



The NO<sub>x</sub> dependence of bromine chemistry in the Arctic atmospheric boundary layer

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## Abstract

Arctic boundary layer nitrogen oxides ( $\text{NO}_x = \text{NO}_2 + \text{NO}$ ) are naturally produced in and released from the sunlit snowpack and range between 10 to 100 pptv in the remote background surface layer air. These nitrogen oxides have significant effects on the partitioning and cycling of reactive radicals such as halogens and  $\text{HO}_x$  ( $\text{OH} + \text{HO}_2$ ). However, little is known about the impacts of local anthropogenic  $\text{NO}_x$  emission sources on gas-phase halogen chemistry in the Arctic, and this is important because these emissions can induce large variability in ambient  $\text{NO}_x$  and thus local chemistry. In this study, a zero-dimensional photochemical kinetics model was used to investigate the influence of  $\text{NO}_x$  on the unique springtime halogen and  $\text{HO}_x$  chemistry in the Arctic. Trace gas measurements obtained during the 2009 OASIS (Ocean–Atmosphere–Sea Ice–Snowpack) field campaign at Barrow, AK were used to constrain many model inputs. We find that elevated  $\text{NO}_x$  significantly impedes gas-phase radical chemistry, through the production of a variety of reservoir species, including  $\text{HNO}_3$ ,  $\text{HO}_2\text{NO}_2$ , peroxyacetyl nitrate (PAN),  $\text{BrNO}_2$ ,  $\text{ClNO}_2$  and reductions in  $\text{BrO}$  and  $\text{HOBr}$ , with a concomitant, decreased net  $\text{O}_3$  loss rate. The effective removal of  $\text{BrO}$  by anthropogenic  $\text{NO}_x$  was directly observed from measurements conducted near Prudhoe Bay, AK during the 2012 Bromine, Ozone, and Mercury Experiment (BROMEX). Thus, while changes in snow-covered sea ice attributable to climate change may alter the availability of molecular halogens for ozone and Hg depletion, predicting the impact of climate change on polar atmospheric chemistry is complex and must take into account the simultaneous impact of changes in the distribution and intensity of anthropogenic combustion sources. This is especially true for the Arctic, where  $\text{NO}_x$  emissions are expected to increase because of increasing oil and gas extraction and shipping activities.

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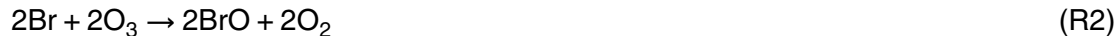
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## 1 Introduction

The episodic depletion of O<sub>3</sub> in the Arctic boundary layer following polar sunrise, referred to as ozone depletion events (ODEs), is attributed to a bromine gas phase reaction scheme, propagated by cycles such as Reactions (R1)–(R3) (Simpson et al., 2007; McConnell et al., 1992).



Ambient measurements at various Arctic sites have revealed maximum BrO mole ratios between 30 to 40 pptv in the springtime (Liao et al., 2012; Pohler et al., 2010). However, modeling studies have shown that heterogeneous chemistry at the surface is needed to facilitate enhanced reactive halogen levels and drive ODEs (Toyota et al., 2014b; Thomas et al., 2012; Michalowski et al., 2000), and recent field observations demonstrated that Br<sub>2</sub> is photochemically produced within the surface snowpack (Pratt et al., 2013; Foster et al., 2001). This heterogeneous chemistry mechanism, known as the “bromine explosion”, is dependent on reactions involving HO<sub>x</sub> (Wennberg, 1999; Tang and McConnell, 1996; Vogt et al., 1996; Fan and Jacob, 1992) to produce hypohalous acids, which then oxidize halide ions at reactive surfaces (Huff and Abbatt, 2002; Abbatt, 1994).



Although gas-phase halogen chemistry in the Arctic has now been studied for several decades (Impey et al., 1997; Hausmann and Platt, 1994; Barrie et al., 1988), few studies have examined the effect of atmospheric NO<sub>x</sub> on these halogen chemical cycles.

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Model studies have shown that NO<sub>x</sub> can react with halogen radicals through several reactions (as shown in Reactions R8–R12), to produce inorganic halogen nitrates or nityl halides, which can, in turn, activate further halogen chemistry through heterogeneous reactions (Cao et al., 2014; Toyota et al., 2014a; Morin et al., 2007, 2012; Thomas et al., 2012; Evans et al., 2003; Aguzzi and Rossi, 1999, 2002; von Glasow et al., 2002; Thorn et al., 1993), and thereby alter gas phase halogen radical reaction pathways.



Reaction (R8) can directly influence the bromine explosion, as lab studies have shown that gas phase BrONO<sub>2</sub> can hydrolyze on acidic surfaces to form HOBr, as shown in Reaction (R12) (X = Br) (Hanson, 2003; Aguzzi and Rossi, 2002; Hanson et al., 1996). Thus, while reactions involving NO<sub>x</sub> can terminate the gas phase radical chain reaction, they can also generate products that contribute to the bromine explosion. Thus, it is not intuitively obvious what impact(s) NO<sub>x</sub> ultimately has on halogen chemistry. These halogen reaction pathways are summarized in Fig. 1 (Abbatt et al., 2012; Grannas et al., 2007; Simpson et al., 2007). As illustrated in Fig. 1, elevated levels of NO<sub>x</sub> can impact the halogen cycle through a variety of reactions. However, the sensitivity of the halogen radical chain reaction to NO<sub>x</sub> is currently not well understood.

The Arctic boundary layer typically has ambient background levels of NO<sub>x</sub> between 10 to 100 pptv resulting from its isolation from major anthropogenic sources, with its primary sources being photochemical production within the snowpack (Villena et al., 2011; Honrath et al., 2002; Ridley et al., 2000), and long range transport of photolyzable species such as organic nitrates (Muthuramu et al., 1994). Arctic field studies have led to observations of NO<sub>x</sub> fluxes from sun-lit snow surfaces (Grannas et al., 2007; Ri-

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dley and Orlando, 2003; Beine et al., 2002; Honrath et al., 2002, 1999), and lab studies have demonstrated that frozen solutions of nitrate and nitrite can release  $\text{NO}_x$  when irradiated with UV light (Dubowski et al., 2002, 2001; Honrath et al., 2000).



