

Measurements of photolyzable chlorine and bromine during the Polar Sunrise Experiment 1995

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Abstract. We report measurements of rapidly photolyzable chlorine (Cl_p ; e.g., Cl_2 and HOCl) and bromine (Br_p ; e.g., Br_2 and HOBr) in the high Arctic using a newly developed photoactive halogen detector (PHD). Ground level ambient air was sampled daily from mid-February through mid-April in the Canadian Arctic at Alert, Northwest Territories (82.5°N , 62.3°W), as part of the Polar Sunrise Experiment (PSE) 1995. Concentrations of “total photolyzable chlorine” varied from <9 to 100 pptv as Cl_2 and that of “total photolyzable bromine” from <4 to 38 pptv as Br_2 . High concentration episodes of chlorine were observed only prior to sunrise (March 21), while high concentration episodes of bromine were measured throughout the study. The high concentrations of photolyzable chlorine and bromine prior to sunrise suggest a “dark” production mechanism that we assume yields Cl_2 and Br_2 . An inverse correlation of bromine with ozone is clearly present in one major ozone depletion episode at the end of March. A trajectory analysis, taken with the differences in measured levels of photolyzable chlorine and bromine after sunrise, imply different production mechanisms for these two types of species. A steady state analysis of the data for one ozone depletion episode suggests a $[\text{Br}]/[\text{Cl}]$ ratio in the range 100–300. The high concentrations of photolyzable bromine after sunrise imply the existence of a precursor other than aerosol bromide.

1. Introduction

The dramatic loss of surface layer ozone at sunrise has been observed in the high Arctic for several years. The episodes occur with the onset of polar sunrise and are associated with large increases in the amount of filterable bromine [Barrie *et al.*, 1988]. Bromine and chlorine atom chemistry has been implicated as the cause of the O_3 destruction episodes. Evidence for halogen atom chemistry has come from measurements of non-methane-hydrocarbons (NMHC) [Jobson *et al.*, 1994], BrO [Hausmann and Platt, 1994], organic nitrates [Muthuramu *et al.*, 1994] as well as organic and inorganic bromine compounds [Li *et al.*, 1994], made during the Polar Sunrise Experiment 1992. Similar observations have been reported by Solberg *et al.* [1996], who find that ozone at Spitsbergen can be depleted from the surface to as high as 2 km.

Modeling studies [Barrie *et al.*, 1988; McConnell *et al.*, 1992; Fan and Jacob, 1992; Tang and McConnell, 1996] have shown that for the observed ozone depletions, the Cl and Br atoms present could originate from a photochemically active “seed” (such as CHBr_3) and that rapid recycling processes can then maintain the catalytic cycle.

To improve our understanding of the halogen atom chemistry occurring in the troposphere, reliable measurements of

photolytically active halogen species such as Cl_2 , Br_2 , HOCl , and HOBr are clearly needed. Recent measurements of inorganic chlorine, which include Cl_2 and HOCl , have been made in the marine boundary layer at Virginia Key, Florida [Pszenny *et al.*, 1993], and over eastern North America [Maben *et al.*, 1995] using a tandem mist chamber described by Keene *et al.*, [1993]. However, there have as yet been no measurements of Br_2 (or Cl_2) in the Arctic, largely as a result of the lack of suitable analytical methodologies. Here we report the first measurements of photolytically active bromine (Br_2 and HOBr) and chlorine (Cl_2 and HOCl) in surface air at Alert, Northwest Territories Canada (82.5°N , 62.3°W), using a newly developed method, the photoactive halogen detector (PHD). This method is described in detail by Impey *et al.* [this issue].

2. Experimental Procedures

The Polar Sunrise Experiment 1995 (PSE 95) was conducted at Alert, Canada, on northern Ellesmere Island (82.5°N , 63.2°W) from February 20 to April 15, 1995. Measurements of photolyzable chlorine and bromine were conducted each day at the Special Studies Laboratory (SSL), situated on a plateau approximately 6 km SSW of the Canadian Forces Station, while ozone and meteorological data were measured continuously from the Baseline Air Pollution Monitoring Network (BAPMoN) laboratory situated within 1 km of the SSL (see Figure 1). Ozone was measured continuously using a TECO model 49 analyzer. The photoactive halogen detector, a new method for measuring photoactive halogens, is described in detail by Impey *et al.* [this issue]. Briefly, the technique involves drawing the sample air through a ~ 2 L cylindrical pyrex reaction vessel at ~ 1 L/min (i.e.,

