1	Interactions of bromine, chlorine, and iodine photochemistry during ozone depletions in
2	Barrow, Alaska
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31	Abstract. The springtime depletion of tropospheric ozone in the Arctic is known to be caused
32	by active halogen photochemistry resulting from halogen atom precursors emitted from snow,

33 ice, or aerosol surfaces. The role of bromine in driving ozone depletion events (ODEs) has been

34 generally accepted, but much less is known about the role of chlorine radicals in ozone depletion 35 chemistry. While the potential impact of iodine in the High Arctic is more uncertain, there have 36 been indications of active iodine chemistry through observed enhancements in filterable iodide. 37 probable detection of tropospheric IO, and recently, observation of snowpack photochemical production of I2. Despite decades of research, significant uncertainty remains regarding the 38 39 chemical mechanisms associated with the bromine-catalyzed depletion of ozone, as well as the 40 complex interactions that occur in the polar boundary layer due to halogen chemistry. To 41 investigate this, we developed a zero-dimensional photochemical model, constrained with 42 measurements from the 2009 OASIS field campaign in Barrow, Alaska. We simulated a 7-day 43 period during late March that included a full ozone depletion event lasting 3 days and subsequent 44 ozone recovery to study the interactions of halogen radicals under these different conditions. In 45 addition, the effects of iodine added to our base model were investigated. While bromine atoms 46 were primarily responsible for ODEs, chlorine and iodine were found to enhance the depletion 47 rates and iodine was found to be more efficient per atom at depleting ozone than Br. The 48 interaction between chlorine and bromine is complex, as the presence of chlorine can increase 49 the recycling and production of Br atoms, while also increasing reactive bromine sinks under 50 certain conditions. Chlorine chemistry was also found to have significant impacts on both HO<sub>2</sub> 51 and RO<sub>2</sub>, with organic compounds serving as the primary reaction partner for Cl atoms. The 52 results of this work highlight the need for future studies on the production mechanisms of Br<sub>2</sub> and Cl<sub>2</sub>, as well as on the potential impact of iodine in the High Arctic. 53

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# 57 1 Introduction

58 The importance of halogen chemistry in Polar Regions has been well established over the 59 past few decades since the observation of near-surface boundary layer ozone depletion in the 60 1980's (Oltmans and Komhyr, 1986; Barrie et al., 1988; Bottenheim et al., 1990). Since that 61 time, ozone depletion events (ODEs) have been observed at numerous Arctic and Antarctic 62 locations (e.g., (Bottenheim et al., 2002; Saiz-Lopez et al., 2007b; Simpson et al., 2007; Oltmans 63 et al., 2012)). ODEs are characterized by episodic depletions of tropospheric ozone from 64 background mole ratios of approximately 35 parts per billion by volume (ppbv) to less than 2 65 ppbv over periods of hours to days. These events are known to occur following the onset of polar sunrise, and continue through polar spring, when temperatures are low and snow and sea 66 67 ice are still present, with a stable atmospheric boundary layer (Simpson et al., 2007).

68 Photochemical reactions involving halogen radicals, notably bromine, are thought to be 69 the primary cause of ODEs (see Simpson et al. (2007) for a review). The chemical destruction of 70  $O_3$  by Br can be described by reactions R1 – R3 (Platt and Hönninger, 2003).

71 
$$Br_2 + hv \rightarrow 2Br$$
 (R1)

72 Br + O<sub>3</sub> 
$$\rightarrow$$
 BrO + O<sub>2</sub> (R2)

73 BrO + BrO 
$$\rightarrow$$
 Br<sub>2</sub> + O<sub>2</sub> (R3)

The efficiency of Br atoms in destroying ozone is due primarily to its relative lack of atmospheric sinks, and thus its relatively high gas-phase concentration, as well as its ability to recycle and regenerate from temporary sink species. Bromine atoms do not react appreciably with methane or other saturated hydrocarbons; thus, its primary sinks (other than O<sub>3</sub>) consist of a few oxygenated volatile organic compounds (OVOCs) (e.g., aldehydes) or unsaturated hydrocarbons, which result in production of HBr, and HO<sub>x</sub> species. BrO can react to regenerate a Br atom (via reaction R3, followed by R1), or react with HO<sub>2</sub> to produce HOBr, which can in
turn lead to the production of two Br atoms through a heterogeneous reaction mechanism termed
the bromine explosion (Tang and McConnell, 1996; Vogt et al., 1996), as shown below.

83 BrO + HO<sub>2</sub> 
$$\rightarrow$$
 HOBr + O<sub>2</sub> (R4)

84 
$$HOBr_{(g)} \rightarrow HOBr_{(aq)}$$
 (R5)

85 
$$\operatorname{HOBr}_{(aq)} + \operatorname{Br}_{(aq)} + \operatorname{H}_{(aq)}^{+} \rightarrow \operatorname{Br}_{2(aq)} + \operatorname{H}_{2}O$$
 (R6)

86 
$$\operatorname{Br}_{2(aq)} \xrightarrow{} \operatorname{Br}_{2(g)}$$
 (R7)

The production of Br<sub>2</sub> can thus be sustained on saline snow, ice, and aerosol surfaces, as has been confirmed in laboratory studies that have observed production of Br<sub>2</sub> and BrCl from aqueous and frozen halide surfaces exposed to HOBr (Fickert et al., 1999; Adams et al., 2002; Huff and Abbatt, 2002), as well as in a recent field-based study that observed Br<sub>2</sub> production from sunlit snowpacks in Barrow, Alaska (Pratt et al., 2013).

92 The presence of chlorine chemistry in the Arctic has been well recognized through 93 indirect measurements of hydrocarbons (Jobson et al., 1994; Ariya et al., 1998; Keil and Shepson, 94 2006; Tackett et al., 2007) and through detection of photolyzable chlorine species (defined as  $[Cl_2 + HOCl]$ ) (Impey et al., 1997); however, few direct measurements of chlorine species have 95 96 been reported. The only currently reported measurements of ClO were by Tuckermann et al. 97 (1997), who detected ClO at Spitsbergen. Unlike bromine, chlorine radicals efficiently oxidize a 98 wide-range of pollutants and volatile organic compounds (VOCs), often with faster rate 99 coefficients than analogous reactions by the hydroxyl radical (OH); thus, chlorine has an 100 Estimates of polar region Cl atom concentrations using abundance of atmospheric sinks. hydrocarbon decay methods are typically in the range of  $10^4 - 10^5$  molecules cm<sup>-3</sup> (Jobson et al., 101

102 1994; Ariya et al., 1998; Boudries and Bottenheim, 2000), approximately 2-3 orders of
103 magnitude lower than analogous estimates of Br (Cavender et al., 2008).

Like bromine, chlorine can react directly with O<sub>3</sub>, generating a ClO radical via Reaction R8. The presence of ClO may also promote bromine-induced depletion of O<sub>3</sub> through the fast cross-reaction of BrO and ClO that serves to regenerate Br atoms (Reaction R9) (Le Bras and Platt, 1995; Platt and Hönninger, 2003).

$$108 \quad \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \tag{R8}$$

109 BrO + ClO 
$$\rightarrow$$
 Br + OClO (or Cl + O<sub>2</sub>) (R9)

110 Due to analytical challenges, few tropospheric observations of Cl<sub>2</sub> and ClO exist, 111 therefore the role of Cl in ozone depletion events remains uncertain and has been much debated. 112 Typical estimated Cl concentrations are likely too low for chlorine to be a significant direct 113 contributor to ozone depletion. However, elevated levels of Cl<sub>2</sub> (exceeding 100 pptv) were 114 recently observed during the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) 2009 campaign in 115 Barrow, Alaska using chemical ionization mass spectrometry (CIMS) (Liao et al., 2014). The 116 impact that such high levels of Cl<sub>2</sub> could have on ODEs or on the oxidation chemistry of the 117 Arctic troposphere has not been fully investigated. Although Reaction (R9) can act to enhance 118 the rate of ozone depletion by propagating the Br cycle, formaldehyde, propanal, acetaldehyde 119 and HO<sub>2</sub> are all produced as by-products of VOC oxidation by Cl and are efficient sinks for Br or 120 BrO radicals (Shepson et al., 1996; Sumner et al., 2002). Therefore, it is likely that the 121 interaction between chlorine and bromine is complex. Modeling studies simulating ozone 122 depletion events often use BrCl as the primary source of Cl atoms (Calvert and Lindberg, 2003; 123 Piot and Von Glasow, 2008), and thus [Cl] is quite low and often insignificant. Few have added

124 significant  $Cl_2$  sources (Sander et al., 1997; Piot and von Glasow, 2009). As a result, our 125 understanding of chlorine chemistry in the Arctic is limited.

126 Iodine may play a significant role in the photochemical reactions leading to ODEs 127 (Sander et al., 1997; Saiz-Lopez et al., 2007b; Saiz-Lopez et al., 2008; Mahajan et al., 2010) 128 based on recent ground-based and satellite observations of IO of up to 20 - 50 pptv over snow 129 and ice-covered surfaces in coastal Antarctica (Saiz-Lopez et al., 2007a, 2007b; Schönhardt et al., 130 2008; Frieß et al., 2010). Although IO has been routinely detected at high levels in Antarctica, 131 there has been no successful set of IO measurements in the High Arctic to date. However, this is 132 possibly due to limitations of current analytical methods rather than an absolute absence of 133 iodine chemistry. Several studies in the Arctic have indicated the presence of iodine species 134 through measurements of springtime peaks in filterable iodine (Sturges and Barrie, 1988; Barrie 135 et al., 1994; Sirois and Barrie, 1999) and total gaseous iodine (Martinez et al., 1999). Hönninger 136 (2002) was able to detect IO during only one instance above the detection limit at Alert in 2000 137 using long path DOAS, corresponding to 0.7 pptv of IO if averaged over the 10 km light path. 138 Mahajan et al. (2010) also observed up to 3.4 pptv IO at the sub-Arctic location of Kujjuarapik, 139 Canada. Most recently,  $I_2$  at levels  $\leq 0.5$  pptv have been observed by our research group at 140 Barrow, Alaska by CIMS, lending direct evidence supporting the presence of at least low levels 141 of iodine chemistry in the Arctic (Raso et al., 2015).

Due to the lack of iodine observations in the Arctic, models often omit iodine chemistry when simulating ODEs. However, this may significantly underestimate the rate of ozone depletion because the BrO + IO cross-reaction (Reaction R10), which propagates the Br chain, has a rate constant that is approximately 2 orders of magnitude faster than the BrO self-reaction.

146  $\operatorname{BrO} + \operatorname{IO} \xrightarrow{} \operatorname{Br} + \operatorname{I} + \operatorname{O}_2$  (R10)

6

Indeed, previous modeling studies have found that significant enhancements in ozone depletion
result from even small concentrations of reactive iodine (Calvert and Lindberg, 2004a; Saiz-

149 Lopez et al., 2008; Mahajan et al., 2010)

Besides causing tropospheric ODEs, halogens can also impact  $HO_x$  and  $NO_x$  chemical cycles. The presence of reactive halogen species has the general effect of shifting the [HO<sub>2</sub>]/[OH] ratio towards OH (Platt and Hönninger, 2003; Thomas et al., 2012), primarily through reactions R11 and R12, where X can be Br, Cl, or I.

154 
$$XO + HO_2 \rightarrow HOX + O_2$$
 (R11)

155 HOX + 
$$hv \rightarrow X$$
 + OH (R12)

Bromine and chlorine atoms can react with formaldehyde (and higher molecular-weight aldehydes), leading to production of hydrogen halides and HO<sub>x</sub>. Alternatively, halogen atom reaction with HO<sub>2</sub> can act as a HO<sub>x</sub> sink. The inclusion of chlorine chemistry further impacts the HO<sub>x</sub> chemistry because RO<sub>2</sub>, HO<sub>2</sub> and carbonyl compounds are produced as side-products of Cl oxidation of VOCs (e.g., Reactions 13 – 15).