With the possibility of increased anthropogenic sources throughout the Arctic, e.g. from coastal development, shipping, and oil and gas exploration, the impacts of increased  $\text{NO}_x$  are likely to be seen (Peters et al., 2011; Corbett et al., 2010). For this study we investigated the effect of elevated  $\text{NO}_x$  mole ratios on Arctic halogen radical chemistry, using a zero-dimensional (0-D) photochemical model, constrained by recent observations of a wide variety of relevant precursors and intermediates, during the Ocean–Atmosphere–Sea Ice–Snowpack (OASIS) 2009 campaign conducted at Barrow, AK. To complement the model studies, observational evidence of the impact of  $\text{NO}_x$  on BrO is shown for aircraft measurements near Prudhoe Bay, AK during the 2012 Bromine, Ozone, and Mercury Experiment (BROMEX).

## 2 Model description

A 0-D photochemical model was developed using the modeling software FACSIMILE. The model has been described in detail by Thompson et al. (2014) and is described briefly here. The model includes known Arctic gas-phase chemistry with 189 gas-phase reactions (Table S1) and 28 photolysis reactions (Table S2). The deposition of 19 gas-phase species to aerosols/snow surfaces (Table S3) and 16 aqueous-phase chemical reactions (Table S4) are also included, where the heterogeneous reactions are treated as aqueous reactions. The model is constrained to observations with time varying mole ratios for a list of gas-phase species (Table S5), including halogen radical precursors ( $\text{Cl}_2$  and  $\text{Br}_2$ ) and a wide range of volatile organic compounds ( $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$ ,  $n\text{-C}_4\text{H}_{10}$ ,  $i\text{-C}_4\text{H}_{10}$ , HCHO,  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{OCH}_3$ , and methyl ethyl ketone),

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as well as calculated, time varying photolysis rates, from the field study OASIS (Ocean–Atmosphere–Sea Ice–Snowpack) in Barrow, AK. Mole ratios of constrained gas-phase species along with the photolysis rates were called into the model every 10 min within the simulation. For this model study, the ten day period from 24 March–2 April 2009 during OASIS 2009 was simulated. During this period, a three-day ozone depletion event ( $O_3 < 5$  ppbv) occurred, followed by a full ozone recovery ( $O_3 > 20$  ppbv) that was due to vertical mixing (discussed in Sect. 3.1), and thus, covers a full range of atmospheric and meteorological conditions. It should be noted that the constrained mole ratio for Br<sub>2</sub> on 30 and 31 March in the model is based on the observed diurnal average of 29 March and 1 April. As discussed in Liao et al. (2012) atmospheric observations for Br<sub>2</sub> on 30 and 31 March were not available.

To investigate the role that atmospheric NO<sub>x</sub> plays in Arctic halogen chemistry, two different NO<sub>x</sub> simulation scenarios were performed. A “low NO<sub>x</sub>” case and a “high NO<sub>x</sub>” case were used to create the two different scenarios. This allowed us to isolate a single variable between the two simulations. However, this approach does not consider other chemical species (i.e. VOCs) that could also be elevated along with anthropogenic NO<sub>x</sub>. The two diurnal-cycle NO<sub>x</sub> profiles were derived from the actual observed NO<sub>x</sub> over the time period being simulated, as shown in Fig. 2. Representative average polluted (high) and clean (low) NO<sub>x</sub> diurnal cycles, which differ by about a factor of 15, were calculated based on observed local NO<sub>x</sub> mole ratio data for the period (Fig. 2). The clean (low NO<sub>x</sub>) and polluted (high NO<sub>x</sub>) days during the 10 day (24 March to 2 April) period studied were selected based on the work of Villena et al. (2011), in which correlations with ambient CO enhancements were used to identify air masses influenced by local emissions (2011). The non-influenced/background days were averaged together to calculate a “low NO<sub>x</sub>” diurnal average that ranged between 50 to 100 pptv. These values were in the range of previous observations of background NO<sub>x</sub> mole ratios (Villena et al., 2011; Honrath et al., 2002; Ridley et al., 2000). The same was done for the days influenced by local anthropogenic emissions, to create the “high NO<sub>x</sub>” diurnal average characterized by NO<sub>x</sub> mole ratios from 700 to 1600 pptv. Each

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diurnal average was fit to a curve to generate temporally smoothed profiles. During the 10 day simulation either the Low NO<sub>x</sub> or High NO<sub>x</sub> diurnal average was applied to each day of the simulation, to generate the two distinct model scenarios. This allowed us to evaluate the NO<sub>x</sub>-dependence of the chemistry, since it was the only parameter altered between the two scenarios.

Molecular halogens respond to changes in the deposition rates and condensed-phase chemistry, the latter of which cannot be well simulated given the current state of knowledge of the snowpack, and physical and chemical processes occurring therein (Domine et al., 2013). Therefore, to ensure proper representation of the gas phase halogen chemistry, the atmospheric molecular halogen (Br<sub>2</sub> and Cl<sub>2</sub>) mole ratios were constrained to observations. The observations for these species reflect the impact of NO<sub>x</sub>-dependent production of reactive reservoir species, and the impact of their deposition to and chemistry within the snowpack. While the model was constrained to observations for stable species (Table S5), it was used to calculate various radical species' (e.g., BrO and Br) mole ratios given the sources and sinks of these radicals. In this way, we calculate the effective NO<sub>x</sub>-dependence of the radical chemistry and rate of ozone depletion, as discussed below.

## 3 Results

### 3.1 Bromine chain length

The chain length for a radical chain reaction is the rate of propagation divided by the rate of termination (or initiation). A chain length of < 1 means that most of the radicals terminate after production. Here we calculate the bromine radical chain length ( $\Phi$ ) for the interconversion of Br and BrO radicals using Eq. (1) (Thompson et al., 2014) for the

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10 day simulation.