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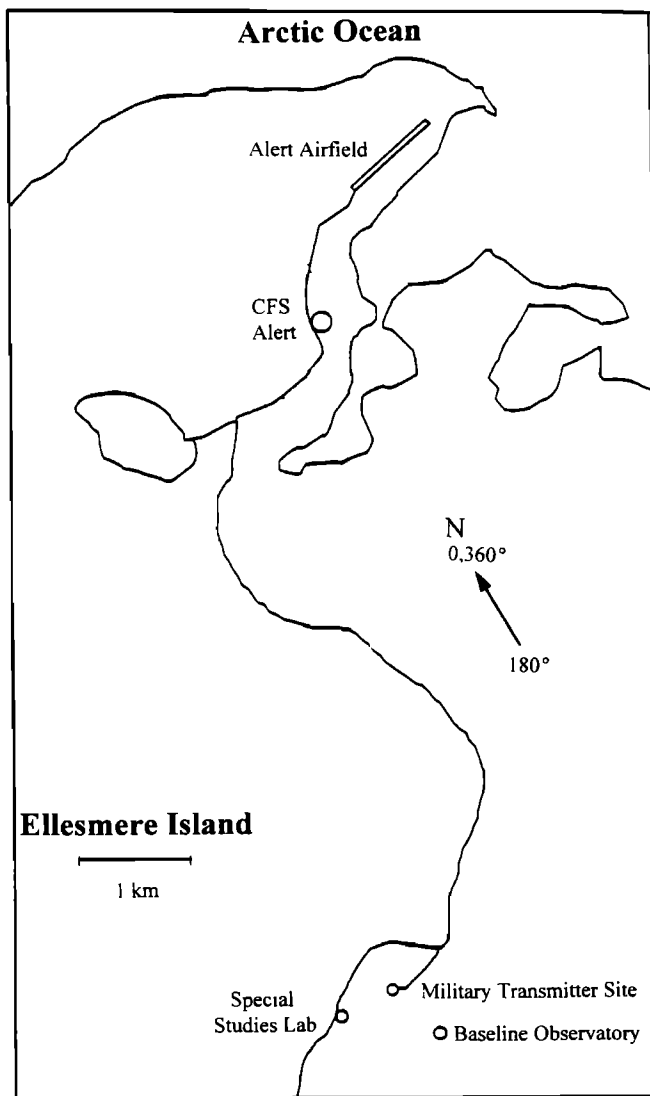


Figure 1. Map of the northern tip of Ellesmere Island. Sampling took place at the Special Studies Laboratory. Ozone was measured continuously from the Baseline Observatory.

a reactor residence time of 2 min). Irradiation of the sample air in the reaction vessel using a 150 W xenon arc lamp photolyzes the ambient Cl_2 and Br_2 (and other photolytically active halogen molecules, such as HOCl , HOBr , ClNO , BrNO , ClNO_2 , BrNO_2 , ClONO_2 , and BrONO_2), to yield free Cl and Br atoms. These Cl and Br atoms then react rapidly in the cell with added propene (C_3H_6) and nitric oxide (NO) to produce, among other products, chloroacetone and bromoacetone. These reaction products are concentrated from 36 L reactor samples onto small adsorbent-filled tubes, extracted, and then measured using capillary gas chromatography with electron capture detection. The system is calibrated through the preparation of low concentration mixtures of Cl_2 and Br_2 in air and sampling these mixtures at the reactor inlet. The method then measures photolytically active Cl and Br sources, "as Cl_2 ," and "as Br_2 ." The detection limits (for a 36 L sample) for Cl_2 and Br_2 are 9 pptv and 4 pptv, respectively.

3. Results and Discussion

Measured ground level ozone and the total photolyzable chlorine concentrations as Cl_2 and the total photolyzable bromine

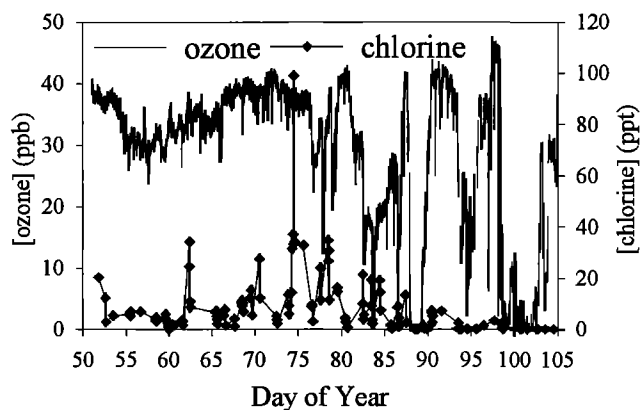


Figure 2. Comparison of ground level ozone and photolyzable chlorine as Cl_2 , measured at Alert.

