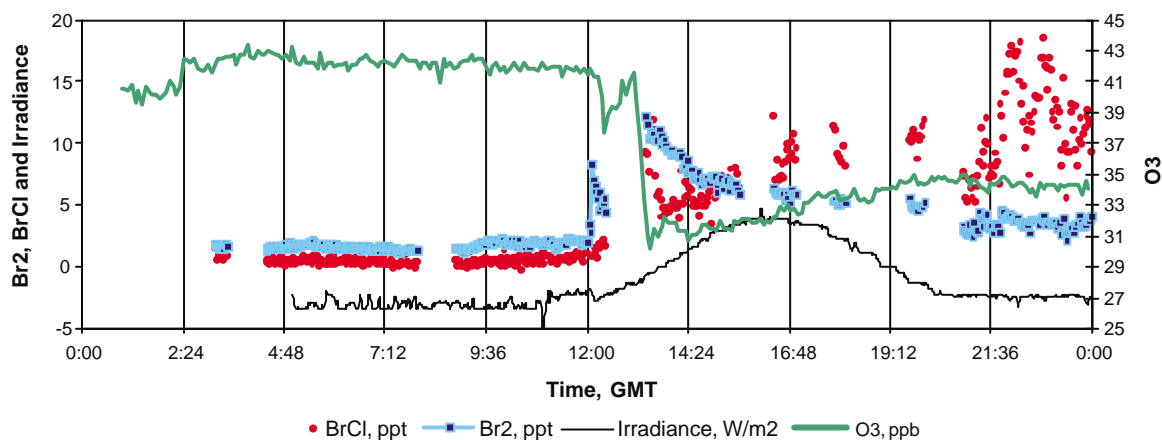


Fig. 5. Time series of O_3 , Br_2 , $BrCl$, and global irradiance at Alert for 29 February 2000. (Note that the global irradiance results have not been adjusted for a negative offset.)

on 3 March. Are the chain reactions triggered by weak indirect sunlight, or by photochemistry at lower latitudes (where polar sunrise occurs earlier), followed by transport of the air to Alert?

To address these questions, we examined two ozone depletion episodes that occurred during our measurement campaign. The earliest of the two took place on 29 February, before first direct sunlight had reached Alert. The data for O_3 , Br_2 , $BrCl$ and global irradiance are shown in Fig. 5. The O_3 mixing ratio was 40–45 ppb before noon GMT, and both Br_2 and $BrCl$ were <2 ppt, although Br_2 was well above its detection limit. Just at noon GMT, as light intensity began to increase, both Br_2 and $BrCl$ increased rapidly and the O_3 mixing ratio began to fall. Over the next 2 h, O_3 continued to decrease until it reached a minimum at about 31 ppb and then began a gradual increase. The slow increase in O_3 mixing ratio lasted almost 24 h, at which time the level was back at 40–45 ppb. The slow 24-h increase is presumably due to mixing of background air from aloft into the O_3 -depleted layer. During the 2-h period when the O_3 mixing ratio decreased, the global irradiance continued to rise. Br_2 and $BrCl$ results are missing for the middle hour because daughter ion scans were being performed, but elevated, decreasing values were measured after 1330 GMT, as if even higher levels had been present.

The modest O_3 depletion event of 29 February appeared to be triggered by a burst of Br_2 and $BrCl$, corresponding to the first appearance of weak twilight. The O_3 decrease did not occur simultaneously with the Br_2 increase, as might be expected if the changes were due to air mass transport alone. The O_3 decrease began 10–15 min after the Br_2 burst, suggesting that chemical reaction was taking place. We speculate that local chemistry caused this depletion event, probably triggered by $HOBr$ photolysis, as discussed shortly. Note that if this event were initiated by photochemical

production of halogens in the snowpack, only very low intensity was required. Fig. 6 shows the global irradiance at Alert from 20 February to 13 March (the data have not been adjusted for a negative offset). No irradiance was detected until 28 February. The O_3 depletion event was observed on 29 February, the second day when weak light intensity was recorded. It is noteworthy that Impey et al. (1999) observed BrO_x radicals during periods of very low radiation.

