In situ measurements of bromine oxide at two high-latitude boundary layer sites: Implications of variability

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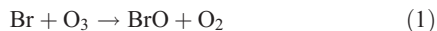
[1] Bromine oxide (BrO) was measured in situ during the Arctic Tropospheric Ozone Chemistry (ARCTOC) '96 campaign in Ny Ålesund, Spitsbergen (April–May 1996), and during the Alert 2000 Polar Sunrise Experiment in Alert, Nunavut, Canada (April–May 2000). Measurements were made in near-surface air during low-ozone events in early May at both sites. The average of the in situ concentrations of BrO at Ny Ålesund is consistent with the path average of near-simultaneous long-path differential optical absorption spectroscopy measurements, but there is considerable scatter in a point-by-point comparison. The differences between these observations are consistent with a strong surface influence on reactive bromine. We see similar variability of the in situ measurements at Alert, which reflects the real variability of both surface sources and sinks. The fluctuations of BrO abundances are used to assess the expected loss rates and associated lifetimes of ozone during depletion events. We show that ozone loss will be underpredicted by any temporal or spatial average of BrO. *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; *KEYWORDS:* bromine oxide, ozone loss, boundary layer ozone, Arctic, halogens

1. Introduction

[2] The phenomenon of sudden boundary-layer ozone loss has been observed at many northern high-latitude sites [*Barrie et al.*, 1988; *Oltmans et al.*, 1989; *Bottenheim et al.*, 1990; *Solberg et al.*, 1996; *Miller et al.*, 1997] and, more recently, at sites in Antarctica [*Kreher et al.*, 1997; *Wessel et al.*, 1998]. Data from field campaigns have linked these ozone loss events to halogen chemistry similar to that responsible for the stratospheric "ozone hole," but dominated by bromine rather than by chlorine [*Barrie et al.*, 1988; *Bottenheim et al.*, 1990; *McConnell et al.*, 1992]. Bromine atoms (Br) can catalytically destroy ozone by the sequence:

$$Br + O_3 \rightarrow BrO + O_2 \tag{1}$$

$$BrO + BrO \rightarrow 2\,Br + O_2 \tag{2}$$

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or through coupling with other halogen oxides (ClO, IO) or by reaction with hydroperoxyl radical (HO_2).

[3] Laboratory and modeling studies have shown that the photolysis rate of bromoform ($CHBr_3$), the most likely organic bromine source, is too slow to account for the observed rate of ozone loss [*McConnell et al.*, 1992]. The most recent observations and model results suggest that the ultimate source of active bromine may be sea-salt that accumulates on and in the snowpack during winter [*Lehrer et al.*, 1997]. Bromine is released auto-catalytically after polar sunrise based on a "seed" of active bromine, perhaps provided by photolysis of biogenic bromocarbons [*Tang and McConnell*, 1996; *Platt and Lehrer*, 1997].

[4] Observational evidence supports a close relationship between active bromine and loss of ozone. The bromine oxide radical (BrO) has been measured with long-path differential optical absorption spectroscopy (DOAS) during the Arctic spring at Alert, Canada [*Hausmann and Platt*, 1994] and Ny Ålesund, Spitsbergen [*Tuckermann et al.*, 1997; *Martinez et al.*, 1999]. In general, a correlation between the appearance of BrO and the loss of ozone has been observed, lending support to the chemical mechanism outlined above. Abundances of BrO as large as 30 parts per trillion (ppt; pmol mol^{-1}) have been seen during depletion episodes, whereas "background" values were typically on the order of a few ppt, at the detection limit of present techniques. Extensive regions of enhanced tropospheric BrO have also been detected by remote sensors [*Richter et al.*, 1998; *Wagner and Platt*, 1998; *McElroy et al.*, 1999]

coincident with areas such as Hudson Bay known to experience dramatic boundary layer ozone losses.