$$\Phi = \frac{\left( 2k[\text{BrO}]^2 + k[\text{BrO}][\text{ClO}] + k[\text{BrO}][\text{CH}_3\text{OO}] + k[\text{BrO}][\text{OH}] + \right)}{k[\text{BrO}][\text{O}(\text{}^3\text{P})] + k[\text{BrO}][\text{CH}_3\text{COOO}] + k[\text{BrO}][\text{NO}] + J[\text{BrO}]} \quad (1)$$
$$\left( \begin{array}{l} k[\text{Br}][\text{HO}_2] + k[\text{Br}][\text{C}_2\text{H}_2] + k[\text{Br}][\text{C}_2\text{H}_4] + k[\text{Br}][\text{C}_3\text{H}_6] + k[\text{Br}][\text{HCHO}] + \\ k[\text{Br}][\text{NO}_2](0.15) + k[\text{Br}][\text{CH}_3\text{CHO}] + k[\text{Br}][\text{C}_3\text{H}_6\text{O}] + k[\text{Br}][\text{C}_4\text{H}_8\text{O}] + \\ k[\text{Br}][\text{CH}_3\text{OOH}] + k[\text{BrO}][\text{HO}_2] + k[\text{BrO}][\text{CH}_3\text{OO}] + k[\text{BrO}][\text{C}_3\text{H}_6] + \\ k[\text{BrO}][\text{NO}_2] \end{array} \right)$$

Termination reactions include those that form non-radical brominated species (e.g., HBr, HOBr, BrONO<sub>2</sub>), with photochemical lifetimes substantially longer than that of BrO or Br. It should be noted that although production of certain species represents a termination of the gas phase Br chain reaction (e.g. HOBr and BrONO<sub>2</sub>), they can also play a crucial role in producing and increasing the Br radicals available for reacting with ozone, either through photolysis or heterogeneous reactions. This emphasizes the complexity of the BrO<sub>x</sub> cycle that takes place in the Arctic. In Eq. (1) the Br + NO<sub>2</sub> reaction is multiplied by the branching ratio (0.15) for the production of BrNO<sub>2</sub> (Orlando and Burkholder, 2000). Orlando and Burkholder (2000) observed that the dominant product for NO<sub>2</sub> reaction with a Br atom is BrONO, and while at lower temperatures isomerization to BrNO<sub>2</sub> is possible, the overall yield would still be minor (2000). The production of BrONO is not considered a sink for BrO<sub>x</sub> because of its rapid thermal decomposition, photolysis and reaction with Br radicals, regenerating BrO<sub>x</sub> (Burkholder and Orlando, 2000; Orlando and Burkholder, 2000). The bromine chain length was only calculated during daylight hours (10:00 to 18:00 AKST) because the bromine radical chain is photochemically initiated via the photolysis of Br<sub>2</sub> (Reaction R1). The bromine radical chain length was calculated throughout the entire 10 day simulation for both the low and high NO<sub>x</sub> simulations, as shown in Fig. 3.

Both the low NO<sub>x</sub> and high NO<sub>x</sub> simulations show a chain length dependence on ozone mole ratio (Fig. 3), with generally higher chain lengths at high O<sub>3</sub>, due to Reaction (R2). When the O<sub>3</sub> mole ratio is > 5 ppbv, the average low NO<sub>x</sub> bromine chain

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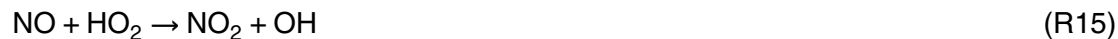
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length was 1.72 ( $\pm$  0.70), while the average high NO<sub>x</sub> bromine chain length was 1.81 ( $\pm$  0.35). The shorter simulated bromine chain lengths ( $<$  1.0) on 26, 27, 28, and 31 March can be explained by the low O<sub>3</sub> mole ratio ( $<$  5 ppbv). One might hypothesize that the high NO<sub>x</sub> simulation would yield a shorter bromine chain length because NO<sub>x</sub> acts as a sink for BrO<sub>x</sub>. Indeed, the model simulation shows that NO<sub>x</sub>, on a percentage basis, is a more dominant sink for BrO<sub>x</sub> during the high NO<sub>x</sub> simulation compared to the low NO<sub>x</sub> simulation (Fig. 4). While the Br + NO<sub>2</sub> reaction occurs more frequently (by a factor of 5) during the high NO<sub>x</sub> case, the BrO + NO<sub>2</sub> reaction is actually 7 % more important as a sink in the low NO<sub>x</sub> simulation. The reaction of HO<sub>2</sub> + BrO additionally influences the results of the bromine chain length in that it occurs more frequently, by a factor of 170, during the low NO<sub>x</sub> simulation. This is due to the suppression of HO<sub>2</sub> in the high NO<sub>x</sub> simulation via Reactions (R15) and (R16).



One point of interest is the much larger bromine chain length on 25 March, when ozone was partially depleted ( $<$  15 ppbv), compared to other days with partially depleted ozone (30 March and 1 April). On this day a very large NO<sub>x</sub> plume ( $\sim$  15 ppbv) from the town of Barrow was observed compared to the relatively low NO<sub>x</sub> conditions observed on 30 March and 1 April. This enhanced bromine chain length can be explained by the fact that we constrain the model to observed Br<sub>2</sub>. If the polluted plume also contains HOBr and BrONO<sub>2</sub> as important temporary halogen reservoirs, then the flux of Br<sub>2</sub> (e.g. via Reactions R6 and R12) from the reactive surfaces would increase, thereby increasing BrO. Spikes were observed for both HOBr and BrO for 25 March (discussed in Sect. 3.3), which may indicate such a situation. The rate of Reaction (R3) is quadratic in BrO mole ratio, and, as discussed by Thompson et al. (2014), and indicated in Eq. (1), the observed chain length increases with BrO mole ratio.

## 3.2 Net O<sub>3</sub> loss rate

Although the bromine chain length is relatively unchanged between the two scenarios, high levels of NO<sub>x</sub> decrease the rate of net O<sub>3</sub> loss within the model. The net O<sub>3</sub> loss rate was calculated in Eq. (2) as the sum of all of the rates of reactions that destroy ozone minus the sum of the rates that produce ozone (Thompson et al., 2014). It should be noted that the reactions in Eq. (2) that “produce” ozone are included as offsets for the depleted ozone destruction rate, which includes XO and NO<sub>2</sub> photolysis.

$$\text{Net O}_3 \text{ Loss Rate} = \left( \frac{k[\text{Br}][\text{O}_3] + k[\text{Cl}][\text{O}_3] + k[\text{O}(^1\text{D})][\text{H}_2\text{O}] + k[\text{OH}][\text{O}_3] + k[\text{HO}_2][\text{O}_3] - k[\text{BrO}][\text{NO}] - J[\text{BrO}] - k[\text{ClO}][\text{NO}] - J[\text{ClO}]}{k[\text{HO}_2][\text{O}_3] - k[\text{BrO}][\text{NO}] - J[\text{BrO}] - k[\text{ClO}][\text{NO}] - J[\text{ClO}]} \right) \quad (2)$$