Another illustrative O_3 depletion event occurred on 10–11 March 2000 (Fig. 7). A rapid drop in O_3 mixing ratio occurred at ≈ 1430 GMT on 10 March, simultaneously with rapid increases in both Br_2 and $BrCl$. The Br_2 and $BrCl$ increases, and the O_3 decrease, occurred as the global irradiance increased rapidly following a period of snow. The O_3 depletion was greatest during the time of maximum radiation and maximum Br_2 and $BrCl$ levels. As darkness set in, the halogen species mixing ratios decreased and O_3 gradually recovered. Back trajectories for this period show that the arriving air had spent the previous 5 days in the polar regions north and northeast of Alert, with little chance of anthropogenic contributions to the air. The air did not pass over any areas that would have experienced direct sunlight. We interpret this depletion event on 10 March as also most likely due to local chemistry. As on 29 February, recovery of the O_3 mixing ratio to pre-episode values required many hours. If radiation triggered the burst of halogen emissions that caused the depletion event, it required greater intensity than the 29 February episode, because the halogen burst did not occur until later in the day when direct sunlight was present.

The second, and much more significant part of this episode began on the morning of 11 March (near midnight local time). Very rapid increases of both Br_2 and $BrCl$ occurred, with Br_2 reaching the highest values observed during our study period (~ 27 ppt) within

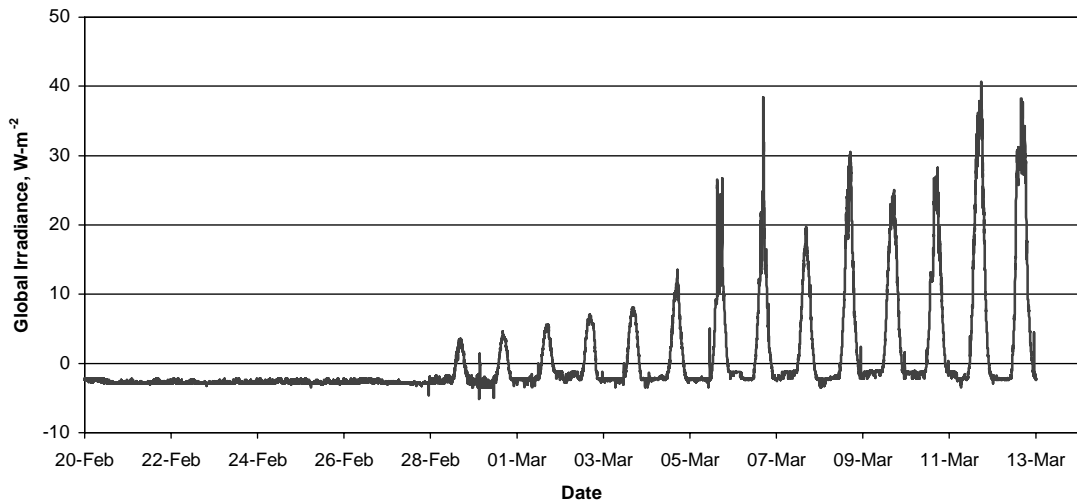


Fig. 6. Global irradiance recorded at Alert for 20 February–13 March 2000. (Note that results have not been adjusted for a negative offset.)