[5] Although evidence for halogen-induced ozone loss is strong, our understanding of the nature of the sources and sinks of the reactive halogens is just emerging. The effects of changing meteorological conditions at a fixed site have complicated interpretation of the measurements of bromine species, such as BrO. Ozone loss occurs on a timescale of days, so transport of airmasses with differing photochemical histories, and mixing between these airmasses, can obscure the effects of local photochemistry. Dynamical activity can also give rise to relationships between species that develop over the course of transport rather than instantaneously at the measurement location [*Bottenheim et al.*, 1990; *Martinez et al.*, 1999; *Langendörfer et al.*, 1999]. Reconciling the observed abundance of halogen oxides with the rate of ozone loss has also proven difficult due to the combination of local photochemistry and advection of previously depleted air masses. Nonetheless, most estimates require sustained BrO levels of 20–30 ppt for one to four days to explain the rates at which ozone is observed to decrease [*Tuckermann et al.*, 1997; *Sander et al.*, 1997; *Martinez et al.*, 1999]. These varying conditions can also confuse efforts to link measurements made by techniques that employ different viewing geometries or observations made at different locations [*Harder et al.*, 1997].

[6] In this paper, we examine the variability of BrO near the snow or ice surface at two high latitude sites to investigate the possible contribution of local sources of reactive bromine to boundary layer ozone losses frequently observed in the Arctic. We describe novel in situ measurements of BrO made during campaigns at two high latitude sites: European Union Arctic Tropospheric Ozone Chemistry (ARCTOC) '96 at Ny Ålesund, Spitsbergen, and Alert 2000 Polar Sunrise Experiment at Alert, Nunavut, Canada. We use these observations to examine the variability of BrO abundances within one meter of the snow surface as an indicator of the influence of the snow surface on gas-phase chemistry. Finally, we calculate ozone lifetimes based on fast-response BrO observations to show that underestimates of BrO variability can dramatically affect calculated ozone loss rates.

2. Experimental Technique

[7] The halogen oxides ClO and BrO were measured by the chemical conversion/resonance fluorescence (CC/RF) technique, which has been used extensively in the stratosphere on balloons and aircraft [*Brune et al.*, 1989; *Toohey et al.*, 1993; *Avallone et al.*, 1995; *McKinney et al.*, 1997]. Nitric oxide (NO) is added to the air flowing through the instrument, converting halogen oxides to atoms (XO + NO → X + NO$_2$, where X = Br or Cl). The atoms are subsequently detected by resonance fluorescence (resonant scatter) in the vacuum ultraviolet, at about 131 nm for Br and 119 nm for Cl. There is considerable absorption by oxygen and water vapor at these wavelengths, as well as rapid quenching of the RF signal at pressures greater than a few hPa. Absorption of RF signal is typically not a problem in the stratosphere, which is relatively dry. In contrast, both the higher absolute humidity and the greater air density complicate sampling in the boundary layer.

[8] To apply the CC/RF technique in the boundary layer, a two-stage sampling system was constructed to achieve an internal pressure low enough that losses of signal resulting from quenching and absorption by water vapor and oxygen were minimal. *Stevens et al.* [1994] adopted a similar strategy for tropospheric measurements of OH and HO$_2$. A high-velocity axial fan draws ambient air through a 1-m long, 15-cm ID halocarbon-wax-coated tube. A small fraction of the air at the center of this flow is expanded through a 2-mm Teflon orifice into the detection system, where the pressure is maintained at about 35 hPa by a rotary-vane pump. The walls of the detection system are coated with halocarbon wax to minimize loss of radical species. Losses of BrO and Br have never been detected in laboratory tests with these coated surfaces; at the flow velocities and pressures employed in these studies, a loss of 1 s^{-1} (the minimum detectable) would result in, at most, a 2% loss of bromine species between the inlet and detector.

[9] Nitric oxide is added to the airstream upstream of the detection region through a series of narrow perforated Teflon tubes at flow rates varying from about 0.5 to 7.5 std cm^3 min^{-1}. These conditions ensure that titration of the halogen oxides to atoms is complete in the 10 ms that elapse from the NO injection point to the RF detection region. Variation of the NO flow rate (and, hence, concentration) permits diagnosis of the kinetics of this conversion process. By modulating NO, we detect differences in signal due only to BrO; with this technique as currently configured we do not detect ambient bromine atoms.