161 Cl + CH<sub>4</sub> (+ O<sub>2</sub>) 
$$\rightarrow$$
 CH<sub>3</sub>OO' + HCl (R13)

162 
$$CH_3OO' + NO \rightarrow CH_3O' + NO_2$$
 (R14)

163 
$$CH_3O' + O_2 \rightarrow HCHO + HO_2$$
 (R15)

Halogen chemistry also generally increases the Leighton ratio ( $[NO_2]/[NO]$ ) through conversion of NO to NO<sub>2</sub> via Reactions R14 and R16 (Platt and Hönninger, 2003), where X is Br, Cl, or I. X or XO can also react with NO<sub>2</sub> to form XNO<sub>2</sub> or XONO<sub>2</sub>, respectively (R17 – R18), however, the net effect of halogen chemistry is an increase in the  $[NO_2]/[NO]$  ratio.

$$168 \quad XO + NO \rightarrow X + NO_2 \tag{R16}$$

$$169 \quad X + NO_2 \rightarrow XNO_2 \tag{R17}$$

170 XO + NO<sub>2</sub>  $\rightarrow$  XONO<sub>2</sub>

(R18)

171 In this work, we utilize a zero-dimensional model to further investigate the chemical 172 interactions occurring in the Arctic related to the chemistry of halogen radicals and the 173 interactions between bromine, chlorine, and iodine. The OASIS 2009 campaign, conducted in 174 March and April in Barrow, Alaska, provides a valuable opportunity to perform a unique study 175 of halogen chemistry using direct observations of a variety of atmospheric species, including 176 HO<sub>x</sub> and XO<sub>x</sub> radicals, and molecular halogens, with high time resolution measured concurrently 177 and from a single location. During OASIS, measurements of a large suite of saturated, 178 unsaturated, and oxygenated VOCs, numerous halogenated species (e.g. Br<sub>2</sub>, Cl<sub>2</sub>, BrCl, HOBr, 179 BrO, ClO), OH, HO<sub>2</sub>, NO, NO<sub>2</sub>, HONO, O<sub>3</sub>, and actinic radiation were conducted. We constrain 180 our model with time-resolved data from OASIS, in order to investigate the following questions: 181 What is the fraction of ozone depleted by each halogen atom, and how do each of the \_ 182 halogens impact the rate and timescale of ozone depletion? 183 How do chlorine and iodine impact bromine chemistry relating to ODEs? -184 What is the effect of halogen species on  $HO_x$  and  $NO_x$  chemistry, and, conversely, what -185 is the effect of  $HO_x$  and  $NO_x$  on halogen chemistry? 186 What is the importance of chlorine chemistry (e.g., is it only the BrO + ClO cross--187 reaction that makes chlorine chemistry important)? 188 Several modeling scenarios were constructed in an effort to address these questions and to 189 dissect the complex chemistry occurring during ODEs. The results of this work have been 190 organized in the following manner:

- 191
- Section 3.1: Comparison of modeled versus observed mole ratios for pertinent species

Section 3.2: Contribution of Br, Cl, and I to ozone depletion and the rate and timescale
of ozone loss

- Section 3.3: Impact of chlorine on bromine chemistry and oxidation capacity

195 - Section 3.4: Impact of iodine and bromine-iodine interactions

196

#### **197 2 Methods**

198 2.1 Field Campaign and Measurements Description

The OASIS (Ocean-Atmosphere-Sea Ice-Snowpack) 2009 campaign occurred during the months of February through April as part of the most recent International Polar Year (2007 – 201 2009). The motivation for OASIS was to investigate the chemical and physical processes leading to ozone and mercury depletion events in polar spring. The OASIS campaign represents the largest suite of simultaneous and co-located atmospheric trace gas measurements conducted in the Arctic to date, and as such, has provided a rich data set for understanding chemical processes in the Arctic troposphere.

The atmospheric measurements employed in this work were conducted from mobile instrument trailers located near the Barrow Arctic Research Consortium (BARC) facility on the Naval Arctic Research Laboratory (NARL) campus. A map of the measurement site is shown in Figure 1. Winds arriving at the measurement site are primarily northeasterly (i.e. from the sea ice), and thus, should represent background conditions with influence from only natural processes and snow/ice interactions. Occasional winds from the west (i.e. from the town of Barrow) are easily identifiable by coincident enhancements in both NO<sub>x</sub> and CO.

Table 5 lists the measurements conducted at OASIS that were used in this modeling study. This is not an exhaustive list of all measurements performed during the campaign. As the 215 methods have all been described previously, they will only be described very briefly here. 216 Ozone, NO, and NO<sub>2</sub> were measured using the well-established chemiluminescence technique as 217 described in Ridley et al. (1992) and Ryerson et al. (2000). O<sub>3</sub> and NO<sub>x</sub> were measured at 3 218 heights (2, 6, and 18 ft) from a fixed tower. The data from the 6 ft height were used in this 219 analysis. Carbon monoxide (CO) concentrations were measured using a standard commercial CO 220 analyzer (Thermo Scientific) with infrared absorption detection. The inorganic halogen species 221 Br<sub>2</sub>, Cl<sub>2</sub>, BrO, and HOBr were measured in situ at a height of ~1.5 m above the snowpack with a 222 chemical ionization mass spectrometer (CIMS) employing I ion chemistry. This method, as 223 used in Barrow, and observations have been published in Liao et al. (2011, 2012, 2014). CIO was 224 measured at a height of  $\sim 3$  m above the snowpack via chemical conversion to a stable, 225 halogenated product followed by online separation and detection by gas chromatography with 226 electron capture detection (Stephens et al., 2012). Formaldehyde (HCHO) concentrations were 227 measured at 1 Hz frequency from the fixed tower using a tunable diode laser absorption 228 spectrometer as described in Fried et al. (1997) and Lancaster et al. (2000). As with the O<sub>3</sub> and NO<sub>x</sub> measurements, only data at 6 ft were used in this analysis. HONO was measured using the 229 230 Long-Path Absorption Photometer (LOPAP) technique described in Villena et al. (2011) with a 231 reported 10% measurement uncertainty. Finally, a large suite of organic compounds were 232 measured both in situ by fast GC-MS (Apel et al. 2010) and via whole air canister samples with 233 offline GC-MS (Russo et al. 2010). Those species that were directly used in this analysis are 234 listed in Table 5.

235

The model used for this study is a zero-dimensional, photochemical model solved using the commercial software FACSIMILE. It incorporates much of the known gas-phase chemistry that occurs in the Arctic in 220 gas-phase reactions and 42 photolysis reactions (Tables 1 and 2). The model also includes deposition/uptake to snow/aerosol surfaces for certain species, aqueous phase halide reactions, (Tables 3 and 4), and a simple dilution rate for long-lived species (e.g., PAN).

243 The model was developed to investigate, as a particularly useful example case study, the 244 period 25 through 31 March, 2009, which included a 3-day ozone depletion event during which 245 O<sub>3</sub> remained below 1 ppbv. This time period was chosen to investigate the changes in halogen 246 interactions under different ozone regimes, i.e. background ozone (~30 - 35 ppbv), ozone 247 depleting periods, full ozone depletion ( $O_3 < 5$  ppbv), and ozone recovery, during which winds 248 were consistently (with the exception of the first half of 25 March) arriving at the measurement 249 site directly from the frozen Arctic Ocean. To enable focused pursuit of specific questions about 250 gas phase free radical chemistry, the model was constrained to observed values of  $O_3$ ,  $C_2H_2$ , 251 C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, *i*-C<sub>4</sub>H<sub>10</sub>, HCHO, CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, methyl ethyl ketone, 252 Cl<sub>2</sub>, Br<sub>2</sub>, NO, NO<sub>2</sub> and CO, as well as calculated time-varying photolysis rate coefficients (J) for 253 O<sub>3</sub> and NO<sub>2</sub>. The in situ measurements that were used to constrain the model are presented in Figure 1. NO<sub>2</sub> mole ratios in Barrow are often quite variable and relatively high compared to 254 255 other polar measurement locations (Beine et al., 2002). At times, winds travel from the 256 southwest direction, bringing air influenced by Barrow emissions over the measurement site. 257 This is the case for the high NO<sub>2</sub> observed at the beginning of 25 March, which correlates to 258 enhanced CO. Observed values were incorporated at 10-minute time steps, calculated as 10-259 minute averages of the reported data, over the entire 7-day period. Constraining the model with

these time-varying observations precludes the need for parameterization of atmospheric transport due to advection, and thus justifies the use of a zero dimensional model for this study. It is important to note that, because our objective was to investigate the halogen chemistry occurring during this time period rather than to attempt to simulate an ozone depletion event, we have constrained our model with the observed ozone mole ratios in order to fully study the fast chemical interactions occurring under these observed conditions, which are strong functions of  $O_3$ .

Mole ratios of CH<sub>4</sub> were held constant at an average value for this time of 1.89 ppmv as reported by the NOAA-ESRL Barrow Observatory. [H<sub>2</sub>O] was calculated for 25 March from observed meteorological conditions of 78% relative humidity and an ambient temperature of

270 -19.5°C (NOAA; Barrow airport data), corresponding to a water vapor concentration of 271  $2.23 \times 10^{16}$  molecules cm<sup>-3</sup>. This was held constant throughout the simulation. Temperature was 272 not varied in the model.

273 The gas-phase chemical reactions and corresponding rate constants used in the model are 274 shown in Table 1. Unless otherwise noted, all rate constants were calculated for a temperature of 275 248K, consistent with average ambient conditions in Barrow for this time (NOAA Barrow 276 Observatory). This mechanism includes halogen, HO<sub>x</sub>, NO<sub>x</sub>, and VOC chemistry associated 277 with ozone depletions in the Arctic spring. The inorganic iodine reaction scheme used here is 278 adapted from McFiggans et al. (2000, 2002), Calvert and Lindberg (2004a), and Saiz-Lopez et al. 279 (2008). Organic iodine compounds are not included. Although some organic iodine compounds 280 have been observed in coastal and marine locations (Carpenter et al., 1999; Jones et al., 2010), I<sub>2</sub> 281 is likely the major source of atmospheric iodine (Saiz-Lopez and Plane, 2004) and, thus, was 282 assumed to be the reactive I source in this model. It should also be noted that while I does not

react appreciably with VOCs, it is likely that I and IO do react with RO<sub>2</sub> radicals (Sommariva et al., 2012). However, these reactions are not included here. Thus, though the iodine reaction scheme agrees with previous studies, it is likely incomplete; therefore, modeled iodine chemistry should be taken only as potential impacts to help direct future research efforts.

287 Photodissociation reactions included in this model are listed in Table 2. For many of the 288 species, time-varying J coefficients were calculated using a modified version of the Tropospheric 289 Ultraviolet and Visible (TUV) Radiation model (Madronich and Flocke, 1999) based on in situ 290 0.1 Hz measurements of downwelling actinic flux conducted throughout the duration of the OASIS campaign and a surface albedo of 0.8. Upwelling flux was estimated as a function of 291 292 solar zenith angle assuming clear sky conditions. The sum of upwelling and downwelling 293 radiation was used by the TUV model to calculate the total photolysis frequencies. J coefficients 294 for solar noon on 25 March (listed as  $J_{max}$ ) are provided in Table 2 as an example. J coefficients 295 were input into the model at 10-minute time steps for  $O_3$  and  $NO_2$ . All other J values were 296 scaled to  $J_{\rm NO2}$  in the modeling code.

297 J coefficients from OASIS were not available for OCIO, HOCI, or iodine compounds. 298 An estimate for  $J_{\text{max}}$  for OCIO was taken from Pöhler et al. (2010) and that for HOCI was taken 299 from an Arctic model study by Lehrer et al. (2004), which were then scaled to  $J_{NO2}$ . J 300 coefficients for iodine compounds were calculated according to the work of Calvert and 301 Lindberg (2004a, 2004b), who also simulated conditions for late March in Barrow, although we 302 note that there is a larger uncertainty for the photolysis coefficients for the iodine species, with 303 the exception of  $I_2$ . Time-varying J coefficients for the iodine species were calculated using a 304 fourth-order polynomial and varying the solar zenith angle from 98.4 to 72.3°.