as Br_2 at Alert are shown in Figures 2 and 3. One hour integrated samples were collected for the period between February 20 and April 14 (days 51-104). This period represents a good sampling for the transition from complete 24 hours of darkness to complete 24 hours of light. March 4 (day 63) was the first day the Sun was visible above the horizon (for a total time of ~15 min). By day 80 the Sun was visible for approximately 8 hours, highest in the sky over Alert at about 1110 LT. Measurements of photolyzable chlorine beyond this day were either low or below the detection limit of the instrument. In contrast, and interestingly, significant concentrations of photolyzable bromine were present after sunrise, even though either likely measured bromine compound (Br_2 or HOBr) has a substantially shorter photolytic lifetime than the corresponding chlorine compound.

The PHD will respond to a number of atmospheric halogen species as noted above. However, their individual contributions to the system response can be very region dependent. As discussed by Shepson *et al.* [1996] the Arctic at sunrise is likely to be an extremely low $[\text{NO}_x]$ environment, which can help rule out some possibilities. Specifically, formation of ClNO , ClNO_2 , ClONO_2 , and similar nitrogen-containing bromine species is unlikely to be important in this particular environment. The PHD will not exhibit a significant response to HCl (HBr) or any organohalogen species. Thus, given what is currently known about the atmospheric chemistry of chlorine and bromine, we assume that Cl_2 and HOCl , and Br_2 and HOBr make up the measured Cl_p and Br_p , respectively.

For March 14 and 15 (days 73-74) we conducted several measurements over the full diel cycle; the results are shown in

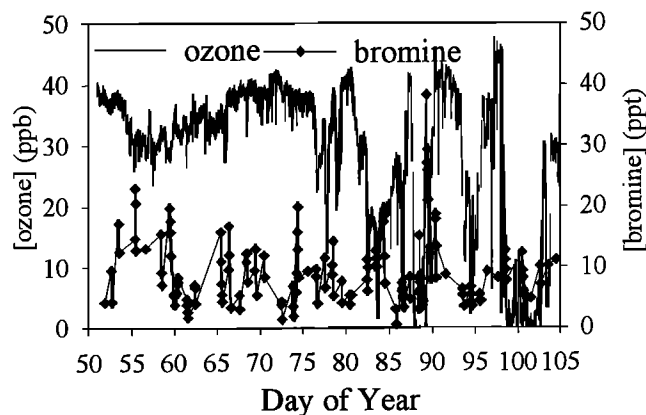


Figure 3. Comparison of ground level ozone and photolyzable bromine as Br_2 , measured at Alert.

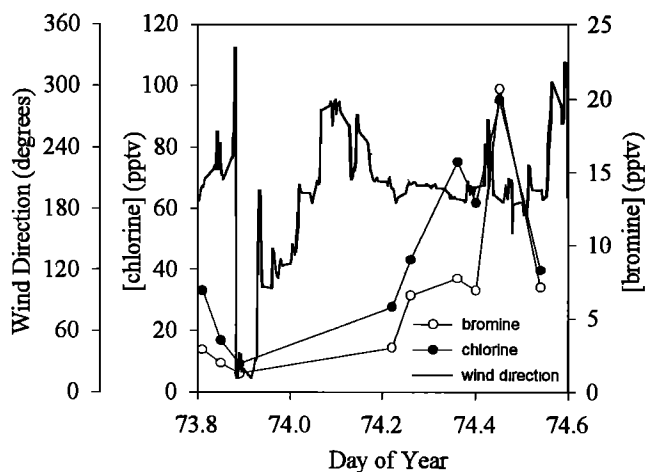


Figure 4a. Wind direction and a complete diel cycle showing the diurnal trend for both chlorine and bromine on days 73-74.