[10] An individual measurement (which incorporates 10 seconds of conversion by NO and 10 seconds of background) typically has an uncertainty of about 5 ppt. The ultimate detection limit of 1 ppt is determined by artifacts resulting from the absorption of chamber scatter (light scattered from internal instrument surfaces) by nitric oxide [*Avallone et al.*, 1995]. The accuracy of the CC/RF measurements is limited by knowledge of the atomic absorption cross-sections, the accuracy of laboratory calibrations, and the accuracy of the rate constants in the BrO/Br/NO/O$_3$ system [*Avallone*, 1993]. Under optimal conditions and with redundant detection axes, BrO concentrations can be determined with an accuracy of 30% (2σ) [*Avallone et al.*, 1995].

[11] The data reported here were obtained with two different optical configurations. Because the light source for Alert 2000 was dimmer than that for ARCTOC '96, longer integration times were required to achieve the same precision. Nonetheless, the precision of the data and the detection limit obey photon-counting statistics, and are consistent with laboratory calibrations. In addition, degradation of the optics in the vacuum ultraviolet was much slower than anticipated, so the instrument was run for the entirety of both campaigns without changing optical windows or resonance lamps. This situation has both advantages and disadvantages. For example, all BrO data from a campaign are directly comparable because they are determined with the same calibration factors. However, any systematic errors in the entire data set are more difficult to discern and must necessarily be considered larger. One particularly important source of error in this measurement is the potential for loss of BrO within the instrument inlet. While it is difficult to prove conclusively that loss is not occurring, all available evidence suggests that it is not:
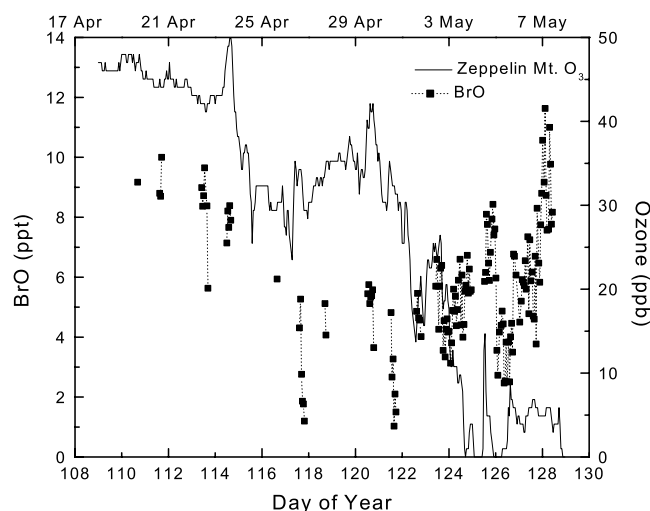
Figure 1. In situ observations of ozone and BrO obtained during ARCTOC '96 at Ny Ålesund, Spitsbergen. Ozone was measured from the Zeppelin Mountain research station (474 m a.s.l.), while BrO was measured 1 m above ground level. Hourly averages are shown.

There are no apparent temperature dependences, nor any drift in the measurement over the course of either campaign. If such a process were occurring, it would lead to an underestimate of the true atmospheric BrO abundance; alternatively, we know of no plausible means by which this technique could overestimate BrO. The overall accuracy of the BrO observations reported here, including systematic errors such as sampling artifacts, is estimated to be about $-30\%/+50\%$ (2σ) for ARCTOC '96 and $\pm35\%$ (2σ) for Alert 2000.

3. Observations

[12] The ARCTOC program sponsored two intensive field campaigns at Ny Ålesund, Spitsbergen (79°N, 12°E) to gain a better understanding of the mechanism of sudden boundary-layer ozone loss [*Platt and Lehrer*, 1997]. Participation in ARCTOC '96 provided an excellent opportunity to test the CC/RF technique in the boundary layer, given that BrO is known to be present during ozone-depletion events and that simultaneous measurements were being made by other techniques. The CC/RF instrument was deployed behind the "Old Blacksmith's Shop" (Gruveverkstedet), about 1.5 km from the main settlement at Ny Ålesund.

[13] In situ measurements of BrO were made between 19 April and 7 May 1996. Due to concerns about the rate of degradation of the CC/RF light source and the notion that BrO abundances would be small except during a low-ozone event (LOE), the instrument was operated intermittently at the beginning of the campaign. The ARCTOC data are shown in Figure 1, along with ozone observations from the Zeppelin Mountain observatory (474 m a.s.l., and approximately 1.5 km from the CC/RF location). Hourly averages of BrO are shown, with continuous measurements connected by line segments; these averages are precise to 0.5 ppt (2σ), suggesting that the observed variability is due to real atmospheric effects. A LOE began late on 1 May

(Day 122), with ozone values dropping below the nominal free tropospheric value of 30 parts per billion (ppb; nmol mol^{-1}), and continued through the end of the measurement period. In situ BrO abundances averaged 5.7 ppt during both the LOE and non-LOE periods and were slightly more variable during the non-LOE period (standard deviations of 2.6 and 3.2 ppt, respectively).