Reaction counters were utilized for all the HO<sub>2</sub>/RO<sub>2</sub> + NO reactions for both NO<sub>x</sub> scenarios to determine the importance of those reactions towards O<sub>3</sub> production. The two different NO<sub>x</sub> cases yielded equal numerical values when the counters were summed, indicating NO<sub>x</sub> did not influence these reactions. The calculated net O<sub>3</sub> loss rate for both NO<sub>x</sub> scenarios is shown in Fig. 5. On average, the net O<sub>3</sub> loss rate is a factor of two times slower for the polluted NO<sub>x</sub> simulation compared with the low NO<sub>x</sub> simulation. To study this effect further, we calculated the net O<sub>3</sub> destruction rate as a function of NO<sub>x</sub> mole ratio by conducting simulations with a wide range of NO<sub>x</sub> mole ratios. The various NO<sub>x</sub> diurnal cycles were calculated by starting with the low NO<sub>x</sub> diurnal profile and step-wise increasing the NO<sub>x</sub> by 250 pptv until the diurnal maximum of 2000 pptv was reached. The results, for the period 11:00–13:00 LT on 30 March, are shown in Fig. 6. 30 March was selected because it fell into the “clean day” category during OASIS and during a time when ozone was decreasing from 30 to 5 ppbv. As shown in Fig. 6, the net O<sub>3</sub> loss rate decreases steeply, by a factor of 1.5 (from 0.80 to 0.52 ppbv h<sup>-1</sup>), during the increase of NO<sub>x</sub> mole ratios of ~ 100–500 pptv, clearly expressing the strong NO<sub>x</sub>-dependence of the chain reaction. We note, however, that this model experiment is directly testing the gas-phase component of this sensitivity on NO<sub>x</sub>, and not the NO<sub>x</sub> dependence of BrONO<sub>2</sub> deposition. However, as discussed

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later, when  $\text{NO}_x$  increases,  $\text{BrO}$  decreases and thus  $\text{BrONO}_2$  is not sensitive to the  $\text{NO}_x$  mole ratio. This does not negate the potential importance of  $\text{BrONO}_2$  during ODEs. Cao et al. (2014) found, from a modeling study, that  $\text{BrONO}_2$  production increased the rate of ozone depletion through the production of  $\text{HOBr}$  from its hydrolysis (Reaction R12) on snow/aerosol surfaces.  $\text{HOBr}$  is a main component of the bromine explosion and leads to an increased production rate of  $\text{Br}_2$  (Reactions R5–R6). However, regression of the observed  $[\text{Br}_2]$  vs. observed  $[\text{NO}_x]$  reveals that the highest mole ratios of  $\text{Br}_2$  do in fact occur when  $\text{NO}_x$  is below 300 pptv (Fig. S1). This observed  $\text{Br}_2$  clearly supports that the  $\text{O}_3$  loss rate is minimized when  $\text{NO}_x$  mole ratios are elevated, as the maximum Br atom production rates will occur at low  $[\text{NO}_x]$ . The net ozone loss is, of course, also extremely low for days when the observed mole ratios of  $\text{O}_3$  were very small ( $< 5$  ppbv), as the rate of ozone destruction will approach zero as  $\text{O}_3$  is nearly completely removed. Based on the results from Figs. 5 and 6, the influence that elevated  $\text{NO}_x$  mole ratios have on decreasing the net ozone loss rate could be a factor in the Arctic as  $\text{NO}_x$  point sources continue to increase in remote Arctic locations.

The  $\text{O}_3$  loss rate for 30 March from 11:00 to 13:00 LT, based on the observations, was approximately  $3.4 \text{ ppbv h}^{-1}$ . This is much larger than the calculated net  $\text{O}_3$  loss rate for the low  $\text{NO}_x$  simulation of  $0.80 \text{ ppbv h}^{-1}$ . The low net  $\text{O}_3$  loss rate for the low  $\text{NO}_x$  simulation could be a result of the constrained model  $\text{Br}_2$  mole ratio not being representative of the ambient air in Barrow at that time; as mentioned previously. If we constrained  $\text{Br}_2$  to an estimated concentration lower than what was actually present during that time, we would expect a decreased depletion rate. This belief is furthered supported by a comparison of the  $\text{BrO}$  data for this time period (discussed later). However, this apparent dramatic ozone loss rate could be the observation of an ozone-depleted air mass being transported to the measurement site (Halfacre et al., 2013).

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### 3.3 Model-simulated species vs. OASIS 2009 observations

To further understand both how  $\text{NO}_x$  decreases the rate of net  $\text{O}_3$  loss and affects the bromine chain length, several species that play a crucial role in the bromine cycle were examined. Molecular bromine and its precursors are produced from Reactions (R6) and (R12). The prominent gas-phase recycling reaction is BrO self-reaction (R3) while the formation and subsequent deposition of HOBr and  $\text{BrONO}_2$  leads to heterogeneous reactions that can form  $\text{Br}_2$  (Reactions R5–R12). Here we simulated the effect of the low and high  $\text{NO}_x$  scenarios on BrO, HOBr and  $\text{BrONO}_2$ , and compared the results with the observed mole ratios during OASIS (Fig. 7a–c). For the majority of the days, simulated BrO for the low  $\text{NO}_x$  case is close to that observed during OASIS, as expected since low  $\text{NO}_x$  conditions were typically observed. However, this is not the case for 30 and 31 March, for which the simulated BrO is lower than what was observed during OASIS. This is likely a result of the fact that atmospheric observations for  $\text{Br}_2$  on 30 and 31 March were not available, as discussed earlier. For those days the constrained  $\text{Br}_2$  was a diurnal average of 29 March and 1 April  $\text{Br}_2$  observations. The high  $\text{NO}_x$  simulation results in a highly suppressed BrO mole ratio (Fig. 7a), compared to the low  $\text{NO}_x$  simulation, by more than an order of magnitude throughout the time period. For the high  $\text{NO}_x$  case, BrO never exceeds 3 pptv, whereas for the low  $\text{NO}_x$  case, BrO ranges from 2.5 to 25 pptv. For high  $\text{NO}_x$  days, the BrO mole ratios are low because of Reactions (R8) and (R10), in which BrO and Br radicals are scavenged by  $\text{NO}_x$ .