Figure 4a. These data show a distinct and similar diurnal cycle for both photolyzable chlorine and bromine, with a maximum near 1100 LT and a minimum near midnight. In Figure 4b we present the average diurnal chlorine and bromine concentrations for all the data obtained for days 63-91. This period is chosen as the period after sunrise where the chlorine concentrations were above the detection limit. The average diurnal profile is similar to that shown in Figure 4a, i.e., a late morning maximum and a minimum near midnight. This is in contrast to what we might expect for rapidly photolyzable species, i.e., low concentrations during the day and high at night. The fact that both chlorine and bromine exhibit similar diurnal characteristics with maxima in the daytime might implies a photo-induced (possibly heterogeneous) source, e.g., as postulated by *McConnell et al.* [1992] and *McConnell and Henderson* [1993]. However, the presence of substantial concentrations of both species well before sunrise (before day 63) clearly indicates that there must be a dark mechanism for their formation. Several cases for which Br_p is high in the dark (e.g., days 55-60) occur when the back trajectories show the air arriving at Alert from an Arctic oceanic origin and thus are not likely to have been sunlit. The wind direction data shown for the one case in Figure 4a imply a change

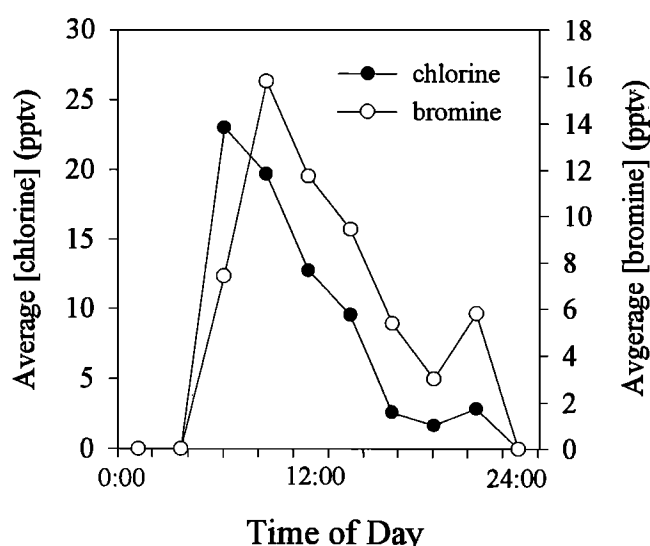
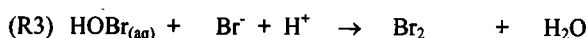
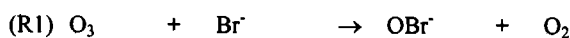


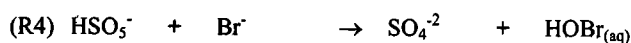
Figure 4b. Average diurnal chlorine and bromine concentrations for days 63-80.

from an oceanic origin to an origin from the Baffin Inlet direction when chlorine and bromine concentrations were highest. However, as discussed below, only the chlorine data indicate that elevated levels appear to be typically correlated with trajectories originating from the Baffin Inlet region. Over the entire sampling period, chlorine and bromine were not well correlated (slope of 0.05 and $R^2 = 0.026$ for a regression of chlorine against bromine).

There are several potential mechanisms for production of photolytically active chlorine and bromine species in the dark. *Taube* [1942] showed that Br^- reacts readily in solution with dissolved ozone (similarly for Cl^- [*Yeatts and Taube*, 1949]), followed by a rapid protonation to produce HOBr . HOBr can then oxidize condensed phase Br^- to Br_2 , as shown in (R3), [*Eigen and Kustin*, 1962; *Fan and Jacob*, 1992]:



Similarly, *Mozurkewich* [1995] suggested that peroxymonosulfuric acid, produced through a free radical chain oxidation of dissolved S(IV) species, could also oxidize bromide ions to HOBr , as shown in (R4). This would then be followed by Br_2 production through (R3).



This requires low temperatures and high SO_2 concentrations which exist only during the winter and early spring in the Arctic region. *Zetzsch et al.* [1988] and *Zetzsch and Behnke* [1993] have found that O_3 can react with HCl on aerosol surfaces to produce Cl_2 in the dark but that the heterogeneous production of Cl_2 can be photocatalyzed. It has been reported by *Livingston and Finlayson-Pitts* [1991] and by *Zetzsch and Behnke* [1993] that reaction of N_2O_5 with $\text{NaCl}(\text{s})$ can produce NO_2Cl , which subsequently photolyzes to yield Cl atoms. However, as discussed by *Shepson et al.* [1996], and as shown by *Honrath and Jaffe* [1992], the levels of available NO_x in the Arctic at sunrise should be very low. It has been recently discussed by *Tang and McConnell* [1996] that only a small Br atom initiation source (e.g., photolysis of CHBr_3) is necessary for significant rates of production of Br_2 after sunrise, if the *Fan and Jacob* [1992] mechanism (reaction (R3)) is operative, since that mechanism is autocatalytic. It thus seems possible that the *Fan and Jacob* mechanism could be operative in the dark but that it is accelerated (at least for bromine) after sunrise.