305 Deposition of species to the snowpack is estimated based on measured dry deposition 306 velocities and applied using Equation (1) to calculate transfer coefficients ( $k_t$ ) from the gas to 307 aqueous phase.

$$308 k_{\rm t} = \frac{V_{\rm d}}{h} (1)$$

 $V_{\rm d}$  is the dry deposition velocity (in cm·s<sup>-1</sup>), and h is the boundary layer height. Most previous 309 estimates of ozone deposition velocities to snow in the Arctic range from 0 to 0.2 cm·s<sup>-1</sup> (Gong 310 et al., 1997; Helmig et al., 2007). Here, we use an average value of 0.05 cm·s<sup>-1</sup> for ozone, 311 312 similar to the modeling studies of Cavender et al. (2008) and Michalowski et al. (2000). 313 However, there is large uncertainty in this parameter and often-contradictory observations from 314 field measurements (Helmig et al., 2007, 2012). For 25 March, the boundary layer height in 315 Barrow was estimated at 300 m based on radiosonde data and model simulations (R. Staebler, Environment Canada, personal communication). This corresponds to a  $k_t$  for ozone of  $1.67 \times 10^{-6}$ 316 317  $s^{-1}$ . Because dry deposition velocities to snow have not been determined for the halogen acids, 318 we use the estimation method of Michalowski et al. (2000) and assume a transfer coefficient 10 times greater than that for ozone. Thus, for HBr, HCl, HOBr, HOCl, and HOI,  $k_t = 1.67 \times 10^{-5} \text{ s}^{-1}$ 319 (Table 3). Similarly, we assume an equivalent deposition velocity for the oxidized acidic 320 321 nitrogen compounds (i.e. HNO<sub>3</sub>, HO<sub>2</sub>NO<sub>2</sub>, HONO, N<sub>2</sub>O<sub>5</sub>), though a full mechanism of aqueous-322 phase nitrate chemistry is not included in this model (see Custard et al. 2015 for a more detailed 323 investigation of nitrate chemistry).

As mentioned above, in the final version of our model we used the observed values of  $Br_2$ and  $Cl_2$  to constrain the halogen precursors, however, our model was initially developed to utilize only multiphase chemistry to produce  $Br_2$  (and  $Cl_2$ ) with a mechanism adapted from Michalowski et al. (2000). Transfer coefficients into and out of the particle phase were 328 calculated as described in Jacob (2000), and the snowpack volume available for heterogeneous 329 reaction was limited to a column 10 cm deep, based on the effective UV extinction depth for 330 Arctic snow (King and Simpson, 2001). Constant concentrations of chloride and bromide ions in 331 the aerosol and snowpack were used throughout the duration of the simulation, as it is likely that 332 these represent an inexhaustible source of chloride and bromide (Lehrer et al., 2004). 333 Concentrations of Br<sup>-</sup> and Cl<sup>-</sup> in the snowpack were calculated by assuming all bromide and 334 chloride from bulk snow measurements over "thick first-year ice" near Barrow (Krnavek et al., 335 2012) were contained within the quasi-liquid layer (QLL) (Cho et al., 2002). We used a pH of 4 336 for the QLL as an estimate, which is in line with previous modeling studies (Thomas et al., 2011, 337 2012). Aerosol halide concentrations were used as reported for the bulk aerosol chloride and 338 bromide measurements from Barrow, Alaska (Li and Winchester, 1989), and we used an 339 estimate of H<sup>+</sup> for Arctic aerosols from the ARCPAC flight campaign (Fisher et al., 2011). 340 Additionally, upward mixing of chemical species emitted from the snowpack heterogeneous 341 reactions was simplified such that it was assumed to be limited only by vertical mixing from the 342 surface and did not include diffusion through the snowpack interstitial air, which is dependent 343 mostly on wind pumping (a parameter not included in this 0-D model). The aqueous phase 344 reactions included in the model are listed in Table 4.

Using this multiphase mechanism, we were able to produce sufficient gas-phase  $Br_2$  in the model solely from the snowpack/aerosol heterogeneous reactions with aqueous bromide, however, we could not reproduce the day-to-day variability in  $[Br_2]$  from only the heterogeneous chemistry; thus, since our main objective was to examine interactions between halogen radical species, we chose to constrain the model to observed  $Br_2$ . This was necessary to ensure that [Br]and [BrO] were accurately represented, so that we could properly examine interactions with

15

other radicals, e.g. HO<sub>2</sub>, ClO, and IO. There was a period of missing Br<sub>2</sub> data during 29 and 30 351 352 March. For these days, we used an average Br<sub>2</sub> diurnal cycle from the previous days, which was 353 then scaled until the modeled BrO was in agreement with observations. It should be noted, also, 354 that the uncertainty in the BrO measurements is high during ODEs as the observed values are 355 very near the detection limit (LOD of  $\sim 2$  pptv with uncertainty of -3/+1 pptv near the LOD), and 356 thus the uncertainty in modeled [Br] would be greatest during these periods. Only daytime BrCl 357 was used as produced in the model multiphase mechanism. BrCl measurements from OASIS are 358 sparse, however, the daytime simulated BrCl mole ratios of 0 - 10 pptv are in agreement with the 359 available observations for the campaign.

360 Volumetric fluxes were also introduced into the model for HONO and I<sub>2</sub>. The fluxes of 361 HONO and I<sub>2</sub> were scaled to J<sub>NO2</sub> since HONO, and likely I<sub>2</sub>, are photochemically produced 362 (Honrath et al., 1999; Zhou et al., 2001; Saiz-Lopez et al., 2011). The HONO flux was adjusted 363 to agree with observed gas-phase concentrations (Villena et al., 2011), with daytime averages 364 near 10 pptv and spikes in excess of 20 pptv, as shown in Figure 3A. Although the flux is 365 included, and is necessary for measured HONO to agree with observations across all seven days 366 of the simulation, the contribution of the flux is small in comparison to gas phase production 367 through NO<sub>x</sub> chemistry, with the exception of 26 - 28 March, when gas phase NO<sub>x</sub> is especially 368 low. Figure 3B shows a time series of the NO and NO<sub>2</sub> observations that has been re-scaled to a 369 smaller range on the y-axis so that the relatively higher NO<sub>x</sub> on 29 and 30 March can be 370 discerned. A recent paper by Lin et al. (2014) speculates a possible additional gas phase source 371 of HONO from the reaction of NO<sub>2</sub> with an HO<sub>2</sub>·H<sub>2</sub>O complex. However, as laboratory studies 372 are still required to quantify the efficiency of this mechanism, the rate constant of this reaction, 373 and the product yield of HONO, this mechanism was not included in our model.

374 To investigate the impacts that different levels of iodine chemistry could have on ozone 375 depletions, two iodine scenarios were used, which will be referred to as "Low Iodine" and "High 376 Iodine." For the Low Iodine case, the I<sub>2</sub> flux was chosen such that average daytime gas-phase 377 mole ratios of IO remain near 1 pptv (i.e., near or below the detection limit of DOAS and in line 378 with previous indications of [IO] in the Arctic) for the majority of days (as shown in Figure 4). 379 Only during the ozone depletion period did simulated IO reach close to 2 pptv, for the chosen  $I_2$ 380 flux. The higher [IO] during ozone-depleted periods is a result of the constant  $I_2$  flux that is 381 utilized for iodine, in contrast to bromine and chlorine species, which use actual observations. Because the I<sub>2</sub> flux is constant during the ODE, while Br<sub>2</sub>, and especially Cl<sub>2</sub> are decreased, 382 383 iodine becomes more dominant for reaction with the remaining  $O_3$  (~1 – 2 ppbv) and [IO] 384 increases. I<sub>2</sub> averages ~0.025 pptv throughout the Low Iodine simulation. The High Iodine 385 scenario uses a flux that is adjusted so that I<sub>2</sub> averages 0.5 pptv across the simulated period. This 386 results in IO mole ratios ranging from 5 to 10 pptv (see Figure 3).

387

### 388 **3 Results and Discussion**

## 389 3.1 Comparison of modeled and observed mole ratios for select species

Those species that are not specifically prescribed in the model (e.g. all radical species and many inorganic halogen compounds) by inputting time-varying observations or by introducing a flux are allowed to freely evolve. Here we compare modeled versus observed mole ratios for only those species that are most important for this analysis on halogen interactions.

394 Since the contribution of each halogen atom to ozone destruction is a function of its 395 concentration, it is important that the model simulates halogen radicals at levels that are 396 consistent with observations. Comparisons of the multi-day model output with observed BrO

397 and ClO are shown in Figures 2B and 2E. ClO observations are limited, but the model captures 398 the occurrence and general shape of the ClO peak observed on 29 March. However, the model 399 generally under predicts ClO where there are available observations. A question to address is the 400 extent to which there are other sources of Cl atoms during this time, such as HOCl or chlorinated 401 organic compounds that are not included here. In Figure 2B, the simulated BrO output generated 402 through bromine chemistry constrained by observed Br<sub>2</sub> is compared with BrO observations. 403 The model represents the overall temporal profile and magnitude of [BrO] throughout this period. 404 This is important for the analysis of the interactions between BrO, ClO, and IO, which is the 405 focus of this work. It has been suggested that daytime Br<sub>2</sub> observed by CIMS contains a 406 contribution from HOBr conversion to Br2 on the inlet, and that daytime Br2 should be below 407 detection limits on average due its fast photolysis rate (Liao et al., 2012). However, this 408 modeling study suggests that Br<sub>2</sub> should indeed be present in the daytime (given the agreement 409 with observed [BrO]), though it is acknowledged that there is some degree of interference from 410 HOBr, as is apparent from the model over-prediction of BrO on 31 March. Considering an efolding photolytic lifetime of Br<sub>2</sub> at solar noon of 23 s ( $J_{max} = 0.044 \text{ s}^{-1}$ ), and using the method of 411 412 Guimbaud et al. (2002), the effective daytime mixing height ( $Z^*$ ) of Br<sub>2</sub> in the stable air typical of the Arctic ( $K_c = 95 \text{ cm}^2 \cdot \text{s}^{-1}$ ) is ~ 0.5 m. Assuming simple first-order kinetics, the [Br<sub>2</sub>] 413 414 remaining after mixing up from the surface to the intake of the CIMS (~1 m or 2 lifetimes) is 415 10% that at the surface. A recent study examining Br<sub>2</sub> production from surface snow in Barrow 416 demonstrates that enhanced Br<sub>2</sub> production is observed in the presence of solar radiation (Pratt et 417 al., 2013). Given that the  $Br_2$  concentrations in the snowpack interstitial air should be elevated due to heterogeneous production mechanisms (e.g., the bromine explosion), and that production 418 419 should be greater during sunlit periods, it seems reasonable to conclude that  $Br_2$  should

sometimes be observable during the day. Indeed,  $Br_2$  mole ratios needed in the model to reproduce BrO observations agree with the "uncorrected"  $Br_2$  observations (shown as the red data in Figure 2A), as reported in Liao et al. (2012).