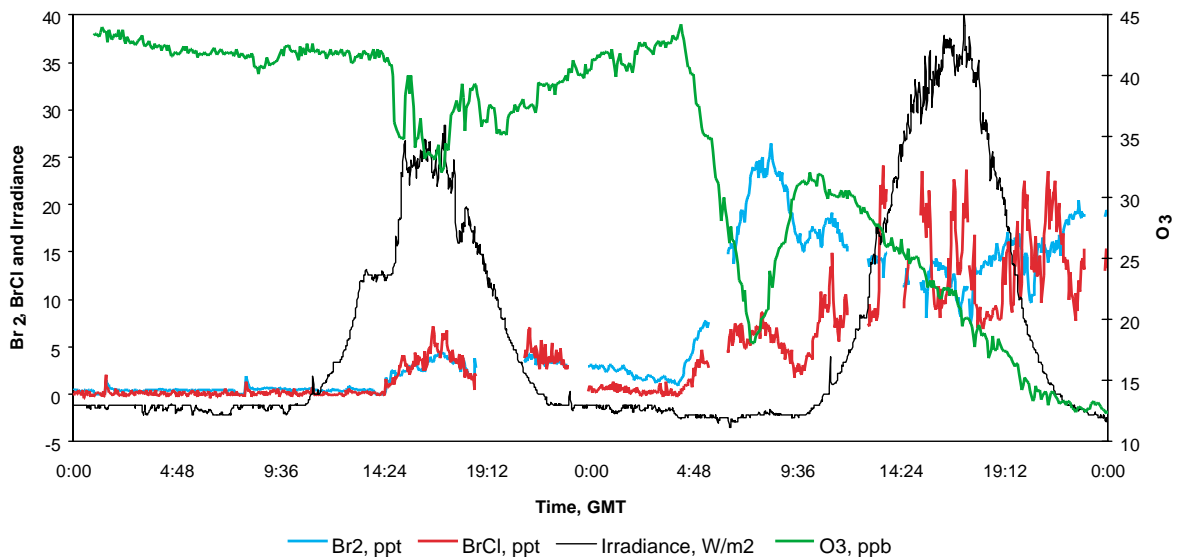


Fig. 7. Time series of O_3 , Br_2 , $BrCl$, and global irradiance at Alert for 10–11 March 2000. (Note that the global irradiance results have not been adjusted for a negative offset.)

about 4 h. O_3 dropped rapidly from 43 to 18 ppb during that same 4-h period. After about 0800 GMT, O_3 began to recover and the halogen species mixing ratios began to decrease, perhaps due to mixing of air from aloft, which would contain higher background O_3 and little if any Br_2 or $BrCl$. At ≈ 1000 GMT, radiation intensity began to rise, and Br_2 and $BrCl$ increased again. Over the next several hours, Br_2 decreased as the radiation intensity increased to its maximum at ~ 1600 GMT. Ozone decreased throughout this interval. The early

portion of this episode from 0400 to 1000 GMT occurred in complete darkness, and is most likely attributable to transport of O_3 -depleted, halogen-enriched air from another location. Trajectories show transport from the north the previous several days. It is possible that the O_3 depletion occurred during the previous day's irradiation at a location where the conditions were appropriate for a bromine explosion. The subsequent portion of this episode, after ~ 0930 GMT, is consistent with a burst of Br_2 and $BrCl$

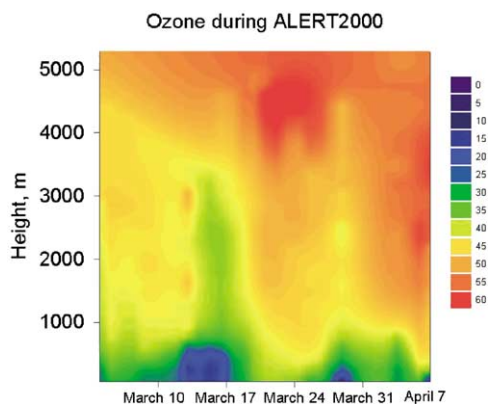


Fig. 8. Vertical structure of O_3 mixing ratio over Alert in March 2000.

triggered by radiation, followed by a period during which the rate of Br_2 photolysis exceeded the rate of production due to the increasing intensity. Once the radiation intensity and consequently the Br_2 photolysis rate began to drop after ~ 1600 GMT, the Br_2 mixing ratio increased until midnight. It is difficult to discern a trend in the $BrCl$ mixing ratio during this last period of O_3 depletion because it was so variable. The behavior of the key chemicals after 0930 GMT on 11 March seems to be consistent with local photochemistry. Production of Br_2 and $BrCl$ in the snowpack (Foster et al., 2001) is triggered by modest light intensity in the morning, followed by transport of the halogens out of the snowpack interstitial air to the near-surface layer of the atmosphere. Subsequent photolysis of these species during the remainder of the daylight period produces O_3 -depleting halogen atoms. That the depletion is occurring in the surface layer of the atmosphere may be determined from the vertical O_3 pattern on 11 March shown in Fig. 8. Reduced O_3 mixing ratios on 11 March appear to be confined to the lowest few hundred meters of the atmosphere over Alert, consistent with a surface source for the species responsible for ozone destruction.