The *Fan and Jacob* [1992] mechanism involves conversion of gas phase XO to HOX , via (R5) and (R6), followed by uptake of



the HOX into the acidic aqueous fine aerosol. Since this mechanism not only destroys O_3 but also requires its presence, it is instructive to examine the relationship between our measurements of the photolytically active halogen species and O_3 . Although photolyzable chlorine was not well correlated with ozone over the entire study, the maximum observed photolyzable bromine concentration (38 pptv as Br_2) occurred during the first major O_3 depletion episode between days 87 and 90 and was inversely correlated with O_3 during this event. An expanded view of the comparison between ozone and bromine concentrations between days 76 and 92 is shown in Figure 5.

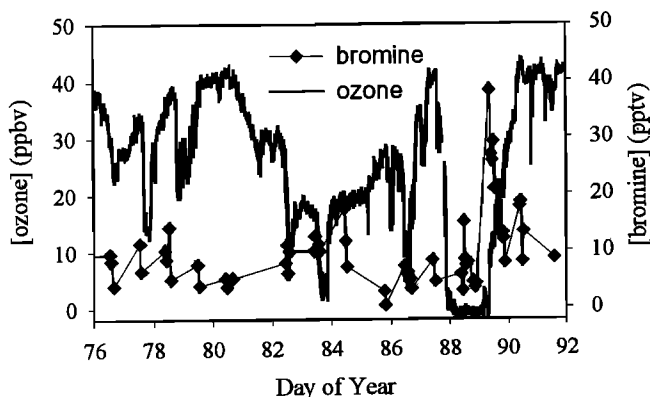


Figure 5. An expanded view for the comparison of ground level ozone and photolyzable bromine for days 76-92.

Three-day back trajectory analysis indicates the sample air arriving from the Arctic ocean region along the north coast of Greenland, in the general direction of Spitsbergen, implying an Arctic source for the photolytically active bromine.

To examine in more detail the origin of high concentrations of the photolytically active halogens, back trajectories were obtained for the end point corresponding to the time of each sample. We then plotted the results as polar plots of [halogen] versus the trajectory origin sector. We arbitrarily divided the back trajectory origins into six equal 45° intervals and determined the average chlorine and bromine concentrations within each sector. The results are presented in Figures 6a and 6b, for bromine and chlorine, respectively. On average the highest bromine concentrations were observed for air parcels arriving at Alert from sector 6 (see Figure 6a). This is interesting in light of the *Mozurkewich* [1995] mechanism and the fact that this trajectory origin is also associated with the highest levels of SO_2 [cf. *Barrie et al.*, 1989]. Unlike bromine, the high chlorine concentrations were observed mainly in the dark period during the earlier part of the study and were from southerly air mass trajectories (sector 1) through the Baffin Inlet (see Figure 6b). Given the fact that Br_2 has a photolytic lifetime (~ 1 -2 min) that is much shorter than that for Cl_2 (the same is true for HOBr relative to HOCl), it is interesting that Br_p is present in significant concentrations after sunrise, while Cl_p is not. These observations imply that there may be distinctly different production mechanisms for photolytically active chlorine and bromine. This conclusion supports the hypothesis of *Shepson et al.* [1996] that the levels of aldehydes in the Arctic ocean region are consistent with Cl atom chemistry occurring in the absence of Br atom chemistry.

To sustain the observed levels of " Br_2 " after sunrise would require a very large source or a continuous recycling from reservoir species like HBr, HOBr and BrONO_2 as in the *Fan and Jacob* [1992] mechanism. As discussed above, for the mechanism of *Fan and Jacob* [1992], the production of Br atoms will cease in the absence of O_3 , since there is no means of producing BrO. This is in fact consistent with our observations for the major ozone depletion event of days 88-89. As shown in Figure 5, while Br_p was close to the detection limit when ozone was completely removed (day 88), it was observed to increase at the end of this event, when ozone was increasing to typical unperturbed levels (note that we were not sampling during the start of this O_3 depletion event). This observation is also consistent with preliminary results from the ARCTOC field