423 Figures 2A and 2D compare the model output for Br and Cl atom concentrations (black 424 trace) with steady-state approximations of [Br] and [Cl] (red trace) following the method of 425 Stephens et al. (2012), as direct observations of Br and Cl atoms have not yet been achieved. In 426 both cases, the model-simulated output is greater than the steady-state approximations on a few 427 days, sometimes by as much as 90%, although both methods capture the diurnal trends and 428 fluctuations. A notable feature of Figure 2A is the rather high Br atom concentrations during the three-day ODE, with concentrations up to  $3x10^9$  molecules cm<sup>-3</sup> (~100 pptv), though as 429 430 mentioned previously, this should be considered an upper limit due to the uncertainty of the Br<sub>2</sub> 431 and BrO measurements and the potentially positive model bias during this time. Nonetheless, 432 higher [Br] (and [I]) is expected during periods of complete ozone depletion due to the loss of this dominant Br atom chemical sink. However, these concentrations are on the high end of 433 previous estimates using hydrocarbon measurements, which range from  $1 \times 10^6$  to  $1 \times 10^9$  for 434 435 ODEs (Jobson et al., 1994; Ariya et al., 1998; Rudolph et al., 1999). While [Br] peaks during 436 periods of low  $O_3$ , [Cl] is enhanced when  $O_3$  is present due to the elevated  $Cl_2$  mole ratios that 437 are observed only when  $O_3$  is above ~10 ppbv (Figure 1A; Liao et al., 2014). The model predicts Cl atom concentrations of  $2x10^5$  to  $6x10^5$  molecules cm<sup>-3</sup>, which is also higher than previous 438 estimates of  $1 \times 10^3$  to  $1 \times 10^5$  determined from hydrocarbon measurements (Jobson et al., 1994; 439 440 Ariya et al., 1998; Rudolph et al., 1999; Boudries and Bottenheim, 2000; Keil and Shepson, 441 2006). As discussed in Stephens et al. (2012), the hydrocarbon-based methods average over the

transport path, which can be aloft and consist of several days, and thus should be lower than that observed near the surface, if the surface is the  $Cl_2$  and  $Br_2$  source.

444 Model simulations of [OH] and [HO<sub>2</sub>] (Figures 2F and 2G) lie within the bounds of 445 measurement uncertainty for the ambient data, with the exception of 29 March when the model under predicts HO<sub>2</sub> by factor of  $\sim$ 3. The accurate simulation of OH and HO<sub>2</sub> is important since 446 447 halogen chemistry, especially that involving chlorine, can have a significant impact on the HO<sub>x</sub> 448 budget. The discrepancy between the modeled and observed HO<sub>2</sub> for 29 March may lead to a 449 less than realistic impact of HO<sub>2</sub> on oxidation chemistry for this day. The model captures the 450 temporal cycle of HOBr well; however, it generally over predicts the daytime peak mole ratios 451 (Figure 2C). It is unclear why this should be the case, given that both BrO and HO<sub>2</sub> are well-452 represented, with the exception of the BrO over-prediction early on 31 March. This suggests that 453 either our simple parameterization of deposition to snow and particle surfaces is slower than that 454 occurring in nature, or that we are missing some other important HOBr sink.

455

# 456 **3.2** Contribution of Br, Cl, and I to ozone depletion and the rate and timescale of ozone 457 loss

An important question regarding ozone depletion events is the contribution of the halogen radicals, Br, Cl, and I, to the total destruction of ozone and the rate of ozone depletion. Based on field measurements of reactive bromine compounds, primarily BrO, it is generally accepted that bromine is the dominant reactant leading to ozone destruction (Simpson et al., 2007). However, this has not been quantified over highly variable chemical conditions, since prior to OASIS, simultaneous high-time resolution measurements of such a large suite of chemical species had not been performed. Few studies have examined the impact of Cl on ozone depletion, and these have not had the benefit of in situ observations of  $Cl_2$  and ClO with which to compare their models. This observational data set and model thus represents a unique opportunity.

467 In this study, "Base Model" runs are those that include both bromine and chlorine. "Br 468 Only" simulations are performed by removing Cl<sub>2</sub> and chloride; likewise "Cl Only" simulations 469 are performed by removing Br<sub>2</sub>, bromide, and organobromine compounds. Simulations with 470 iodine are conducted by introducing fluxes of I<sub>2</sub> of a magnitude necessary to keep the average 471 daytime IO near 1 pptv (Low Iodine) or at 0.5 pptv I<sub>2</sub> (High Iodine), as described previously 472 (reference Figure 4). It is important to note that the model is adjusted to fit observations using the 473 Base Model only. No re-adjustments are made to the model when either bromine or chlorine is 474 turned off, or when iodine is turned on, to observe the effect of a one variable change.

The time-varying fraction of ozone depleted by bromine, chlorine, and iodine was calculated by considering those reactions that destroy ozone (i.e. Reaction R2 for Br and the analogous reactions for Cl and I) while correcting for those reactions that result in the regeneration of O<sub>3</sub>. Here, photolysis of BrO, ClO, or IO, as well as reaction of XO with NO, ultimately lead to O<sub>3</sub> production. The rate of O<sub>3</sub> loss by halogen X is determined by Equation (2), where X = Br, Cl, or I, and the total chemical O<sub>3</sub> loss rate is calculated using Equation (3). The fractional contribution for each halogen is then determined by dividing the two quantities.

482 Rate of 
$$O_3$$
 loss by  $X = k[X][O_3] - k[XO][NO] - J[XO]$  (2)

483 Total 
$$O_3$$
 loss rate =  $k[Br][O_3] + k[Cl][O_3] + k[I][O_3] + k[O(^1D)][H_2O]$  (3)  
484  $+ k[OH][O_3] + k[HO_2][O_3] - k[BrO][NO] - J[BrO]$   
485  $- k[ClO][NO] - J[ClO] - k[IO][NO] - J[IO]$ 

While we recognize that considering only the sum of the rates of XO + XO reactions (where X =Br, Cl, or I) has generally be used in previous studies to estimate the rate of ozone destruction (Le Bras and Platt, 1995; Platt and Janssen, 1995), we have chosen to use Equations 2 and 3 as it is likely that these complex interactions are oversimplified by the XO + XO method. Indeed, we show in a forthcoming manuscript (Thompson et al., Bromine atom production and chain propagation during springtime Arctic ozone depletion events in Barrow, Alaska, *manuscript in preparation*) that the XO + XO method underestimates chemical ozone loss by Br and Cl atoms when compared to Equation 2.

494 Figure 5 shows the fraction of the rate of O<sub>3</sub> depletion by Br and Cl for the Base, the Base 495 + Low Iodine, and the Base + High Iodine model scenarios as a diurnal average for the daytime 496 hours of only 25 and 29 – 30 March, for conditions in which  $O_3$  is > 5 ppbv, since this quantity is 497 only meaningful when  $O_3$  is present. Br accounts for the vast majority of  $O_3$  depletion in the 498 Base scenario, at about 95%, whereas Cl only accounts for 5 - 10% of ozone loss on average. In 499 the Low Iodine plot it can be seen that the levels of iodine considered (1 ppt IO) contribute more 500 to  $O_3$  destruction than does chlorine on average, with a contribution of to 20 - 40%. This also 501 decreases the Br contribution to 60 - 80%. When High Iodine is included, the relative 502 importance of Br and I switch, such that I now contributes ~60% to ozone loss, whereas Br is 503 reduced to 30 - 40%. Thus, it is clear that iodine can have a significant contribution to ozone 504 depletion even at low levels.

To investigate this in further detail, we used a focused version of our model that simulated a 1.5 h period fixed at mid-day conditions to facilitate instantaneous calculations of ozone depletion. We used chemical mole ratios similar to those of 29 March. This day has  $Br_2$  at 6.7 pptv and  $Cl_2$  at 80 pptv, and ozone at background concentrations near 30 ppbv. We chose not to use 25 March, as this day was impacted by local pollution during the first half of the day (as evidenced by  $NO_x$  and CO in Figure 1). The mid-day version of our model was run with constant molecular halogen and VOC concentrations, thus, although the conditions are similar to29 March, the results are not directly comparable.

The fractional contribution of each halogen to ozone destruction was calculated using Equation (4) for ten different model scenarios with different combinations of halogens present and with no halogens. In Equation (4), *P*, *Q*, *R*, *S*, *T*, *U*, and *V* represent the total value for model "counters" for each process in parentheses, and the denominator is the sum of chemical ozone loss terms. Because photolysis of O<sub>3</sub> can result in fast reformation of O<sub>3</sub> through the reaction of  $O(^{3}P) + O_{2}$ , the  $O(^{1}D) + H_{2}O$  reaction is used to represent the ozone that is destroyed via photolysis.

520 
$$F_{X} = \frac{P(X+O_{3}) - Q(J_{XO}) - R(XO+NO)}{P(X+O_{3}) - Q(J_{XO}) - R(XO+NO) + S(O_{3}+OH) + T(O_{3}+HO_{2}) + U(O_{3}+NO_{2}) + V(O^{1}D+H_{2}O)}$$
(4)

S21 Results of this calculation are shown in Table 6 for the scenarios studied. In addition to the S22 fraction of O<sub>3</sub> loss by each halogen, Table 6 also shows the total change in O<sub>3</sub> across the S23 simulated period ( $\Delta O_3$ ), the total O<sub>3</sub> production via the O(<sup>3</sup>P) + O<sub>2</sub> reaction, and the sum of the S24 O<sub>3</sub> loss terms (denominator of Equation 4).

525 It is clear from Table 6 that Br is the primary driver of O<sub>3</sub> loss with at least 64% contribution in all cases that it is present, reaching up to 87% in the "Br and Cl" (Base) scenario, 526 527 and 97% in the "Br Only" simulation. In the "Br and Cl" run, Cl accounts for 11.5% of the loss 528 (at Cl2 levels somewhat enhanced at 80 pptv), which is a minor, though significant, contribution. 529 On an absolute basis, the addition of chlorine chemistry also enhances the  $O_3$  depletion caused 530 by bromine, with the total ozone depleted by Br increasing from 2.21 ppbv in the Br Only 531 scenario to 3.61 ppbv in the Br and Cl scenario (data not shown). This is primarily a result of the 532 efficient cross-reaction between BrO and ClO that regenerates Br and thereby increases the

[Br]/[BrO] ratio. Comparing "Br Only" with "Br and Low I", it is apparent that iodine chemistry 533 534 directly contributes a significant amount to ozone depletion, at a fractional contribution of 11.9% 535 with just 1 ppt IO present, due to both the fast reaction between I and O<sub>3</sub>, and IO and BrO, as 536 well as the lack of known competing sinks for I. When iodine is increased, as in the "Br and 537 High I" scenario, the iodine contribution jumps to 35.0%. From examination of the fractional 538 ozone depletion, it appears that iodine chemistry decreases the Br-destruction of ozone; however, 539 on an absolute basis, there is an increase in the total amount of ozone destroyed by Br in the "Br 540 and Low I" simulation (2.55 ppbv O<sub>3</sub> destroyed) compared to the "Br Only" simulation (2.21 541 ppbv O<sub>3</sub>); this is even greater in the "Br and High I" scenario, at 3.92 ppbv O<sub>3</sub>. The  $\Delta O_3$  also 542 increases by a factor of 1.3 for the "Br and Low I" case and 2.8 for the "Br and High I" case over 543 the integrated 1.5 h simulation period. When low iodine is added to the base model, there is a 544 factor of 1.2 increase in  $\Delta O_3$ , with iodine contributing ~9% to the ozone depletion; this increases 545 to a factor of 3.3 increase in  $\Delta O_3$  and 28.8% contribution from I when high iodine is included. In 546 the "Br, Cl, and Low I" case, Cl atoms actually contribute more to the ozone depletion, however, 547 this is a function of the much higher  $Cl_2$  (80 pptv) than  $I_2$  (0.025 pptv) in this scenario. On a per 548 atom basis, iodine is more efficient than chlorine at depleting ozone. That is partly due to the 549 fact that ~50-100% of I atoms are lost via reaction with O<sub>3</sub>, while only ~20% of Cl atoms are lost 550 via O<sub>3</sub> reaction.