[14] The Alert 2000 Polar Sunrise Experiment was designed to explore photochemistry in snow, ice, and near-surface air during the Arctic springtime, and specifically, to gain a better understanding of the role of snow and ice in boundary-layer ozone depletion [*Bottenheim et al.*, 2002b]. Measurements of BrO, ozone, mercury, and meteorological parameters were made from an "ice camp," set up about 6.5 km from the main base of Canadian Forces Station Alert (82.5°N, 62°W) on the annual sea ice in Black Cliffs Bay. Observations were made at this site during the "light phase" (mid-April to early May 2000) of the study only.

[15] In situ observations of BrO were made at the ice camp from 26 April to 9 May 2000, with nearly continuous data obtained from 4–9 May. These results are shown in Figure 2, along with ozone observations from the 10-cm level of the University of Virginia meteorological tower, which was located approximately 10 m from the BrO instrument. The data shown in Figure 2 were taken during an unusually long ozone depletion episode, which began on 26 April and continued until 12 May 2000, past the end of the measurement campaign. The BrO values obtained in Alert, averaging 12.1 ppt (with a standard deviation of 6.6 ppt), are substantially greater than those measured during the ARCTOC '96 LOE. Unlike the ARCTOC LOE, however, the ozone at Alert remained uniformly low, averaging about 6 ppb. The occasional spikes of larger ozone are generally correlated with wind blowing from the direction of the ice camp generator tent and are believed to be the result of in situ
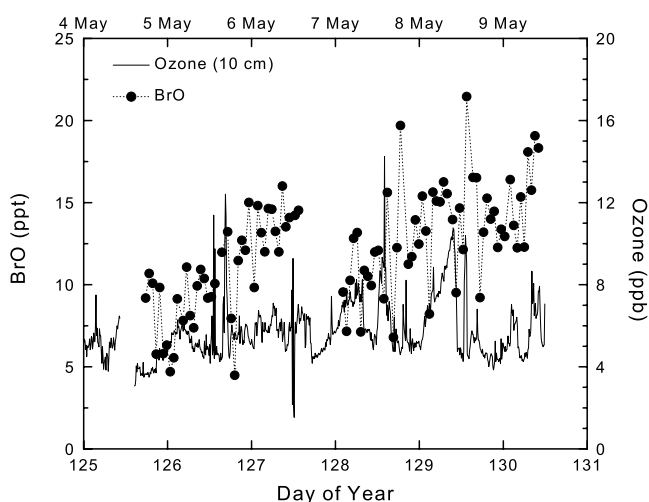
Figure 2. In situ observations of ozone and BrO obtained during Alert 2000 at Alert, Nunavut, Canada. Ozone (every 10 minutes) was measured from a meteorological tower, 10 cm above the surface, while BrO was measured 25 cm above ground level. Hourly averages of BrO are shown.

production via the interaction of hydrocarbons and NO_x from the generator exhaust.

4. Results and Discussion

[16] One of our main goals during ARCTOC '96 was to test whether the CC/RF technique would be of value for local measurements of BrO in the boundary layer. BrO measurements were also made by two long-path DOAS instruments, designed to characterize regional chemistry, one from the University of Heidelberg Institut für Umweltphysik (IUP; *Tuckermann et al.* [1997]); the other from the Max-Planck-Institut für Chemie (MPI; *Martinez et al.* [1999]). Although one would not necessarily expect a local measurement, with a sampling scale of meters, to agree with one sampling over kilometers [*Harder et al.*, 1997], there may be occasions when the BrO abundances are uniform enough that the in situ and long-path remote measurements would coincide. A comparison of all of the corresponding in situ and IUP DOAS measurements obtained between 19 April and 7 May 1996 is plotted in Figure 3; comparison to the MPI DOAS yields a similar pattern, but with considerably more scatter. In situ data have been averaged for 40 to 50 min to match the DOAS signal-averaging time; errorbars represent the 2σ precision of the measurements. Within the mutual errorbars, there is broad agreement between the in situ and long-path measurements, with many of them lying close to the one-to-one line. However, it is apparent that there are also statistically significant deviations from that correspondence. The fact that the comparisons between the in situ observations and those from both DOAS instruments show considerable scatter leads us to conclude that the variability is real and not a result of any one technique failing to characterize the BrO in its sampling volume.