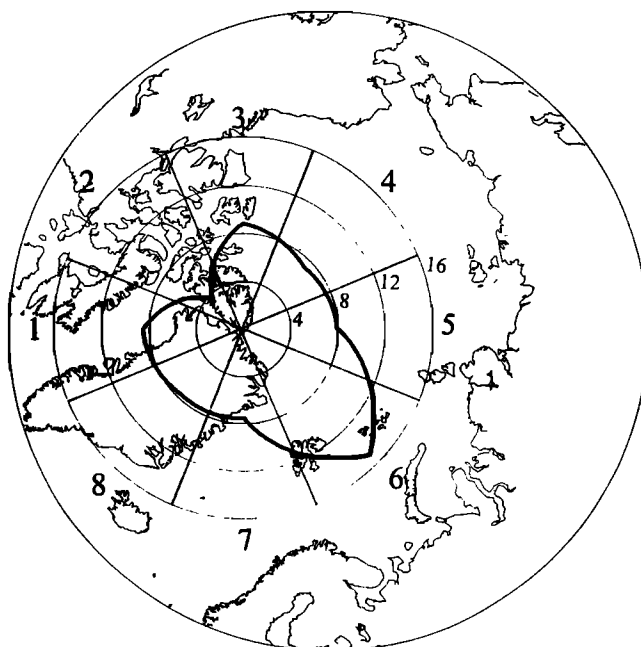


Figure 6a. Average bromine concentration (0-16 pptv) by sector region.

campaign in Ny-Ålesund, Spitsbergen (in April 1995) [(*H. Lorenzen-Schmidt et al.*, unpublished manuscript, 1995)] during which significant levels of BrO (as much as ~ 40 pptv) were observed on the wings of the ozone depletion episodes. It should be noted that there is only a small period of time when we would expect a good correlation between photolyzable bromine and ozone, i.e., only after sunrise when ozone depletion chemistry occurs but before the solar flux is so large that the lifetime of Br_p becomes too small to sustain high Br_p levels.

Since our method does not discriminate between Br_2 and HOBr (or Cl_2 and HOCl), we examined the importance of the different photochemically active sources, using a simple box

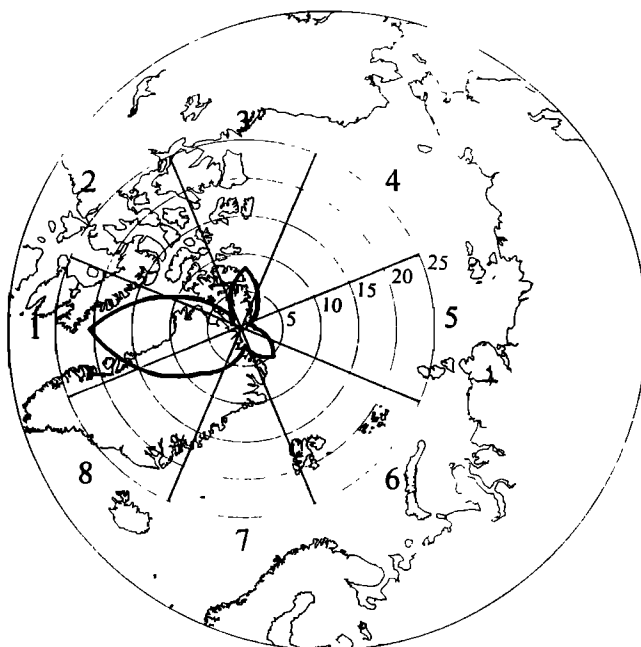


Figure 6b. Average chlorine concentration (0-25 pptv) by sector region.

model. The model contains 78 reactions with 49 species, including the standard gas phase ClO_x , BrO_x , NO_x , and HO_x chemistry. Constant Br_2 and Cl_2 fluxes of 22 pptv/h and 6 pptv/h, respectively, are used to maintain the Br and Cl atom concentrations at 10^7 and 10^4 molecules/cm³, respectively, in accord with the estimates of *Jobson et al.* [1994]. Photodissociation rate coefficients are as used in the modeling study of *Tang and McConnell* [1996] (with an update for HOBr photolysis from *Lock et al.* [1996]). Concentrations of formaldehyde (HCHO) and acetaldehyde (CH_3CHO), which are major sinks for Br atoms, are maintained at 200 pptv and 100 pptv, respectively [Shepson *et al.*, 1996]. Also, all relevant hydrocarbon, NO_x and O_3 initial concentrations are consistent with measurements from PSE 1992 [see *Barrie et al.*, 1994] and with the measurements conducted at Alert in 1995.