The presence of multiple halogen species leads to synergistic effects, where the total amount of  $O_3$  destroyed is greater than the sum of the species run in isolation. This synergism is primarily due to the efficient cross-reactions between BrO, ClO, and IO that reform  $O_3$ -depleting halogen atoms. The absolute ozone destruction by Br is enhanced more by iodine than by chlorine as a result of the very fast reaction between BrO and IO. Indeed, the increase of 1.41 556 ppbv of  $O_3$  destroyed by Br when chlorine is included ("Br and Cl" case vs. "Br Only" case) 557 corresponds to an increase of only 0.02 ppbv of  $O_3$  destroyed per pptv of  $Cl_2$ , whereas the 558 enhancement in ozone destruction by Br provided by low iodine is nearly 7 ppbv of  $O_3$  per pptv 559 of  $I_2$ . Therefore, while Cl acts primarily to enhance Br chemistry, I both increases the efficiency 560 of bromine catalyzed ozone destruction, and directly depletes ozone.

561 Chlorine is an especially interesting case because it contributes to both O<sub>3</sub> depletion 562 (though relatively minor) and O<sub>3</sub> production. Indeed, in the "Cl Only" run, there is a net increase 563 in O<sub>3</sub> that is greater than in the "No Halogens" scenario by a factor of nearly 8. This increase is 564 due to the efficient reaction of Cl with nearly all VOCs, and the resultant production of RO<sub>2</sub> and 565 HO<sub>2</sub>. Br, in contrast, does not react appreciably with most VOCs, although its reaction with 566 HCHO will also lead to HO<sub>2</sub> production, as evidenced by the increase in O<sub>3</sub> production in the 567 "Br Only" scenario compared to the "No Halogens" case. I does not react to produce HO<sub>2</sub>, thus, 568 there is no additional O<sub>3</sub> production in the "Low I Only" case, and only a slight increase in the 569 "High I Only" case, likely as a result of IO reaction with NO to form NO<sub>2</sub>. It is clear that fully 570 understanding ODE chemistry will require a complete understanding of all three halogen radical 571 families.

Platt and Janssen (1995) indicate that ~99% of Br atoms react with  $O_3$  when present at background levels, while only ~50% of Cl atoms react with  $O_3$  due to efficient reactions with many VOCs. However, this quantity is highly dependent on the mole ratios of  $O_3$ , HCHO, CH<sub>3</sub>CHO, and the VOCs, which can fluctuate independently of each other. To further investigate how the three halogens contribute to ozone depletion, we considered the fraction of available Br, Cl, and I atoms that react with  $O_3$  over all other competing pathways across the seven-day simulation with iodine included (Low Iodine) as shown in Figure 6. The inclusion of 579 iodine does not significantly change the result for Br and Cl, thus only the simulation including I 580 is shown. Br atoms were simulated to react with  $O_3$  55 – 95% of the time when  $O_3$  is not 581 depleted, but this fraction fluctuates significantly and is at times below 25% when O<sub>3</sub> is depleted 582 (i.e., < 5 ppbv). Cl atom reaction with O<sub>3</sub> varies between 10-20% on average, and is always less 583 than 30% for this time period. These numbers are lower than those estimated previously, likely 584 because we are using actual measurements of all of the known Br and Cl atom sinks that 585 contribute to this quantity, e.g. HCHO, CH<sub>3</sub>CHO, numerous VOCs and NO<sub>x</sub>. Based on our 586 chemical mechanism, I atoms can react with O<sub>3</sub> up to 100% of the time, and usually up to 90% 587 (though with high variability during O<sub>3</sub> depleted periods), consistent with the estimates of Platt 588 and Janssen (1995), who determined 99% for I. However, as stated previously, it is likely that 589 our iodine reaction scheme is incomplete, e.g. for IO reaction with peroxy radicals.

590 Not all halogen atom reactions with  $O_3$  result in a net loss of ozone. Though up to 90% 591 of Br atoms react with O<sub>3</sub>, most of these reactions do not ultimately destroy ozone as it can be 592 reformed via e.g., BrO photolysis or BrO reaction with NO. When considering only Br and Cl in 593 our mid-day model, 70% of the BrO formed regenerates O<sub>3</sub> through photolysis or reaction with 594 NO, whereas this quantity is only 12% for ClO, which photolyzes much more slowly. While this 595 suggests that Cl atoms are actually more efficient at destroying ozone on a per atom basis, the 596 lower concentration of Cl due to the numerous competing Cl-atom sinks and the low fraction of 597 Cl atoms that react with O<sub>3</sub> make it a minor player in ozone depletion. When iodine is included 598 at low levels, thus opening the BrO + IO cross-reaction, the percentage of BrO that reforms  $O_3$ 599 drops to 64% and that for IO is comparable at 65%.

600 A highly significant finding from the OASIS 2009 campaign was the observation of 601 unexpectedly high levels of  $Cl_2$  (Liao et al., 2014). Given the observed [ $Cl_2$ ] maxima of 100 – 602 400 pptv, a sensitivity study was performed to investigate the impact that such high 603 concentrations could have on ozone depletion chemistry. Table 7 shows the results of modeling 604 runs for midday of 29 March performed by varying Cl<sub>2</sub> between 25 to 400 pptv (recall that the 605 Base scenario here for 29 March has 80 pptv Cl<sub>2</sub>). These particular runs included only bromine 606 and chlorine chemistry. Here it can be seen that the high Cl<sub>2</sub> levels observed in Barrow can have 607 significant impacts on  $O_3$  depletion, with Cl atoms accounting for over 30% of  $O_3$  loss when 608 present at 400 pptv. At Cl<sub>2</sub> levels less than 100 pptv, however, Cl destruction of  $O_3$  is  $\leq 11\%$ , thus, 609 chlorine must be relatively elevated to make an appreciable impact on O<sub>3</sub> depletion. While the 610 amount of O<sub>3</sub> production also increases at higher Cl<sub>2</sub> (by an additional 0.58 ppbv O<sub>3</sub> at 400 pptv 611 Cl<sub>2</sub> compared to 25 pptv Cl<sub>2</sub>), the increase in the O<sub>3</sub> destruction by both the additional Cl atoms 612  $(2.8 \text{ ppbv } O_3)$  and by the enhanced efficiency of Br atoms through the synergy of the halogen 613 cross-reactions (4.37 ppbv  $O_3$ ), far outweighs the  $O_3$  production. Thus, when both bromine and 614 chlorine are present, our modeling results do not show indications of a "chlorine counter-cycle" 615 hindering ozone depletion as suggested by Piot and von Glasow (2009).

616 It is useful to also consider the rate of ozone depletion. Often, fast apparent ozone 617 depletions, in which O<sub>3</sub> is observed to decrease over timescales of hours, have been attributed to 618 air mass transport of ozone-depleted air, whereas local chemistry is believed to result in a more 619 gradual depletion (Bottenheim and Chan, 2006; Simpson et al., 2007; Halfacre et al., 2014). The 620 ozone depletion rate and the resulting timescale for depletion induced by Br, Cl, and I, both in 621 isolation (for Br and I) and when allowed to interact was investigated with model runs conducted 622 for "Br Only" and "I Only", as well as with different combinations of the above, including both 623 Low Iodine and High Iodine conditions. Cl was not run in isolation here, since as was shown in 624 Table 6, the "Cl Only" simulation did not result in a net loss of O<sub>3</sub>. Here, we considered only the ozone depletion rate at mid-day of 29 March, determined using the delta  $O_3$  for the 1.3 h simulation time (as shown in Table 6), to calculate the depletion timescale. Table 8 shows the resulting ozone depletion rates in ppbv·h<sup>-1</sup> for the different permutations of halogen radicals studied, along with the resultant timescale for total ozone depletion from a background of 35 ppbv to 5 ppbv, our definition of a major ODE (assuming a constant ozone depletion rate, which represents an upper limit as the rate of ozone depletion decreases as  $[O_3]$  decreases).

631 For the chemical conditions observed on this day, bromine chemistry alone is capable of depleting ozone on a timescale of 16.2 h at a rate of 1.85 ppbv  $h^{-1}$ , whereas low iodine levels 632 would require 13.9 days at a rate of 0.09  $ppbv \cdot h^{-1}$ . High iodine alone depletes ozone at a rate of 633 1.72 ppbv  $h^{-1}$  in 17.4 hours. Again, the synergy that exists between the halogen species is 634 635 apparent, such that the combination of any halogen species depletes ozone at a faster rate than 636 the sum of the components run in isolation. This is a result that was previously found for the 637 interaction of bromine and iodine in modeling studies by Calvert and Lindberg (2004a, 2004b), 638 Saiz-Lopez et al. (2008) and Mahajan et al. (2010). The greatest ozone depletion rate of 6.07  $ppbv \cdot h^{-1}$ , with a timescale for complete depletion of only 4.9 h, results when all three halogens 639 640 are present, with I<sub>2</sub> set at the High Iodine level of 0.5 pptv. Based on these results, it can be 641 concluded that iodine has the potential to have a much greater impact on ozone depletion than 642 chlorine. The combination of Br, Cl and low iodine, resulting in an 8.5 hr depletion timescale is 643 consistent with the fast-end timescales observed over the Beaufort Sea by Halfacre et al. (2014).

It should be noted, however, that the ozone lifetimes discussed above simply represent the calculated ozone lifetime, as determined from measurements conducted within the surface layer. As discussed in detail in Tackett et al. (2007), the current view of the boundary layer is one that is very chemically stratified, with the most important source of Br<sub>2</sub> and Cl<sub>2</sub> likely from 648 the snowpack surface. Thus, the concept of "boundary layer" is one that has been defined in 649 terms of the height over which ozone is observed to be depleted, i.e. typically ~400 m 650 (Bottenheim et al., 2002; Helmig et al., 2012). It is likely, however, that ozone is depleted 651 largely in the very near surface layer, and the time scale for that depletion is thus determined in 652 significant part by the time scale for downward diffusion of ozone in the 0 - 400 m range to the 653 near-surface layer in which BrO<sub>x</sub> concentrations are large. In short, when averaged over the 654 entire boundary layer, the actual ozone depletion timescale may potentially be slower than that 655 calculated here using only surface measurements, because of diffusion limitation.

656 In Table 9, we show the average ozone depletion rate (calculated as discussed for Table 657 8) for the five different scenarios with varying  $[Cl_2]$ . When  $Cl_2$  is present at only 25 pptv, the 658 timescale for depletion is 13.2 h, which is longer than for the Base model (with 80 pptv Cl<sub>2</sub>), but 659 still less than one day, primarily due to the activity of bromine. 100 pptv Cl<sub>2</sub> decreases the 660 timescale for depletion to 9.55 h, while at 400 pptv, the timescale is only 5.24 h (again assuming 661 constant  $Cl_2$  mole ratios). For comparison, the Base Model with low iodine as shown in Table 8, 662 has an ozone depletion timescale of 8.47 h, whereas the Base with high iodine has a depletion 663 timescale of 4.94 h. Thus, the presence of only 0.025 pptv of  $I_2$  has a greater effect on the ozone 664 depletion rate than does 100 pptv of Cl<sub>2</sub>, and sustained levels of Cl<sub>2</sub> greater than 400 pptv would 665 be required to have a comparable impact on ozone depletion as does 0.5 pptv  $I_2$ .

Although the depletion timescales reported here, both for base model conditions and for elevated  $[Cl_2]$ , represent relatively fast ozone depletion and, as stated, represent an upper limit assuming a constant ozone depletion rate, total ozone depletions are often observed to occur on timescales of a day or less (Tang and McConnell, 1996; Simpson et al., 2007; Halfacre et al., 2014), and a fast ozone depletion of ~7 h attributed to local chemistry was reported over the 671 Arctic Ocean by Jacobi et al. (2006). Thus, the ozone depletion rates calculated here (including 672 for elevated [Cl<sub>2</sub>]) show that rapid photochemical ozone depletion events are possible, and thus 673 one should not assume that all fast ODEs represent transport, without appropriate supporting 674 information. Back-trajectories for periods of very high [Cl<sub>2</sub>] during OASIS indicate air mass 675 transport over the surface of the Arctic Ocean (Stephens et al., 2012). Ozone instruments on-676 board the O-Buoy network of sea ice-tethered buoys (Knepp et al., 2010) in the Arctic Ocean 677 have also indicated very fast ozone depletions, with a median timescale of 10.4 hours and 678 numerous individual events much faster than that (Halfacre et al., 2014). Unfortunately, we are 679 limited by a lack of Cl<sub>2</sub> measurements from across the frozen Arctic Ocean, and thus, it is not 680 possible to speculate how widespread this elevated Cl<sub>2</sub> may be.