3.1. Mechanistic implications

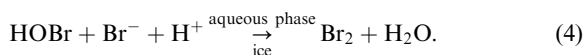
The earliest mechanisms for bromine activation included the photolysis of organobromine compounds such as bromoform (Barrie et al., 1988) and reactions of sea salt with gases (Finlayson-Pitts et al., 1990). While it is now generally accepted that sea salt is the source of bromine, the specific reactions leading to activation of sea salt bromide are not well established. The molar ratio of bromine to chlorine in sea salt is only 1:650. To cause almost complete destruction of ppb levels of ozone, enhancement of the ratio of bromine to chlorine must take place. In addition, there needs to be a set of chain reactions that lead to an autocatalytic release of

bromine, the so-called ‘‘bromine explosion’’ (Platt and Lehrer, 1996; Wennberg, 1999).

Impey et al. (1997) and Oum et al. (1998) proposed that the reaction initiating the formation of gas-phase bromine compounds is the reaction of ozone with bromide on the surface of seawater ice, a reaction well known to occur in solution (Haag and Hoigne, 1983; Taube, 1942; vonGuntzen and Hoigne, 1994):

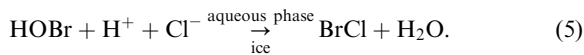


Laboratory studies (Koop et al., 2000) suggest that sea salt particles on the Arctic snowpack are likely to be liquid and hence the chemistry of HOBr in solutions or in the quasi-liquid layer on ice surfaces is relevant. HOBr is known to react with Br^- to generate Br_2 both in solution (Beckwith et al., 1996; Eigen and Kustin, 1962; Fickert et al., 1999; Hanson and Ravishankara, 1995) and when the bromide is present in salts or ice (Abbatt, 1994; Abbatt and Waschewsky, 1998; Allanic et al., 1997; Kirchner et al., 1997; Mochida et al., 1998):



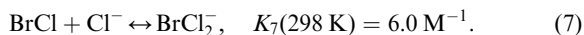
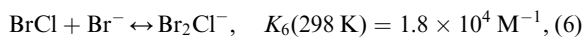
McConnell and coworkers and Fan and Jacob proposed reaction (4) as a key reaction in the autocatalytic release of bromine from aerosols and the snowpack (Fan and Jacob, 1992; McConnell et al., 1992; Tang and McConnell, 1996).

However, if HOBr is formed by reactions (2) and (3) where sea salt is the source of bromide ions, there will also be an excess of chloride ions present. HOBr also reacts with chloride ions, giving $BrCl$ (Abbatt, 1994; Abbatt and Waschewsky, 1998; Allanic et al., 1997; Chu and Chu, 1999; Fickert et al., 1999; Hanson and Ravishankara, 1995; Kirchner et al., 1997; Mochida et al., 1998):

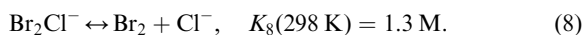


Given the large Cl:Br ratio in sea salt, reaction (5) might be expected to predominate and the concentration of $BrCl$ would then greatly exceed that of Br_2 . However, in the present studies, Br_2 and $BrCl$ were present at Alert at similar concentrations. There are a number of factors that may contribute to the higher than the expected $Br_2/BrCl$ ratios. One is the solubility of $BrCl$ compared to Br_2 . Based on recent laboratory measurements (Bartlett and Margerum, 1999), the Henry's Law constant for $BrCl$ at 245 K is calculated to be 60 M atm^{-1} , compared to 13 M atm^{-1} for Br_2 . This decreased solubility of Br_2 compared to $BrCl$ favors gas-phase Br_2 relative to $BrCl$. More important, the increased solubility of $BrCl$ increases the opportunities for it to undergo secondary reactions in the surface film

(Wang and Margerum, 1994):



The Br_2Cl^- formed in reaction (6) decomposes to Br_2 and Cl^- :



The equilibrium constant K_6 is a factor of 3000 larger than K_7 at room temperature. If this is also the case at the lower temperatures ($\sim 240 \text{ K}$) characteristic of the Arctic at this time of year, it more than overcomes the smaller concentrations of bromide ion in seawater.

An additional factor that favors Br_2 production over BrCl is the selective ion segregation that occurs during phase transitions of salt solutions. Koop et al. (2000) suggest, based on studies of phase transitions in seawater, that chloride will be concentrated by a factor of ~ 11 and bromide by a factor of ~ 38 in seawater deposited on the ice pack under conditions of polar sunrise. This would decrease the Cl^-/Br^- ratio available for reaction in the surface film from 650:1 to 188:1; indeed, the Cl/Br ratio in snow at Alert has been found to be as low as 30/1 (Toom-Sauntry, 2001). Furthermore, in laboratory studies of bromine-doped NaCl crystals, preferential surface segregation of bromide was observed on exposure to water vapor (Ghosal et al., 2000). Molecular dynamics simulations also suggest that in concentrated sea salt aerosols, bromide ions will preferentially reside at the air–water interface and hence be readily available for reaction with gases such as HOBr (Jungwirth and Tobias, 2001).