HOBr responds in similar fashion to changes in  $\text{NO}_x$  as does BrO, with the low  $\text{NO}_x$  simulated HOBr being within  $\pm 5$  pptv of the OASIS observations while the high  $\text{NO}_x$  simulated HOBr is much lower. Occasionally the low  $\text{NO}_x$  simulation HOBr is slightly elevated compared to the observed HOBr (26 and 29 March) because the low  $\text{NO}_x$  simulation has a greater  $\text{HO}_2$  mole ratio compared to the observations.

Figure 7b shows that the high  $\text{NO}_x$  condition completely suppresses HOBr, and that is what is observed for the high  $\text{NO}_x$  mole ratios day, 24 March. However, in contrast to the case for BrO and HOBr,  $\text{BrONO}_2$  is not suppressed by high  $\text{NO}_x$  mole ratios

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(Fig. 7c), since while increased  $\text{NO}_x$  suppresses BrO, the rate of Reaction (R8) is compensated by the increase in  $\text{NO}_x$  mole ratios, therefore Reaction (R8) is largely unchanged. This is shown in Fig. 7c as the  $\text{BrONO}_2$  mole ratio is similar for both the high and low  $\text{NO}_x$  simulations. Additionally, when the model simulated  $\text{BrONO}_2$  mole ratio for both  $\text{NO}_x$  simulations is plotted against the  $\text{BrONO}_2$  production rate ( $k_{\text{BrO}+\text{NO}_2}[\text{BrO}][\text{NO}_2]$ ), it affirms that the  $\text{BrONO}_2$  mole ratios follow  $k_{\text{BrO}+\text{NO}_2}[\text{BrO}][\text{NO}_2]$  (Fig. S2).

### 3.4 $\text{BrO}_x$ and $\text{NO}_x$ sinks

It is clear from the discussions above that  $\text{NO}_x$  influences  $\text{BrO}_x$  partitioning. The sinks of  $\text{BrO}_x$  and  $\text{NO}_x$  were quantified to evaluate their  $\text{NO}_x$ -dependence by including reaction counters on the relevant reactions in the model that convert  $\text{BrO}_x$  and  $\text{NO}_x$  to reservoir species. Over the 10 day simulation period for both low and high  $\text{NO}_x$  cases,  $\text{NO}_x$  is a significant sink for  $\text{BrO}_x$  radicals ( $> 27\%$ ), although for the high  $\text{NO}_x$  case it contributes more than  $50\%$  (Fig. 4). However, both products of Reactions (R8) and (R10) result in species that can regenerate  $\text{Br}_2$ . As expected,  $\text{CH}_3\text{CHO}$  plays a major role as a  $\text{BrO}_x$  sink as well (Shepson et al., 1996), contributing to more than  $> 35\%$  in both simulations. Though anthropogenic emissions are known sources of acetaldehyde, observed  $\text{CH}_3\text{CHO}$  mixing ratios were unaffected by Barrow emissions throughout the 10 day simulation period. Thus it is likely that the snowpack is the dominant  $\text{CH}_3\text{CHO}$  source in this study (Grannas et al., 2002). For  $\text{NO}_x$ , while reactions with  $\text{HO}_2$  are important ( $\sim 20\%$ ), reactions of  $\text{NO}_2$  with Br and BrO still represent significant  $\text{NO}_x$  sinks ( $\sim 30\%$ ). Peroxynitrates result from an important sink pathway of  $\text{NO}_2$ , e.g. via Reactions (R17) and (R18), below. Reaction (R17) will be the subject of a separate study.



## 4 BROMEX 2012 field observations

To further examine the interactions between  $\text{NO}_x$  and reactive bromine,  $\text{NO}_2$  and  $\text{BrO}$  were measured within and around a large combustion plume in the coastal Arctic atmosphere. During the spring 2012 Bromine, Ozone, and Mercury Experiment (BROMEX) field campaign in Barrow, Alaska, airborne measurements of  $\text{BrO}$  and  $\text{NO}_2$  column density (from  $\sim 700$  m to the surface) were conducted using an aircraft-mounted MAX-DOAS (General et al., 2014) in nadir view. The results for the derived  $\text{BrO}$  and  $\text{NO}_2$  differential slant column density (DSCD), the integrated mole ratio along a vertical line, for a section of a flight on 30 March near Prudhoe Bay, AK, are shown in Fig. 8. Prudhoe Bay is the largest oil field on the North Slope, located  $\sim 330$  km southeast of Barrow, AK, and produces significant  $\text{CO}_2$ ,  $\text{NO}_x$ , and  $\text{CH}_4$  (Brooks et al., 1997; Jaffe et al., 1995). Anthropogenic emission plumes can easily be observed from the flight by increased  $\text{NO}_2$  column density. This is a good example of the type of point source that is increasing in prevalence in the Arctic (Roiger et al., 2014; Harsem et al., 2011). It can be seen from Fig. 8 that an increase in the column density of atmospheric  $\text{NO}_2$ , corresponding to a plume near Prudhoe Bay, coincided with a decrease in the column density of atmospheric  $\text{BrO}$ . The  $\text{BrO}$  mole ratio suppression is further expressed in the Fig. 8 insert that shows a plot of  $\text{BrO}$  vs.  $\text{NO}_2$  DSCD. This can be explained by Reactions (R8) and (R10) and supports our findings that  $\text{BrO}$  is suppressed by elevated levels of  $\text{NO}_x$  (Fig. 7a). Thus, while  $\text{BrONO}_2$  and  $\text{BrNO}_2$  can be recycled on surfaces to re-emit  $\text{Br}_2$ , it seems clear that the net effect of high  $\text{NO}_x$  mole ratios is to slow down the overall halogen chain chemistry, as demonstrated in Figs. 8 and S1. It should be noted that in very large  $\text{NO}_x$  plumes  $\text{O}_3$  can be removed by the reaction of  $\text{NO}$  with  $\text{O}_3$ , as shown in Reaction (R19), although in day light, a photosteady state will develop from  $\text{NO}_2$  photolysis.