681

# 682 **3.3** The impact of chlorine chemistry on oxidative capacity

683 One of the primary objectives of this work was to assess the impact of chlorine on 684 bromine chemical cycles relating to ODEs in light of the recent discovery of unexpectedly high 685 [Cl<sub>2</sub>] in Barrow during OASIS. We discussed the contribution of observed levels of chlorine to 686 ozone depletion in Section 3.2 and the impact of varying concentrations of Cl<sub>2</sub> on the rate and 687 timescale of ozone depletion. These results show that chlorine itself plays only a minor role in 688 the direct destruction of ozone until  $Cl_2$  reaches over 100 pptv. That Cl atoms do not directly 689 contribute significantly to ozone depletions is not surprising, given their lower ambient 690 concentration compared to Br (see Figure 2), due to the multitude of Cl atom sinks. In the model, 691 the rate of Cl atom production from Cl<sub>2</sub> and BrCl (assumed to be surface emitted species) is also 692 on average only 20% of the rate of Br production from Br<sub>2</sub> and BrCl. The Br/Cl ratio for the 693 Arctic has been estimated to range from 80 to 1200 when ozone is not fully depleted (Jobson et

694 al., 1994; Keil and Shepson, 2006; Cavender et al., 2008) based on observations of halocarbons 695 and hydrocarbon decay. Our model predicts daytime Br/Cl ratios for non-O<sub>3</sub> depleted days 696 ranging from a low of 18 up to 1300, consistent with previous estimates. When ozone is fully 697 depleted (i.e., < 5 ppbv), [Br] becomes much greater than [BrO], due to the loss of its primary 698 atmospheric sink and the resultant lack of production of BrO, and the Br/Cl ratio increases dramatically to  $8x10^3 - 2.5x10^5$ . During these periods when the ozone concentration is low, 699 700 CH<sub>3</sub>CHO becomes an important Br atom sink, with a rate of reaction with Br comparable to that 701 of  $Br + O_3$  (Figure 7). This supports the hypothesis by Shepson et al. (1996) that aldehydic 702 compounds, including CH<sub>3</sub>CHO, represent important Br sinks during ODEs. HCHO is at times a 703 major Br atom sink, but only when ambient concentrations are high enough to compete with 704 CH<sub>3</sub>CHO (e.g., towards the second half of 28 March where [HCHO]/[CH<sub>3</sub>CHO] =  $\sim 0.8$ ). 705 Interestingly, NO<sub>2</sub> also represents a major Br sink during ODEs. In comparison to other Arctic 706 locations, Barrow can have relatively high NO<sub>x</sub>, and thus NO<sub>2</sub> would likely not be as important a 707 Br sink in more pristine Arctic environments. A detailed study into the impact of these increased 708 NO<sub>x</sub> levels in Barrow is the subject of Custard et al. (2015), and thus is not discussed extensively 709 here.

Although Cl chemistry can generate HCHO and CH<sub>3</sub>CHO in the gas phase through oxidation of methane and ethane, respectively (e.g., Reactions R13 – R15), it is likely not the case that these important Br sinks are the result of such reactions during ODEs. From the time series of ambient Cl<sub>2</sub> observations (Figure 1A), and as discussed in Liao et al. (2014), it is apparent that substantial mole ratios of Cl<sub>2</sub> are only observed when O<sub>3</sub> and radiation are present. When O<sub>3</sub> is fully depleted during 26 - 28 March, Cl<sub>2</sub> is nearly absent. Moreover, the efficiency of production of HCHO and CH<sub>3</sub>CHO is NO<sub>x</sub>-dependent, with hydroperoxide production more important at low NO<sub>x</sub> levels typical of more remote Arctic environments. Thus, while some significant gas-phase production of HCHO and CH<sub>3</sub>CHO can occur if [Cl] is high (Sumner et al., 2002), it is far more likely that in the Arctic, surface concentrations of these compounds are primarily derived from snowpack emissions (Grannas et al., 2007; Barret et al., 2011). The production of HCHO and CH<sub>3</sub>CHO from the snowpack has been documented in previous studies (Sumner and Shepson, 1999; Grannas et al., 2002) and strong vertical fluxes of both compounds were observed during OASIS (Barret et al., 2011; Gao et al., 2012).

724 As discussed previously, and shown in Figure 6, only a small fraction of available Cl 725 atoms react with  $O_3$ . This is due to the very efficient reactions of Cl with numerous organics, 726 with rate constants much faster than analogous oxidation by OH. In Figure 8, we investigate the 727 most important Cl atom sinks. Indeed, reaction with organic compounds dominates the Cl atom 728 reactivity for both non-ODE and ODE days. Reactions with reduced hydrocarbons (red trace) 729 are the primary sink under both circumstances, at 63% and 78% respectively. When O<sub>3</sub> is present, 730 the  $O_3$  reaction sink accounts for ~27% of Cl atom reaction (calculated as the median across 29) 731 and 30 March), with oxygenated organic compounds (OVOCs) accounting for 9%. When ozone 732 is depleted, the OVOCs make up 22% of the Cl atom reactivity. The remaining sinks (i.e., HO<sub>x</sub>, 733 NO<sub>v</sub>, and other inorganic halogen compounds) are insignificant in comparison. Thus, one of the 734 most important impacts of Cl chemistry in this environment is its direct contribution to the 735 oxidative capacity of the near surface boundary layer via oxidation of organic compounds.

Based on the reaction scheme shown in R13 - R15, and similar VOC oxidation pathways involving Cl atoms, Cl chemistry generates HO<sub>2</sub> as a by-product, a very significant BrO sink (though relatively unimportant for Br atoms) and itself an important atmospheric oxidant; however, this too is dependent on NO<sub>x</sub>. It has been suggested that the presence of chlorine will 740 significantly increase HO<sub>2</sub> (Rudolph et al., 1999; Piot and von Glasow, 2009). Figure 9A 741 presents results of a sensitivity study in which simulations with different combinations of 742 halogens present were performed to investigate the impact on HO<sub>2</sub>. For days when O<sub>3</sub> is not 743 fully depleted (i.e., 25, 29, and 30 March), and when Cl<sub>2</sub> is present, the "Cl Only" simulation results in HO<sub>2</sub> concentrations up to  $3 \times 10^8$  molecules cm<sup>-3</sup> (~10 pptv) for [Cl<sub>2</sub>] nearing 100 pptv 744 745 (March 29 and 30). Especially for 29 and 30 March, it is apparent that the "Br Only" simulations have much lower daytime HO<sub>2</sub>, generally remaining below  $1 \times 10^8$  molecules cm<sup>-3</sup>. When Cl<sub>2</sub> is 746 present (i.e., when O<sub>3</sub> is not depleted), the "Cl Only" simulation is nearly indistinguishable from 747 748 the Base model, indicating the chlorine is dominating the halogen contribution to  $HO_2$ . However, 749 in some cases, specifically when  $O_3$  is depleted (and thus  $Cl_2$  is absent as discussed above)  $HO_2$ 750 is indistinguishable from a "Br Only" case. During the 26-28 March period, there would be little 751 HO<sub>x</sub> production from O<sub>3</sub> photolysis, and as Cl<sub>2</sub> is also nearly absent, bromine chemistry and 752 photolysis of HOx precursors from the snowpack (e.g., HCHO or HONO) become the primary 753 sources of HO<sub>x</sub> production.

754 The production of HO<sub>2</sub> as a result of chlorine chemistry is also apparent when examining 755 the [HO<sub>2</sub>]/[OH] ratio in simulations performed with and without chlorine. Table 10 presents 756 [HO<sub>2</sub>]\[OH], [BrO]\[Br], [ClO]\[Cl], and [IO]\[I] ratios, calculated for mid-day of 29 March, for 757 a variety of model scenarios with no halogen chemistry and different combinations of halogens 758 present. When halogen chemistry was excluded from the model, the [HO<sub>2</sub>]\[OH] ratio was 115; 759 this nearly doubled to 230 when only chlorine chemistry was added. This effect is in contrast to 760 the "Br Only", "Low Iodine Only", and "High Iodine Only" simulations, where the addition of 761 bromine or iodine served to decrease the [HO<sub>2</sub>]/[OH] ratio. Futhermore, the addition of chlorine to any scenario shifted this ratio towards HO2. For example, "Br Only" decreased this ratio from 762

763 115 to 63; upon the addition of chlorine for the "Br and Cl (Base)" scenario, the ratio was 764 increased to 104. It is important to note that NO<sub>x</sub> chemistry has a very significant impact on both 765 HO<sub>x</sub> and halogen chemistry. For these calculations NO and NO<sub>2</sub> were held constant (at 25 and 50 766 ppty, respectively) so that we could investigate the impacts of just adding or removing halogens 767 without concomitant changes in  $NO_x$ . If  $NO_x$  is not constrained, the removal of halogens has the 768 effect of leading to increased  $NO_x$  levels (through removal of this sink), which then decreases 769  $HO_x$ . This leads to a confounding influence on the  $HO_x$  ratio that is due to increased  $NO_x$ 770 chemistry rather than removal of halogens.

771 To investigate further, time-varying rates of production of OH and HO<sub>2</sub> were determined 772 from their primary source reactions (Figure 10). Under our modeling conditions for the 7 days 773 studied, when  $O_3$  is not fully depleted,  $HO_x$  is produced primarily through photolysis of HONO 774 (as postulated by Zhou et al., 2001 and Villena et al., 2011) and as a product of Br reaction with 775 HCHO (orange and blue traces in Figure 8, 29% and 41% respectively for 30 March), with 776 significant production from photolysis of HCHO (15% for 30 March), as well, confirming the 777 importance of snowpack-emitted carbonyl compounds for the oxidation capacity of the Arctic 778 boundary layer (Sumner and Shepson, 1999). When O<sub>3</sub> is fully depleted, HCHO is the primary 779 direct HO<sub>x</sub> source via reaction with Br (84% for 27 March). This result explains the observation 780 in Figure 8A, that on O<sub>3</sub>-depleted days, the "Br Only" and Base simulations give essentially 781 identical results for [HO<sub>2</sub>]. Although these modeling results clearly indicate that Br oxidation is 782 the dominant HO<sub>2</sub> source during ODEs, the absolute value of the HO<sub>2</sub> production from this 783 pathway during the ozone-depleted days should be regarded as an upper limit, since, as explained 784 previously, the uncertainty in the BrO measurements is high during this time and it is possible that [Br] is somewhat overestimated. Indeed, this is likely the reason behind the high bias of the model  $HO_2$  compared to measurements for 26 - 28 March (Figure 2G).

Finally, an additional significant impact of chlorine chemistry on the oxidation capacity of the polar boundary layer (PBL) is the production of RO<sub>2</sub> through Reaction R13 and analogous oxidation reactions with higher order hydrocarbons. RO<sub>2</sub> reaction with BrO can also lead to production of HOBr through Reaction R17, which could enhance the heterogeneous production of Br through HOBr deposition and the bromine explosion mechanism.