[17] A direct comparison of the DOAS and in situ BrO data is complicated by a number of factors. First, the instruments were not collocated; the in situ instrument was situated about 1.5 km from either of the two DOAS detectors (see *Platt and Lehrer* [1997] for a map) and measured about 1 m above the surface, compared to average heights ranging from 20 to 200 m for the various DOAS paths. Second, shading of the regions sampled by the instruments, or of the instruments themselves, occurred as the sun passed behind nearby mountain peaks and buildings. The lifetime of BrO is sufficiently short (ranging from minutes to about 1 hour) that local fluctuations in its abundance can occur. Thus the CC/RF and DOAS data were taken under different photochemical conditions much of the time, and, on that basis alone, might not be expected to agree.

[18] In addition to these environmental factors, the dissimilar nature of the two detection methods can also contribute to the observed differences. DOAS samples over long paths in the atmosphere, ranging from 3 to 12 km for the BrO data shown here, whereas the in situ instrument measures air from within meters of its location. The DOAS technique necessarily provides an average value of the measured constituent over the entire optical path, integrating over any naturally occurring spatial and/or temporal variations, whereas the in situ instrument would be sensitive to these variations. Thus, sampling of different airmasses is the most likely reason for the deviations from a one-to-one correspondence between the in situ and DOAS instruments. These types of differences have been seen in previous
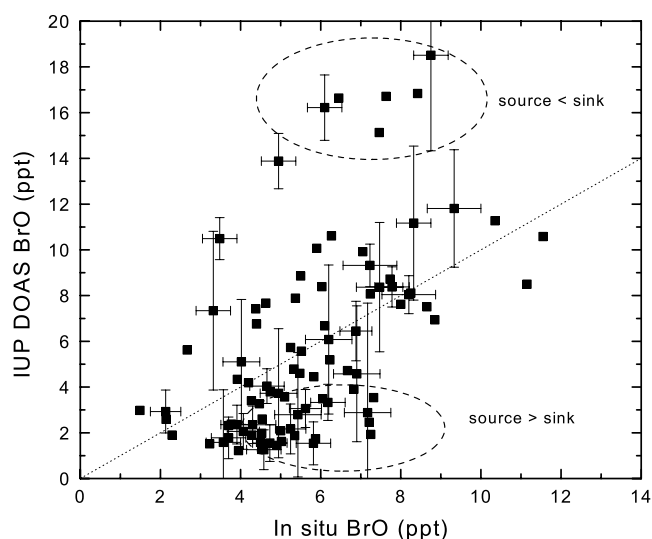
Figure 3. Scatterplot of in situ and IUP DOAS BrO observations from ARCTOC '96. The dashed line indicates a 1:1 correspondence. Errorbars are 2σ precision. See text for discussion of encircled regions.

comparisons of long-path and in situ measurements; for example, *Harder et al.* [1997] showed that, as the lifetime of the measured molecule decreased, the disagreement between long-path and in situ observations increased. This was most notable for NO_2, which was heavily influenced by local sources, and has a photochemical lifetime in urban areas that is comparable to that of BrO in the high-latitude boundary layer. Disagreement between long-path and in situ sensors was also seen for H_2O, a quite long-lived gas whose abundance can nonetheless be affected by underlying terrain and local meteorology.

[19] While it is possible that horizontal inhomogeneities caused by varying terrain and winds exist within the fjord at Ny Ålesund, we do not have any direct evidence (such as in situ measurements from a moving platform) of this. Thus, we infer that vertical gradients in BrO within the boundary layer exist, so that the in situ instrument (sampling 1 m above the ground) measures different BrO abundances than the average throughout the column (20 m or more above the surface) sampled by DOAS. The observed differences between the two techniques could then be explained by either surface or near-surface chemical loss or near-surface production of BrO, as illustrated by the encircled areas in Figure 3.