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If no ozone is present the  $\text{BrO}_x$  can repartition from  $\text{BrO}$  towards  $\text{Br}$ , via photolysis of  $\text{BrO}$ . During the 30 March 2012 flight the air mass depleted of  $\text{BrO}$  also had lower ambient  $\text{O}_3$  mole ratios which could explain the  $\text{BrO}$  depletion.

In Prudhoe Bay, the sources of  $\text{NO}_x$  are buoyant plumes, located aloft of the surface (smoke stacks), where natural aerosol extinction would be less compared to the surface (Breider et al., 2014). This would limit the availability of surfaces on which  $\text{BrONO}_2$  could react to re-emit  $\text{Br}_2$ . However, these  $\text{NO}_x$  sources also produce aerosols (data not shown) (Peters et al., 2011); if these sources continue to increase in number, a shift in the aerosol extinction could occur, providing increased available aerosol surfaces for reaction of  $\text{BrONO}_2$ .

## 5 Atmospheric implications

It is clear that elevated levels of atmospheric  $\text{NO}_x$  have a significant effect on the atmospheric chemistry that occurs in the Arctic relating to halogen species. With the possibility of more anthropogenic sources appearing in the Arctic as sea ice area continues to decrease, due to gas and oil exploration and increased shipping traffic, a shift in the atmospheric oxidation capacity and chemical pathways could occur. The main springtime atmospheric oxidizers could change from halogens in the surface layer to a greater contribution from  $\text{OH}$  via  $\text{O}_3$  photolysis, via Reaction (R20), along with a potential decrease in the frequency of ODEs. Further, open water produces convective mixing, bringing  $\text{O}_3$  from aloft down to the surface (Moore et al., 2014). However, the climate change impacts on the Arctic atmosphere and associated chemistry are complex. As multiyear ice retreats, the fraction of first year ice is increasing, leading to more saline ice surfaces. However, the findings of Pratt et al. (2013) indicate that the surface snowpack on the sea ice needs to be acidified for halogen activation to occur, and this likely depends on the depth of the snowpack, which is impacted by snowfall rates and timing, as well as the presence of sea ice. It is now known that snowpack depths in the Beaufort and Chukchi seas have been decreasing at a significant rate (Webster

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et al., 2014). The acidification of the surface snow also depends on long range transport of acidic species, such as SO<sub>2</sub> and HNO<sub>3</sub> (Worthy et al., 1994), which are likely to change. Moreover, increasing latent heat fluxes (Serreze and Barry, 2011) resulting from more open water will increase the OH production rate in the Arctic because of the humidity dependence of ozone photolysis as shown in Reactions (R18)–(R20), although a significant increase in humidity would be needed for Reactions (R20)–(R22) to have an impact on Arctic OH production.



Thus, there are multiple competing variables that influence Arctic atmospheric chemistry, and it is surely the case that we will need to continue to integrate simulations with observations to understand the coupling of physical and chemical processes, as the Arctic continues to warm and undergo change at the surface. Finally, we note that the deposition rates and aqueous phase chemistry for the products from the reaction between atmospheric NO<sub>x</sub> and halogen radicals are not well known, and fluxes of molecular halogens from Arctic surface snow have not been measured to date. Thus further efforts in this area are necessary to gain a greater understanding of these chemical processes to improve models.

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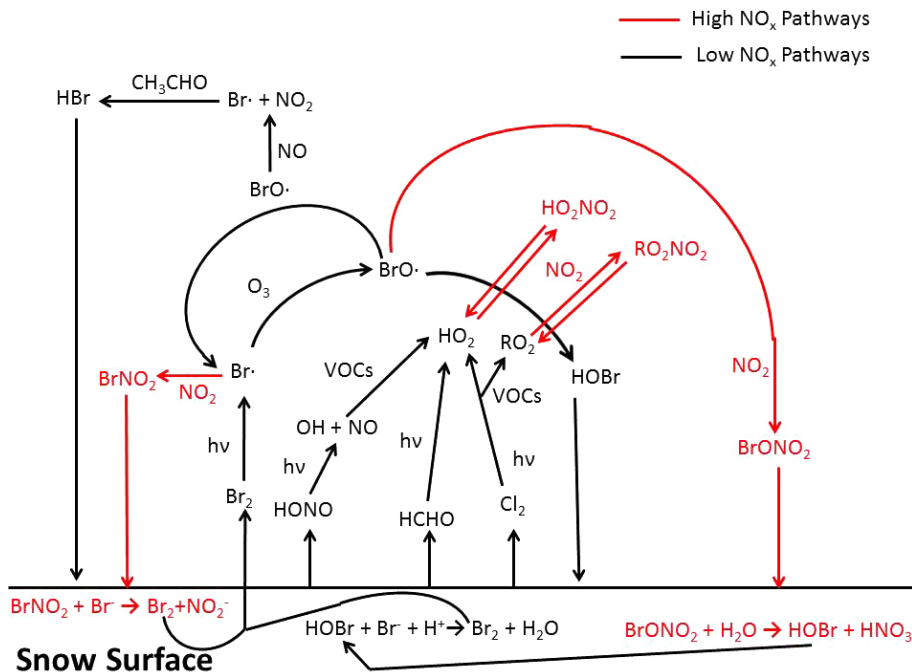
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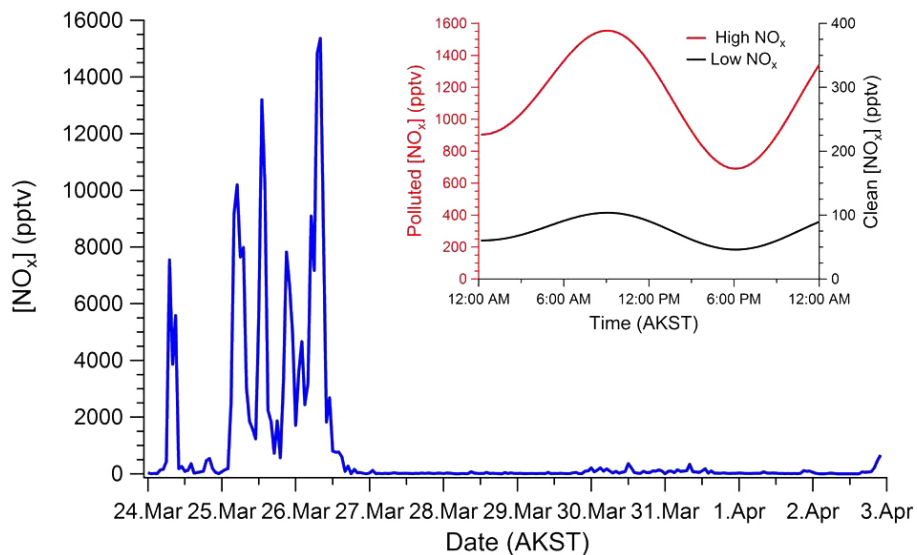
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**Figure 1.** Halogen cycle in the Arctic boundary layer with (red trace) and without (black trace) the influence of anthropogenic NO<sub>x</sub> (Abbatt et al., 2012; Simpson et al., 2007; Grannas et al., 2007).