The input conditions discussed above simulate the observed ozone decay. The model predicts a steady state concentration of ≈ 0.5 pptv for Br_2 . The simulated HOBr concentration depends on the value for the effective first-order transfer coefficient for HOBr accommodation into the fine aerosol. Using the value of $1.4 \times 10^{-4} \text{ s}^{-1}$ used by *Fan and Jacob* [1992] results in an HOBr concentration, when O_3 is present, of only ≈ 10 pptv. However, laboratory measurements by *Abbatt* [1994] indicate that the uptake coefficient is considerably larger than that (0.01) used by *Fan and Jacob*. If we use an upper limit uptake coefficient for HOBr of 1, the first-order transfer coefficient would be $2.2 \times 10^{-3} \text{ s}^{-1}$, using the method described by *Sander and Crutzen* [1996]. This value then results in a simulated HOBr concentration of only ≈ 1 pptv. That $[\text{HOBr}] > [\text{Br}_2]$ results from the fact that Br atoms are relatively efficiently converted to HOBr via (R5) and (R6) and because Br_2 photolysis is 25-30 times faster than that for HOBr.

To examine the relative effects of photolytically active bromine in the form of Br_2 or HOBr, we can convert our measurements of total photolyzable bromine from "as Br_2 " to "as HOBr". Taking into account the different photolysis rates of Br_2 and HOBr and the residence time within the photoactive halogen detector (PHD), as discussed by *Impey et al.* [this issue], we find that ["as HOBr"] = $3.4 \cdot$ ["as Br_2 "], so that the 38 pptv "as Br_2 " observed on day 89 is the equivalent of 129 pptv "as HOBr". Similarly, ["as HOCl"] = $5.0 \cdot$ ["as Cl_2 "]. Although our measurements during PSE 95 did not allow us to discriminate between Br_2 and HOBr, it is important to do so, as ambient Br_2 photolysis produces Br atoms ≈ 50 times faster than does an identical concentration of HOBr. Thus for day 89 we calculate that 38 ppt of Br_2 will result in a photolytic Br atom production rate of 2.7×10^7 molecules/cm³·s, while 129 ppt of HOBr would produce only 1.7×10^6 molecules/cm³·s.

As discussed by *Jobson et al.* [1994] and *Shepson et al.* [1996], the relative rates of decay of various reactive hydrocarbons (e.g., alkanes and acetylene; aldehydes and ketones) are highly dependent on the $[\text{Br}]/[\text{Cl}]$ ratio. For days when there is radiation and when the photolytically active halogens are well above the detection limit, it is possible to estimate the resulting steady state Br and Cl atom concentrations. A good case for this is day 83, when the ozone concentration ranged between ≈ 5 -20 ppb. Using the measured maximum concentrations on day 83 of 43 and 97 pptv of HOBr and HOCl, respectively (i.e., assuming these represent Br_p and Cl_p), a steady state concentration of Br and Cl atoms can be estimated from equations (1) and (2):

$$[\text{Br}] = \frac{J_{\text{HOBr}}[\text{HOBr}]}{k_{\text{Br}}[\text{O}_3] + k_{\text{Br}}[\text{HCHO}] + k_{\text{Br}}[\text{CH}_3\text{CHO}] + k_{\text{Br}}[\text{C}_2\text{H}_2]} \quad (1)$$

$$[\text{Cl}] = \frac{J_{\text{HOCl}}[\text{HOCl}]}{\{k_{\text{Cl}}[\text{O}_3] + k_{\text{Cl}}[\text{HCHO}] + k_{\text{Cl}}[\text{CH}_3\text{CHO}] + k_{\text{Cl}}[\text{CH}_4] + \sum k_{\text{Cl}(i)}[\text{RH}]\}} \quad (2)$$