[20] Gas exchange across the snow/atmosphere boundary is significant for several chemical species, among them, reactive nitrogen [*Dibb et al.*, 1998; *Honrath et al.*, 1999; *Jones et al.*, 2001], formaldehyde [*Sumner and Shepson*, 1999], which is known to be a bromine sink, and Br_2 [*Foster et al.*, 2001], a precursor of BrO. None of these was measured during ARCTOC '96 to corroborate our hypothesis about the importance of the snow surface to BrO. However, snow samples taken during that campaign revealed a correlation between bromide ion in fresh snow and gas-phase ozone, as well as deeper layers of snow apparently depleted in bromide, which may indicate mobilization of bromine to the gas phase [*Platt and Lehrer*, 1997]. Although the exact form of the bromine in snow is

not known, its presence suggests a reservoir that could influence the gas-phase bromine concentrations above the snow surface.

[21] The main reason to measure BrO near the surface and to understand its sources and sinks is to better quantify bromine's role in boundary layer ozone losses. Observations by long-path DOAS instruments have, on many occasions, shown an anticorrelation between ozone and BrO [*Hausmann and Platt*, 1994; *Tuckermann et al.*, 1997; *Hönninger and Platt*, 2002], which helped to establish a causative link between bromine and ozone loss. However, no similar relationship between ozone and in situ BrO has been seen. Although larger abundances of BrO are observed by the CC/RF technique during the Ny Ålesund LOE than immediately preceding it (see Figure 1), similar large amounts were also measured under background (high ozone) conditions earlier in the experiment. The data shown in Figure 2 illustrate the lack of a clear correlation between ozone and in situ BrO during the Alert LOE.

[22] The lack of correspondence between ozone and BrO is perhaps not surprising, given the widely different lifetimes of reactive bromine and ozone. Under conditions typical of LOEs at high Arctic sites, boundary layer abundances of hydrocarbons and formaldehyde are large and variable [e.g., *Ramacher et al.*, 1999; *Sumner and Shepson*, 1999; *Bottenheim et al.*, 2002a] such that reactive bromine (Br + BrO) has a lifetime of a few minutes to half a day. However, the lifetime of ozone is quite long, on the order of a week, even when as much as 15 ppt of BrO is present. Consequently, transport can play a major role in the redistribution of ozone and reactive bromine reservoirs and precursors, such that a high degree of correlation between BrO and ozone is not necessary, despite the linkage of their photochemistry during depletion events.

[23] Why, then, have some DOAS observations shown clear relationships between BrO and ozone? It seems likely that chemistry and dynamics are quite different within a meter of the surface and 20 to 200 m aloft. For example, hydrocarbon emissions from the snowpack can have a significant impact on the bromine partitioning (and, hence, BrO abundances) near the surface, but are unlikely to affect to the same extent a 10-km path 50 m above varying terrain. Under conditions where the boundary layer is stable, as is often the case during LOEs [*Strong et al.*, 2002], *Sumner et al.* [2002] estimate that formaldehyde mixes only about 20 m in the vertical in one photochemical lifetime. Because formaldehyde is a significant sink for bromine (through its rapid reaction with bromine atoms), it would not be surprising to see a greater effect close to the surface, from which formaldehyde is emitted, than tens of meters above it.

[24] On the other hand, the DOAS measurements will be considerably more sensitive to large-scale changes in airmass than the near-surface in situ observations. Thus, the long-path DOAS observations are much more likely to reveal correlations that result from advection of and mixing between ozone-rich and ozone-poor airmasses, both of which have been transported over long distances, than relationships that develop locally. Indeed, *Hönninger and Platt* [2002] compared their multi-axis DOAS observations of BrO made at the Ice Camp during Alert 2000 with in situ ozone measurements taken 9 km (horizontal) and 175 m (vertical) away, at the Global Atmospheric Watch (GAW) site to the southeast of the main base at CFS Alert. This resulted in an apparent anti-correlation between ozone and BrO abundances that could not have arisen from local chemistry, given the wide separation of measurement locations. Moreover, a comparison of the ozone observed at the GAW site (Figure 5a of Hönninger and Platt) with that from the Ice Camp (Figure 2 of this work) shows that ozone had recovered to background values at the higher altitude station, but remained depleted near the ice surface.