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**Figure 2.** Observed (blue)  $\text{NO}_x$  mole ratios for the 10 day OASIS period in Barrow, AK, as well as model scenario diurnal  $\text{NO}_x$  mole ratios for low (black) and high (red) cases.

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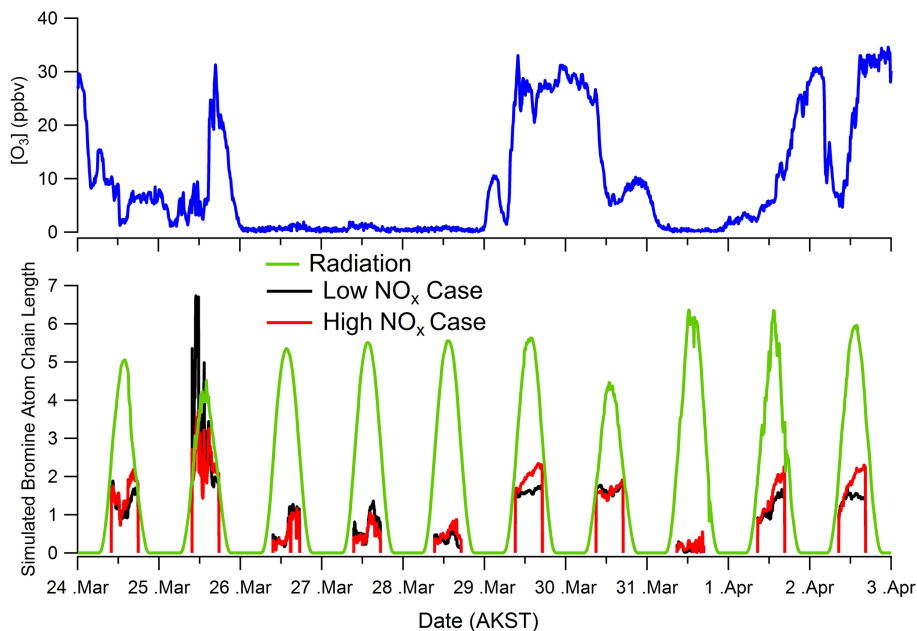
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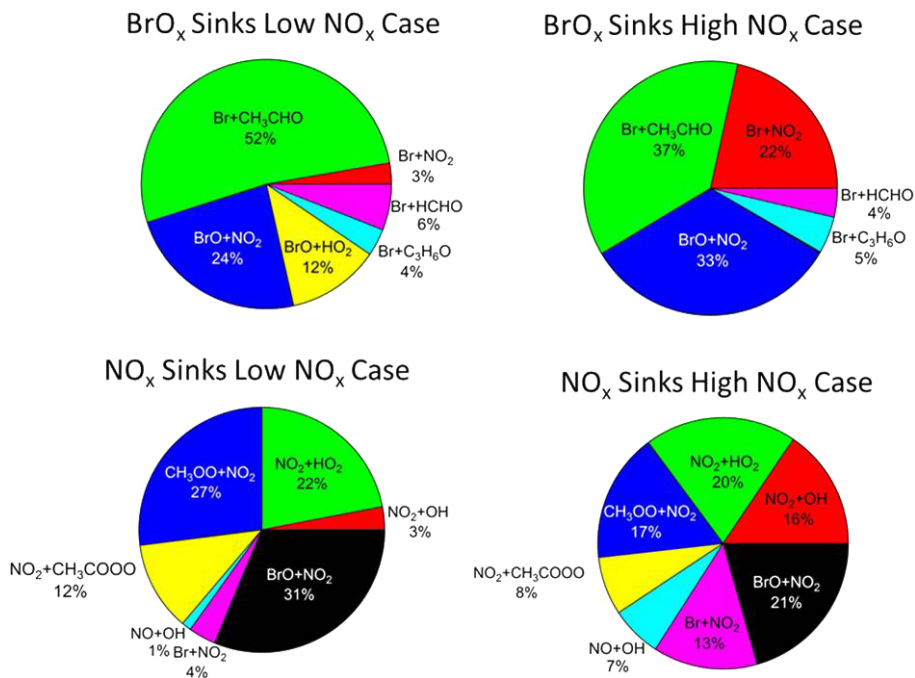


**Figure 3.** Calculated bromine chain length for the low NO<sub>x</sub> simulation and the high NO<sub>x</sub> simulation along with observed O<sub>3</sub> and radiation.

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**Figure 4.** Fractional contributions of BrO<sub>x</sub> and NO<sub>x</sub> sink reactions from the low and high NO<sub>x</sub> simulation cases.

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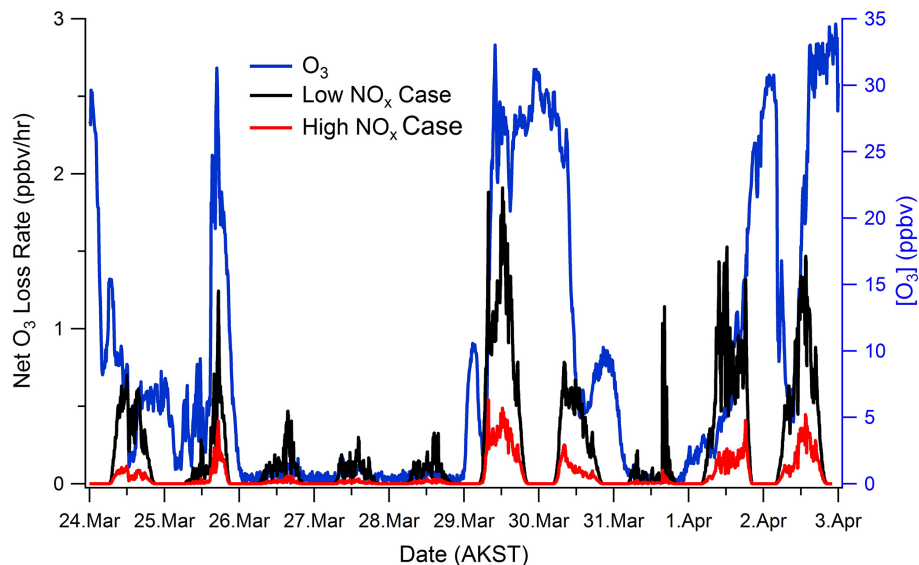
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**Figure 5.** Calculated net O<sub>3</sub> loss rate for the low NO<sub>x</sub> and high NO<sub>x</sub> simulations, along with the observed O<sub>3</sub> mole ratios.