Here k_x corresponds to the rate constant for Br or Cl atom reaction with that particular reacting species. The last term in the denominator of equation (2) includes all alkanes from C_2 to C_8 , as well as C_2H_4 , C_3H_6 , and C_2H_2 . Br atoms are assumed to be removed only through reaction with O_3 , HCHO, CH_3CHO , and C_2H_2 . Corresponding calculated values for Br and Cl atom concentrations can be obtained assuming that the measured photolytically active species are Br_2 and Cl_2 , by appropriate substitution, e.g., of $J_{\text{Br}_2} \cdot [\text{Br}_2]$ into the numerator of equation (1). Using our estimates for the J values, and the measured hydrocarbon data at Alert, the calculated steady state Br atom concentration for the day 83 episode is between 1.0×10^6 atoms/cm³ (assuming the precursor is HOBr) and 1.8×10^7 atoms/cm³ (assuming it is Br_2). The corresponding values for $[\text{Cl}]$ are 1.0×10^4 atoms/cm³ (HOCl) and 6.1×10^4 atoms/cm³ (Cl_2). Because of the large range of estimated values, we can only say that our estimates for the absolute concentrations are consistent with the estimates of *Jobson et al.* [1994]. However, the calculated ratio $[\text{Br}]/[\text{Cl}]$ is much less sensitive to the identity of the precursor, i.e., we obtain $[\text{Br}]/[\text{Cl}] \approx 100$ if the precursors are HOBr and HOCl, and ≈ 300 if the precursors are Br_2 and Cl_2 . This range of $[\text{Br}]/[\text{Cl}]$ atom ratios is slightly lower than the *Jobson et al.* [1994] estimate of about 800. This result may, however, depend on the availability of ozone in the air mass (see discussion above) and could be quite variable. For example, if we assume the measured photolyzable chlorine concentration on day 89 (a maximum HOBr of 129 ppt) to be ≈ 9 pptv as Cl_2 (i.e., at the detection limit, corresponding to 45 ppt HOCl), the calculated (steady state) $[\text{Br}]/[\text{Cl}]$ ratio has an upper limit of approximately 2000. Thus we can only say that the Br/Cl atom ratio appears to be consistent with the estimates of *Jobson et al.* [1994].

Our model predicts a maximum HOBr concentration ranging between 1 and 10 pptv (when $[\text{Br}]$ is fixed near the *Jobson et al.* [1994] estimate of 10^7), but our measurements indicate that as much as 129 pptv of HOBr may be present during an ozone depletion episode when we are sampling air from the Arctic ocean region. Increasing the Br_2 flux in the model to as much as 170 pptv/h (yielding a simulated $[\text{Br}]$ near the upper limit of the literature estimates of 6×10^7 atoms/cm³) still produces only 40 pptv of HOBr. The *Fan and Jacob* [1992] mechanism involves uptake of HOBr onto acidic aerosol that contains Br^- , followed by (R3). One test of this mechanism is to compare the estimated Br_2 production rate with the amount of available aerosol bromine. If the Br_2 is generated from (R3), the lifetime of bromine in the aerosol would then be given by $\tau_{\text{aerosol Br}} = [\text{aerosol Br}]/2 \cdot [\text{Br}_2 \text{ flux}]$. Using the *Li et al.* [1994] measured aerosol Br concentration of about 1.25×10^{-9} mol Br/m³ during an ozone depletion event when air was coming from the Arctic ocean boundary layer and assuming a Br_2 production rate from the aerosol of 170 pptv/h (2.82×10^{-10} mol Br/m³ min) leads to an effective lifetime for the aerosol Br of 2.2 minutes. However, following the method of *Sander and Crutzen* [1996], our estimated characteristic time for gas-phase diffusion of the limiting reactant HOBr to the aerosol surface is 8 min (using an average particle radius of 1.5×10^{-5} cm, an accommodation coefficient α of 1, and dimensionless LWC = 4×10^{-12} [Staebler *et al.*, 1994]). Using this value for α yields the lower limit to the HOBr characteristic transport time to the aerosol. However,

since our lower limit estimate is greater than the effective aerosol Br lifetime, it appears that the available aerosol bromine would be rapidly depleted if the only mechanism for generating photolytically active bromine was (R3) occurring on aerosol particles. Therefore it appears that other mechanisms, such as oxidation of Br⁻ in the surface ice [Tang and McConnell, 1996], may play a more important role in generation of photolytically active bromine in the Arctic.

4. Conclusions

This work provides conclusive evidence for the presence of substantial concentrations of photolytically active chlorine and bromine in the Arctic near the time of polar sunrise. For both photolytically active chlorine and bromine it is apparent that there exist dark production mechanisms, as large concentrations were observed before sunrise. Furthermore, large concentrations of photolytically active bromine were observed after sunrise, when the lifetime of these species (presumably Br₂ or HOBr) are short, implying a large source, and indicating a large Br atom source. For example, for day 89, the ~38 pptv of bromine ("as Br₂") would be equivalent to 3.8 ppbv of CHBr₃ (~3 orders of magnitude greater than observed) in terms of the relative rates of photolytic generation of Br atoms. It is thus clear from our data that CHBr₃ (or other organo-bromine compounds) is an unimportant source of bromine atoms in the Arctic at polar sunrise.

The observation of high bromine on the "wings" of an ozone depletion episode seems to indicate either that we are measuring HOBr or that ozone is an important oxidant (or directly related to the oxidant) involved in production of Br₂. It is important that the exact nature of this Br atom source be determined (i.e., Br₂ versus HOBr).

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