792 BrO + R-CH<sub>2</sub>OO 
$$\rightarrow$$
 HOBr + R-CHOO (R17)

793 However, the presence of chlorine chemistry also decreases the [BrO]/[Br] ratio through the BrO 794 + ClO reaction, so Reaction R17 may affect [HOBr] most under certain chemical conditions (e.g., 795 lower [ClO]). [RO<sub>2</sub>] (calculated as the sum of methyl through butyl forms) for simulations 796 conducted with and without chlorine is shown in Figure 9B. This figure illustrates that when Cl<sub>2</sub> 797 is high, i.e. 25, 29, and 30 March, there is sometimes a large impact on RO<sub>2</sub>, as can by seen by 798 comparing the "Br Only" case (blue trace) with Base model (black trace). Again, [Cl<sub>2</sub>] is very 799 low when ozone is depleted, so simulated [RO<sub>2</sub>] during ozone-depleted days becomes nearly 800 indistinguishable for the Base and "Br Only" scenarios, as was shown already for HO<sub>2</sub>. These 801 results support the hypothesis that Cl can substantially increase the oxidation capacity of the 802 Arctic troposphere when present at elevated mixing ratios. The levels of  $RO_2$  that are present 803 when Cl is not included in the model are primarily a result of both Br- and OH-oxidation 804 chemistry; the RO<sub>2</sub> spike on 31 March that is seen in the "Br Only' simulation, for example, is a 805 result of the observed spike in  $CH_3CHO$  and reaction with Br. The impact of the increased  $RO_2$ 806 due to Cl chemistry appears to be less significant as a BrO sink, however, as CH<sub>3</sub>OO (the 807 dominant RO<sub>2</sub> species) represents only a minor sink for BrO (Thompson et al., *manuscript in* 

808 *preparation*), and BrO is likewise a minor sink for  $CH_3OO$  in comparison to  $HO_2$  and NO 809 (median sink contribution of BrO to  $CH_3OO$  is 0.05%).

810 Based on our analysis, it appears possible that the presence of chlorine can promote the 811 production of reactive bromine species through two distinct mechanisms: 1) oxidation chemistry 812 due to chlorine, which under certain chemical conditions can (e.g., high  $Cl_2$ , elevated  $NO_x$ ) 813 increase [HO<sub>2</sub>] and/or [RO<sub>2</sub>], thereby increasing the production of HOBr, and thus, the 814 heterogeneous recycling of bromine, and 2) gas-phase HOCl can react with Br<sup>-</sup> in the aqueous 815 phase to produce BrCl, thus producing reactive bromine (though this pathway is not as 816 significant for Br atom production as is Br<sub>2</sub>). Conversely, the presence of both chloride and 817 bromide ions in the aqueous phase can lead to a competition between the production of Br<sub>2</sub>, BrCl, 818 or Cl<sub>2</sub>. When we initially ran our model with only heterogeneous production of molecular 819 halogens, large increases in gas-phase [Br] were produced when aerosol chloride was decreased 820 by three orders of magnitude, but no difference in [Br] occurred when snowpack phase chloride 821 was decreased by an equivalent amount. The snowpack is by far the primary source of both Br 822 and Cl atom precursors in our model, as shown in Michalowski et al. (2000); however, the 823 greater sensitivity to the aerosol chloride loading suggests that the aerosol could be a potentially 824 important source of Cl atom precursors to the atmosphere. This may likely be related to the 825 aerosol pH. Laboratory and field studies would be required to test this hypothesis. It is clear that 826 the interactions between bromine and chlorine are quite complex in that chlorine chemistry can 827 produce reactive bromine sinks (when at elevated concentrations), but the presence of chlorine 828 can also increase Br atom production under certain circumstances, thereby increasing the rate of 829 ozone depletion in an indirect fashion.

830
## 831 **3.4** The impact of iodine chemistry and bromine-iodine interactions

832 Several modeling studies have also investigated the potential impact of iodine on ozone 833 depletion in the troposphere (e.g., (Chameides and Davis, 1980; Davis et al., 1996; Sander et al., 834 1997; Calvert and Lindberg, 2004b; Saiz-Lopez et al., 2008)), in each case concluding that it 835 could be very important. Iodine is potentially one of the most important species in Arctic ozone 836 chemistry, and yet there is very little observational information. To date, no conclusive 837 measurements of IO in the High Arctic have been achieved, though recently our group has 838 detected substantial concentrations of I<sub>2</sub> in the snowpack air in Barrow with CIMS (Raso et al., 839 2015), thus, there is evidence that iodine chemistry is present to some extent.

840 As discussed in section 3.2, iodine chemistry can greatly enhance the rate of ozone 841 depletion, both through the direct reaction of I with ozone (given that ozone is the primary I atom 842 sink, Figure 4) and through the indirect effect of increasing available Br atoms through the cross-843 reaction of IO and BrO. This can be seen in Table 10, where it is shown that the [BrO]/[Br] ratio 844 is decreased from 7.65 in the "Br Only" simulation to 7.34 or 6.12 upon addition of low iodine or 845 high iodine levels, respectively. In a similar fashion, iodine chemistry also shifts the  $ClO_x$ 846 partitioning, decreasing the mid-day [CIO]\[CI] for 29 March from 247 in the base model (Br and 847 Cl) to 244 or 230 when low or high levels are iodine are present, respectively, due to the IO + 848 ClO reaction and decreased  $[O_3]$ . The decreased  $[ClO]\setminus[Cl]$  ratio could then impact the radical 849 distribution through RO<sub>2</sub> production. The  $[IO] \setminus [I]$  ratio is much lower than either the BrO<sub>x</sub> or 850 ClO<sub>x</sub> ratio due to fast photolysis of IO and far fewer known I atom sinks (Vogt, 1999). Under 851 the conditions employed here on 29 March, the [IO]\[I] ratio ranges from 1.57 to 2.60.

Previous modeling studies have concluded that iodine chemistry can impact the partitioning of important atmospheric oxidants by decreasing the [HO<sub>2</sub>]\[OH] ratio through the 854 formation of HOI and subsequent photolysis. The rate constant for the  $IO + HO_2$  reaction is a 855 factor of ~2.5 and 10 faster than the analogous BrO and ClO reactions, respectively, thus, iodine 856 has the potential to have a significant impact on the [HO<sub>2</sub>]\[OH] ratio, and HO<sub>2</sub> can represent a 857 primary IO sink during periods of low [IO] and [BrO] (Vogt, 1999). As mentioned above and 858 shown in Table 10, the [HO<sub>2</sub>]/[OH] ratio at mid-day on 29 March with no halogens present is 859 115. The presence of bromine alone decreases this ratio to 63, and inclusion of iodine further 860 decreases this to 60.8 or 53.1 when at low or high levels, respectively. There of course can be 861 wide variability in the absolute ratios depending on specific chemical conditions, such as NO<sub>x</sub> or 862 VOC levels. Saiz-Lopez et al. (2007b) determined a [HO<sub>2</sub>]/[OH] ratio of 33 due to bromine-863 iodine chemistry in Antarctica.

864 The decrease in the ClO<sub>x</sub> ratio affected by iodine could also impact the oxidizing capacity 865 of the PBL. In fact, we see a slight increase in [RO<sub>2</sub>] when iodine is present at high levels in the 866 multiday model, with a greater increase during O<sub>3</sub>-depleted days when iodine is included (green 867 trace, Figure 9B). Because iodine atoms do not oxidize VOCs, the increased RO<sub>2</sub> is likely a 868 result of the combined effects of a shift in the ClO<sub>x</sub> ratio toward Cl, and a shift in the HO<sub>x</sub> ratio 869 toward OH, resulting in a decrease of RO<sub>2</sub> sinks, and increase in production. These impacts 870 suggest an important indirect role for iodine in mediating the oxidation potential of the PBL, in 871 the presence of the other halogens.

We note, however, that the observed  $[Cl_2]$  and  $[Br_2]$  are lower during ozone-depleted days, than during non-ozone depleted days. This suggests a surface activation mechanism controlled by O<sub>3</sub>, presumably in part through a snowpack halogen explosion mechanism, such as has been observed in laboratory studies by, e.g., Oum et al. (1998a, 1998b) and the recent Pratt et al. (2013) study using natural Barrow snow. In our model, because the production mechanism of 877  $I_2$  is undefined and we have no observations with which to compare, the  $I_2$  flux is of the same 878 magnitude each day, independent of  $[O_3]$ . Therefore, during the  $O_3$  depleted days when  $[Br_2]$ 879 and [Cl<sub>2</sub>] are much reduced, iodine chemistry becomes dramatically more important in relative 880 terms. However, laboratory studies have indicated that I<sub>2</sub> can be produced via O<sub>3</sub> oxidation of 881 aqueous iodide (Garland and Curtis, 1981; Martino et al., 2009; Carpenter et al., 2013). If it 882 were indeed the case that I<sub>2</sub> is also produced through an O<sub>3</sub>-mediated activation mechanism, this 883 would likely eliminate the large difference between depleted and non-depleted days that is seen 884 here. More studies are required to determine the dominant mechanism and kinetics for the 885 heterogeneous surface production of I<sub>2</sub>.

886 As discussed previously, the calculations in Table 10 were performed by fixing NO and NO2 concentrations so that we could investigate halogen impacts on HOx. However, we did 887 888 examine the impact of halogen chemistry on the [NO<sub>2</sub>]/[NO] ratio. This was performed simply 889 by initiating the model with NO and NO<sub>2</sub> mole ratios of 25 and 50 pptv, respectively, and then 890 allowing them to freely evolve. For these sensitivity studies, the presence of halogen chemistry 891 in our model increased the [NO<sub>2</sub>]/[NO] ratio, primarily through Reaction R16, though Cl 892 chemistry can further increase this ratio through the production of RO<sub>2</sub> (e.g., Reactions R13 – 893 R14). However, though bromine increases the mid-day  $NO_x$  ratio from 0.68 to 1.81 for 29 894 March compared to a model run conducted with no halogens, the further addition of low iodine 895 only increases it to 1.85. The absolute concentrations of [NO<sub>2</sub>] and [NO] both decrease with the 896 addition of halogens, but the [NO<sub>2</sub>]/[NO] ratio increases because XO reaction with NO is 897 generally faster than reaction with NO<sub>2</sub>. However, in the case of iodine, IO reaction with NO<sub>2</sub> is 898 faster than its reaction with NO, and I atoms also react very efficiently with NO<sub>2</sub>. Thus, chlorine 899 should have a greater effect on increasing the NO<sub>x</sub> ratio than iodine. Indeed, when the model 900 was run with bromine and chlorine (the Base scenario), the [NO<sub>2</sub>]\[NO] ratio significantly 901 increased to 8.4.

## 902 4 Conclusions

903 The goal of this work was to investigate the interactions and impacts of halogen 904 chemistry on ozone depletion using a model that is constrained to a very unique set of observed, 905 time-varying chemical conditions at the time of the event. With this approach, we have been 906 able to dissect some of the important chemical pathways pertaining to ODEs, focusing on the 907 interactions between the halogen radicals. It is clear that the interactions between bromine, 908 chlorine, and iodine are very complex and highly dependent on the concurrent conditions of 909 relevant species, such as O<sub>3</sub>, HO<sub>x</sub>, NO<sub>x</sub>, and the VOCs. As these species fluctuate, the 910 partitioning of halogen species will also change, and so too will their impact on chemistry of the 911 PBL. Thus, a full understanding of halogen chemistry requires the careful measurement of all 912 these species (including Cl<sub>2</sub>, Br<sub>2</sub>, HOBr and HOCl).