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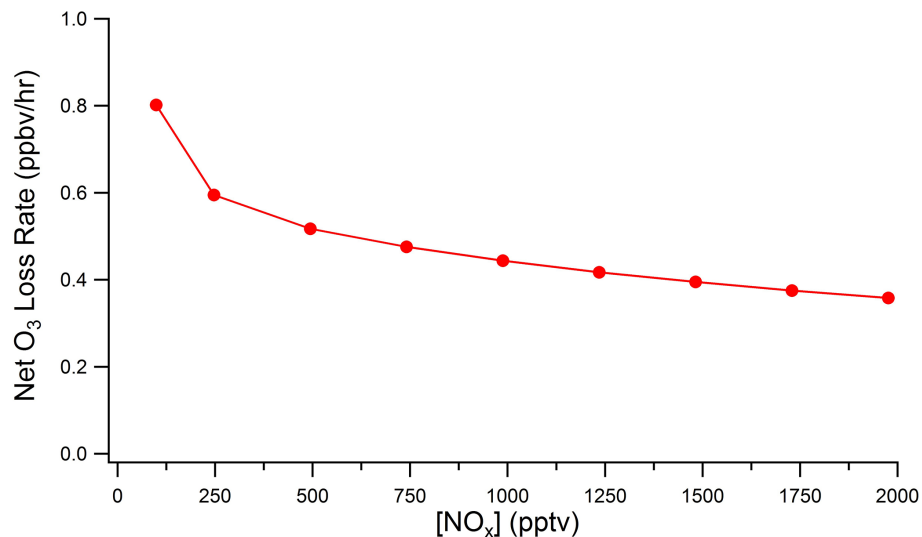
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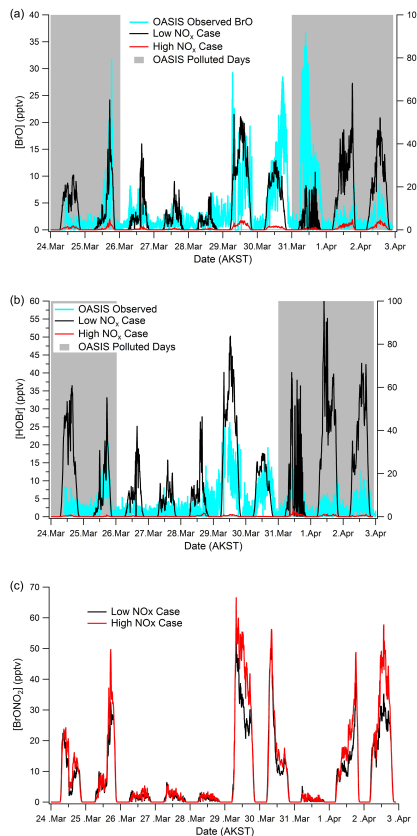


**Figure 6.** Net O<sub>3</sub> loss rate as a function of the NO<sub>x</sub> mole ratio, for 30 March mid-day (11:00 to 13:00 AKST) conditions.

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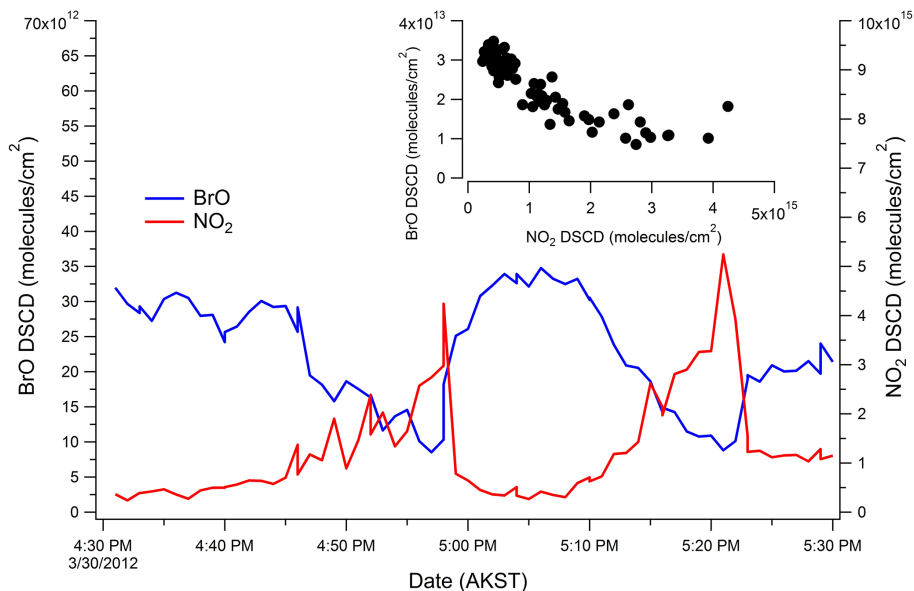
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**Figure 7.** (a) Simulated BrO mole ratio (low NO<sub>x</sub> and high NO<sub>x</sub> cases) and the observations during the study period. (b) HOBr levels from the model simulations (low NO<sub>x</sub> and high NO<sub>x</sub> cases) and the observations during the simulation dates. (c) BrONO<sub>2</sub> mole ratio from the two simulation cases.

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**Figure 8.** BrO and NO<sub>2</sub> measured mole ratios via MAX-DOAS during the BROMEX field campaign, near Prudhoe Bay (70° N, 149° W), AK at 700 m above the surface on 30 March 2012. The insert of the NO<sub>2</sub> vs. BrO shows the anti-correlation between the two species.