In short, there are a number of factors, both physical and chemical, which enable the production of gas-phase Br_2 to compete with production of BrCl in the snowpack, consistent with our observations that these two compounds are present in air at Alert at similar concentrations around the time of polar sunrise. That such chemistry in the snowpack is the source of gas-phase halogens is also supported by our measured enhancement of Br_2 in snowpack interstitial air compared to the air above it (Foster et al., 2001). Our measurements of similar concentrations of Br_2 and BrCl , showing an $\approx 3:1$ ratio of bromine to chlorine compared to 1:650 in sea salt, are consistent with an autocatalytic production of bromine and the proposed “bromine explosion” hypothesis (Platt and Lehrer, 1996; Wennberg, 1999).

We investigated gas-phase halogen behavior in this environment using a 0-D box model that includes the gas-phase chemistry as described by Michalowski et al. (2000), with updates as described in Grannas et al. (this issue). The effect of the measured snowpack halogen sources (Br_2 and BrCl) on gas-phase chemistry was investigated by including fluxes of these species in the

gas-phase chemistry model. Of interest is whether the model simulations of the relative amounts of Br and Cl atoms are in accord with estimates from measurements of hydrocarbon decay rates. The full multiphase model used by Michalowski et al. (2000) involves condensed phase reactions of HOBr with Cl^- , followed by a series of inter-halogen reactions, producing either Br_2 or BrCl (as discussed above), which then efflux to the gas phase. The modified full model of Michalowski et al. (2000) yields an average Br_2/BrCl concentration ratio of 1.5 averaged over a 4-day period in mid-March, consistent with our measurements. We have found that although the model can produce Br atom concentrations comparable to what are believed to exist during O_3 depletion events (i.e. $\sim 10^7 \text{ cm}^{-3}$; Jobson et al., 1994), it underpredicts Cl atoms. The available literature, discussed by Summer et al. (this issue), suggests that the actual $[\text{Br}]/[\text{Cl}]$ for modest O_3 depletion will be 200–350. However, the gas-phase model predicts a ratio of ~ 1400 for the lower limit case where we only permit emissions of BrCl from the snowpack. If Br_2 emissions from the snowpack are also included, consistent with our observations during ALERT 2000, the modeled ratio is even higher. This discrepancy indicates that either the gas-phase chemistry that modulates halogen atom concentrations is incomplete (e.g. we are missing Br atom sinks), or that we are missing a source of chlorine in this environment. For example, the ion–molecule chemistry of HOCl is such that it does not have a parent peak in APCI-MS and would not have been observed in these studies (Caldwell et al., 1999).

4. Conclusions

The molecular halogens Br_2 , BrCl , and Cl_2 were monitored by a highly selective and sensitive tandem mass spectrometric technique for a period of 33 days during the transition from winter (total darkness) to spring (several hours of direct sunlight) in the high Arctic. Formation of Br_2 and BrCl in the absence of light was observed. Molecular chlorine, Cl_2 , was not observed above the 2 ppt detection limit during this period. Results from O_3 depletion events during the campaign show that bursts of Br_2 and BrCl occur at the onset of O_3 depletion episodes, and these halogen bursts can coincide with increasing radiation intensity, even very weak radiation associated with twilight. Other depletion events occurred in the dark, and may be associated with transport of O_3 -depleted and halogen-enriched air from another location, or possibly, transport of air enriched in HOBr , which triggers a “bromine explosion” in the dark. A strong inverse relationship was observed between O_3 and Br_2 ($R^2 = 0.7$) and a weaker correlation was found between O_3 and BrCl ($R^2 = 0.4$). The slopes of the corresponding regressions show

≈ 1 ppb O_3 decrement for each 1 ppt of either Br_2 or $BrCl$. Our observations seem to be generally consistent with the “bromine explosion” hypothesis (Platt and Lehrer, 1996; Wennberg, 1999).

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