[25] Mixing processes referred to above may explain the apparent discrepancies between ozone-loss rates calculated from long-path measurements of BrO and observations of the rate of ozone loss at a particular site [*Martinez et al.*, 1999]. However, the fast-response in situ measurements of BrO allow us to examine atmospheric variability and fine scale structure, which can provide insight into the mechanisms of and timescales for ozone loss. First, the substantial variability seen during both campaigns implies that BrO is not the sole reservoir of gas-phase bromine in near-surface air. Indeed, measurements of total gas-phase bromine [*Martinez et al.*, 1999] and "photolyzable bromine" [*Impey et al.*, 1997] range from 30 to 100 ppt, considerably greater than the observed BrO amounts. The Br_2 and BrCl seen by *Foster et al.* [2001] in Alert imply that as much as 80 ppt of active bromine may be present. Second, measurements during the Alert LOE made from 25 cm above the surface displayed much larger variability than those made during the Ny Ålesund LOE, 1 m above the surface. Mixing processes are likely to be slower near the surface than aloft, implying a greater influence of the surface, and any chemicals emanating from it, on gas-phase BrO abundances. Further, there is no correlation between BrO abundances and horizontal wind speeds, implying that the observed variability is likely due to changes in the local photochemical environment. Comparisons with simultaneous solar flux observations from the University of Virginia tower (data not shown here) reveal no significant diel behavior in the Alert BrO data. Measurements of snowpack formaldehyde made at a nearby site [*Sumner et al.*, 2002], however, do show a diel dependence. Snowpack temperature may also be important [*Hutterli et al.*, 1999]. Thus, it is likely that the observed variability in near-surface BrO arises due to changes in the environmental variables that govern the rates of bromine formation and destruction. These variables include solar irradiance, snowpack temperature, wind speed, and speed of air mass movement, which exerts control on long-range transport of bromine reservoirs and other photochemically related species.

[26] While the large variability of BrO near the surface is strong evidence for surface sources and sinks, it is also important for ozone loss calculations. Figures 4a and 4b show histograms of observed BrO and calculated ozone lifetimes, respectively, during the LOEs at Ny Ålesund and Alert. The ozone lifetimes have been computed based on measured BrO, ozone, temperature, and pressure, with rate coefficients for the self-reaction of BrO and the reaction of BrO with ClO taken from the IUPAC assessment [*Atkinson et al.*, 2000]. Very little ClO was observed during either LOE (a few ppt), so its abundance has been fixed at 1 ppt, and we ignore the reaction of BrO with HO_2, due to lack of HO_2 observations. This reaction may be important, however, and would serve to further shorten the ozone lifetimes calculated here.

a

b
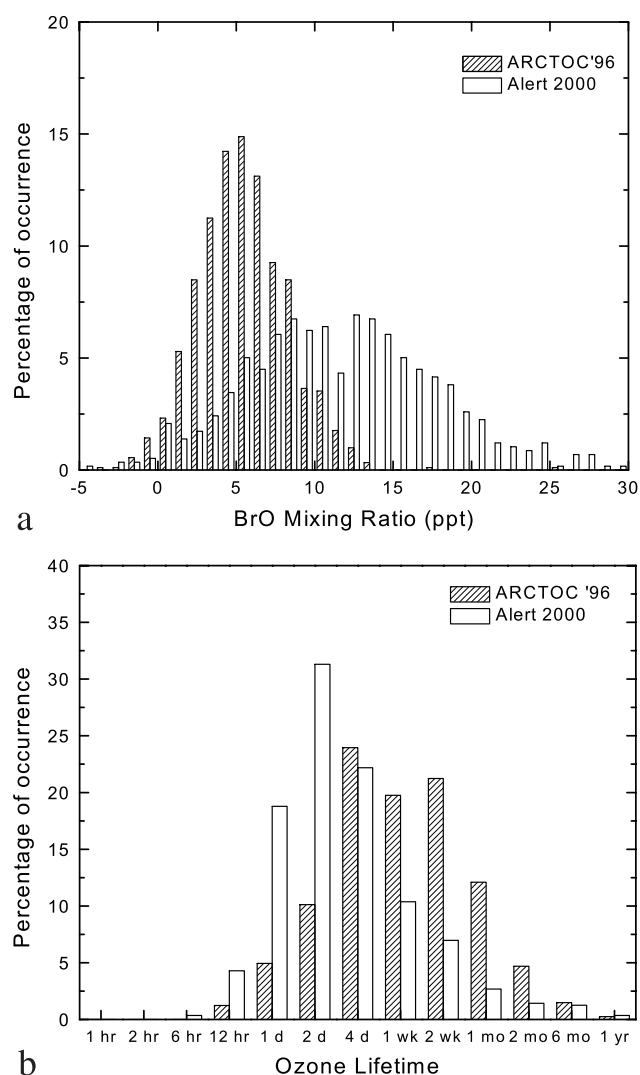
Figure 4. Histograms of (a) observed BrO mixing ratios and (b) ozone lifetimes calculated from observed BrO and ClO at ARCTOC '96 (hashed bar) and Alert 2000 (open bar). See text for discussion.

[27] Frequency distributions of observed BrO (Figure 4a) fall off sharply at abundances of 15 ppt (for ARCTOC) and 30 ppt (for Alert), which translate into ozone lifetimes of about 12 hours (the difference in the two campaigns is the ozone concentration at which these BrO values occurred). At larger values of BrO, such as the 50–100 ppt reported by *McElroy et al.* [1999], ozone lifetimes would be on the order of hours. Thus, when BrO increases beyond a certain threshold value, rapid loss of ozone will result. When ozone is removed from the system, BrO cannot be sustained, because it is formed by the reaction of bromine atoms with ozone. The fact that very few of these short lifetime points occur in the distributions is consistent with the postulated bromine-catalyzed ozone loss. Conversely, the preponderance of ozone lifetimes long enough for significant transport to occur demonstrates that the two LOEs were not solely the result of local photochemistry, but rather were caused by a mixture of photochemistry and transport from distant locations.

[28] Because the chemical loss of ozone depends on the square of BrO ($d[O_3]/dt \propto k[BrO]^2$), calculations of ozone

loss rates during these LOEs based on temporally or spatially averaged BrO values will necessarily underestimate them. This is due to the fact that, for a normal distribution of BrO values, $\langle[BrO]\rangle^2$ is less than $\langle[BrO]^2\rangle$, where the brackets ($\langle\rangle$) denote an average value. Calculations using lower resolution BrO values, which miss some real atmospheric variability, will result in an underestimate of the true ozone loss rates, and hence, an overestimate of the true ozone lifetimes [*Sparling et al.*, 1998]. We conclude that significant ozone loss occurs in small regions that contain relatively large abundances of BrO. Such "parcels" will necessarily go undetected by any technique that spatially and/or temporally averages.

5. Summary

[29] The in situ observations from ARCTOC '96 and Alert 2000 paint a complicated picture of what controls the abundance of BrO in near-surface air. Observations of BrO near the snow surface agree on the average with those obtained by long-path DOAS measuring 20 to 200 m above the surface, but the scales of spatial and temporal variability are not comparable.

[30] Comparison of near-surface BrO during LOEs at two different locations and two different heights hints at the presence of a surface source of bromine. This is consistent with the measurements by *Foster et al.* [2001], which show substantial Br_2 in the interstitial air of the top few cm of the snowpack at a nearby site. The work of *Sumner and Shepson* [1999] and *Sumner et al.* [2002] clearly indicates that the snowpack is a source of formaldehyde, which reacts rapidly with bromine atoms. It is likely that other bromine-reactive hydrocarbons, such as ethene and acetaldehyde, emanate from the snowpack [*Boudries et al.*, 2002; *Bottenheim et al.*, 2002a], although the factors controlling this are not yet clear. Thus, the snowpack influences both the sources and sinks of reactive bromine (Br + BrO), making interpretation of the gas-phase BrO observations at a single altitude impossible without simultaneous measurements of other bromine reservoirs, such as HBr and HOBr, and correlative species, such as HO_x, NO_x, and H_2CO.

[31] Because near-surface BrO appears to be controlled by local sources and sinks, it is not a good predictor of large-scale ozone-loss rates during LOEs. However, the variability observed in the near-surface BrO illustrates the importance of resolving small-scale structure to adequately calculate ozone loss.

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