913 This work has demonstrated that bromine chemistry is clearly the dominant destruction 914 pathway for ozone depletion episodes, but that chlorine and, especially, iodine, can contribute 915 significantly to both the rate and timescale of ozone depletion. The new observations of high 916 chlorine levels at Barrow potentially change the way we view ODEs. Often, observations of 917 rapid decline in ozone at various locations have been attributed to transport because bromine 918 chemistry alone was not enough to account for the ozone depletion rate (Hausmann and Platt, 919 1994; Tuckermann et al., 1997; Bottenheim et al., 2002). As we have shown, complete ozone 920 depletions can occur on timescales of much less than a day, and at elevated chlorine levels, even 921 as short as several hours. This result suggests that more of the ODEs that are observed could be 922 the result of local scale chemistry, however, as noted previously, our calculated timescales for

923 ozone depletion are based upon measurements conducted within the near surface layer and may 924 not necessarily reflect the overall depletion timescale through the boundary layer. While 925 chlorine is clearly not necessary to cause ozone depletion, it can impact the rate of ozone 926 depletion through synergistic effects of cross-reactions that enhance Br atom recycling. 927 Moreover, the presence of elevated chlorine levels can impact important Arctic chemical budgets, 928 including HO<sub>x</sub>, NO<sub>x</sub> and VOCs, with implications for the oxidative capacity of the PBL. More 929 field measurements, including over the frozen Arctic Ocean, are necessary to evaluate the 930 ubiquity of these elevated chlorine levels. In light of these new data, it is crucial that future 931 Arctic modeling studies take into account the activity of chlorine.

In our model, we prescribed a  $Cl_2$  mixing ratio that was varied from 25 pptv – 400 pptv for 29 March in sensitivity studies to investigate the impact of elevated  $Cl_2$ . However, we also determined the  $Cl_2$  fluxes that would be necessary to produce the desired gas-phase [ $Cl_2$ ]. In our model, volumetric fluxes ranging from  $5.5 \times 10^5$  molecules  $\cdot$  cm<sup>-3</sup>  $\cdot$  s<sup>-1</sup> to  $1.45 \times 10^6$ 

molecules  $cm^{-3} s^{-1}$  were required. If we assume a boundary layer mixing height of 300 m, the 936 corresponding surface fluxes would be  $1.65 \times 10^{10} - 4.35 \times 10^{10}$  molecules cm<sup>-2</sup> s<sup>-1</sup>. Similarly, the 937 fluxes necessary for Br<sub>2</sub> range from  $1.0 \times 10^3 - 9.0 \times 10^6$  molecules cm<sup>-3</sup> s<sup>-1</sup>. These numbers are 938 939 consistent with those used by Piot and von Glasow (2009). However, there are no Br<sub>2</sub> or Cl<sub>2</sub> 940 measurements aloft of the surface in the Arctic. Utilizing the method of Guimbaud et al. (2002), 941 the effective mixing height,  $Z^*$ , for Cl<sub>2</sub> at midday is only 2.15 m, making the calculated Cl<sub>2</sub> fluxes  $1.2 \times 10^8 - 3.1 \times 10^8$  molecules cm<sup>-2</sup>·s<sup>-1</sup>; Z\* for Br<sub>2</sub> is 0.5 m, leading to a calculated Br<sub>2</sub> flux 942 of 5.0 x  $10^4 - 4.5$  x  $10^8$  molecules cm<sup>-2</sup>·s<sup>-1</sup>. Therefore, field studies aimed at determining the 943 944 magnitude of the surface flux of Cl<sub>2</sub> and Br<sub>2</sub> are warranted. This disparity also points out the 945 importance of measurements of the vertical profiles of molecular halogens above the 946 snowpack/sea ice surface.

947 Finally, we find that iodine could be the most efficient halogen for depleting ozone on a 948 per atom basis, given our assumed fluxes. We assume very low [IO] in our model ( $\leq 1$  pptv), 949 below the detection limit of the DOAS instrumentation, and yet the resulting enhancements in 950 ozone depletion are quite significant. Higher levels of iodine would certainly have a dramatic 951 effect on ozone chemistry, as illustrated by our simulations incorporating 0.5 pptv I<sub>2</sub> (~10 pptv 952 IO). A possible mechanism for the production of  $I_2$  in the polar regions is the activity of ice 953 algae and phytoplankton that produce iodine-compounds, which are then wicked to the surface 954 through brine channels (Mahajan et al., 2010). It has also been suggested that the primary 955 productivity in Antarctic ice and waters may be higher than in the Arctic (Arrigo et al., 1997; 956 Gosselin et al., 1997; Lizotte, 2001; Mahajan et al., 2010), possibly accounting for the difference 957 in apparent iodine activity between the two poles. However, as the ice in the Arctic continues to 958 thin, and as more multiyear ice has been replaced by seasonal sea ice (Nghiem et al., 2012), the 959 algae and phytoplankton productivity in the Arctic has increased (Arrigo et al., 2008; Arrigo et 960 al., 2012). This could lead to an increase in iodine emissions in the future, and thus to a greater 961 occurrence of springtime ODEs. The further development of analytical methods capable of 962 measuring the very low [IO] and [I<sub>2</sub>] potentially present in the Arctic should be a high priority 963 for the further advancement of this research.

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**Table 1.** Gas-phase chemical reactions used in the model. All rate constants are calculated for a temperature of 248 K unless otherwise noted and are expressed in units of  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>.

1563	Reaction	Rate Constant	Reference
1564	$O(^{1}D) + M \rightarrow O(^{3}P)$	7.22 x 10 <sup>-11</sup>	Dunlea et al. (2002)
1565	$O(^{3}P) + O_{2} \rightarrow O_{3}$	$2.12 \times 10^{-14}$	Atkinson et al. (2004)
1566	$O(^{1}D) + H_{2}O \rightarrow 2OH$	$2.2 \times 10^{-10}$	Atkinson et al. (2004)
1567	$OH + O_3 \rightarrow HO_2$	$3.84 \times 10^{-14}$	Atkinson et al. (2004)
1568	$OH + HO_2 \rightarrow H_2O$	$1.34 \ge 10^{-10}$	Atkinson et al. (2004)
1569	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$1.52 \times 10^{-12}$	Atkinson et al. (2004)
1570	$OH + O(^{3}P) \rightarrow O_{2}$	$3.74 \times 10^{-11}$	Atkinson et al. (2004)
1571	$OH + OH \rightarrow H_2O + O(^3P)$	$1.74 \times 10^{-12}$	Atkinson et al. (2004)
1572	$OH + OH \rightarrow H_2O_2$	$1.86 \ge 10^{-11}$	Atkinson et al. (2004)
1573	$OH + NO_3 \rightarrow HO_2 + NO_2$	$2.0 \times 10^{-11}$	Atkinson et al. (2004)
1574	$HO_2 + NO_3 \rightarrow HNO_3$	$4.0 \times 10^{-12}$	Atkinson et al. (2004)
1575	$HO_2 + O_3 \rightarrow OH + 2O_2$	$1.39 \times 10^{-15}$	Atkinson et al. (2004)
1576	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.58 \times 10^{-12}$	Atkinson et al. (2004)
1577			
1578	$NO + OH \rightarrow HONO$	3.49 x 10 <sup>-11</sup>	Atkinson et al. (2004)
1579	$NO + HO_2 \rightarrow NO_2 + OH$	9.59 x 10 <sup>-12</sup>	Atkinson et al. (2004)
1580	$NO + O_3 \rightarrow NO_2$	$7.09 \times 10^{-15}$	Sander et al. (2006)
1581	$NO + NO_3 \rightarrow NO_2 + NO_2$	$2.98 \times 10^{-11}$	Sander et al. (2006)
1582	$NO_2 + OH \rightarrow HNO_3$	$1.2 \times 10^{-10}$	Atkinson et al. (2004)
1583	$NO_2 + HO_2 \leftrightarrow HO_4$	f: 8.6 x 10 <sup>-12</sup> r: 1.32 x 10	$^{-4}$ Atkinson et al. (2004)
1584	$NO_2 + O_3 \rightarrow NO_3$	$6.15 \ge 10^{-18}$	Sander et al. (2006)
1585	$NO_2 + NO_3 \leftrightarrow N_2O_5$	f: 1.83 x 10 <sup>-12</sup> r: 3.76 x 1	$0^{-5}$ Atkinson et al. (2004)
1586	$NO_2 + CH_3COOO \leftrightarrow PAN$	f: 1.4 x 10 <sup>-11</sup> r: 3.1 x 10 <sup>-8</sup>	Atkinson et al. (2004)
1587	$NO_3 + NO_3 \rightarrow NO_2 + NO_2$	4.36 x 10 <sup>-17</sup>	Sander et al. (2006)
1588	$N_2O_5 + H_2O \rightarrow HNO_3 + HNO_3$	2.6 x 10 <sup>-22</sup>	Atkinson et al. (2004)
1589	HONO + OH $\rightarrow$ NO <sub>2</sub> + H <sub>2</sub> O	3.74 x 10 <sup>-12</sup>	Sander et al. (2006)
1590	$HNO_3 + OH \rightarrow NO_3 + H_2O$	$1.5 \times 10^{-13}$	Atkinson et al. (2004)
1591	$HNO_4 + OH \rightarrow NO_2 + H_2O$	$6.2 \times 10^{-12}$	Atkinson et al. (2004)
1592			
1593	$CO + OH \rightarrow HO_2 + CO_2$	2.4 x 10 <sup>-13</sup>	Atkinson et al. (2004)
1594	$CH_4 + OH \rightarrow CH_3OO + H_2O$	1.87 x 10 <sup>-15</sup>	Sander et al. (2006)
1595	$C_2H_2 + OH \rightarrow C_2H_2OH$	$7.8 \times 10^{-13}$	Atkinson et al. (2004)
1596	$C_{2}H_{6} + OH \rightarrow C_{2}H_{5}OO$	$1.18 \times 10^{-13}$	Lurmann et al. (1986)
1597	$C_2H_4 + OH \rightarrow C_2H_4OH$	$1.02 \ge 10^{-11}$	Vakhtin et al. (2003)
1598	$C_3H_8 + OH \rightarrow nC_3H_7O_2$	1.56 x 10 <sup>-13</sup>	Harris and Kerr (1988)
1599	$C_3H_8 + OH \rightarrow iC_3H_7O_2$	$6.64 \ge 10^{-13}$	Harris and Kerr (1988)
1600	$C_{3}H_{6} + OH \rightarrow C_{3}H_{6}OH$	$3.63 \times 10^{-11}$	Atkinson et al. (2004)
1601	$C_3H_6O + OH \rightarrow Products$	2.51 x 10 <sup>-11</sup>	Atkinson et al. (2004)
1602	$nC_3H_7O_2 + NO \rightarrow NO_2 + C_3H_6O + HO_2$	5.4 x 10 <sup>-11</sup>	Eberhard et al. (1996)
1603	$iC_3H_7O_2 + NO \rightarrow NO_2 + CH_3COCH_3 + HO_2$	$1.2 \ge 10^{-11}$	Eberhard and Howard (1996)
1604	$nC_4H_{10} + OH \rightarrow nC_4H_9OO$	1.64 x 10 <sup>-12</sup>	Donahue et al. (1998)
1605	$iC_4H_{10} + OH \rightarrow CH_3COCH_3 + CH_3OO$	$1.65 \ge 10^{-12}$	Donahue et al. (1998)
1606	$nC_4H_9OO + NO \rightarrow n$ -Butanal + $NO_2 + HO_2$	$5.4 \times 10^{-11}$	Michalowski et al. (2000)
1607	$nC_4H_9OO + CH_3OO \rightarrow n$ -Butanal + HCHO + HO <sub>2</sub> + HO <sub>2</sub>	$6.7 \ge 10^{-13}$	Michalowski et al. (2000)
1608	$nC_4H_9OO + CH_3OO \rightarrow n$ -Butanal + $CH_3OH$	2.3 x 10 <sup>-13</sup>	Michalowski et al. (2000)
1609	$nC_4H_9OO + CH_3OO \rightarrow nC_4H_9OH + HCHO$	$2.3 \times 10^{-13}$	Michalowski et al. (2000)
1610	$CH_3OH + OH \rightarrow CH_3O$	$7.09 \times 10^{-13}$	Atkinson et al. (2004)
1611	n-Butanal + OH $\rightarrow$ Products	$2.0 \times 10^{-11}$	Michalowski et al. (2000)
1612	$CH_3OO + HO_2 \rightarrow CH_3OOH$	8.82 x 10 <sup>-12</sup>	Atkinson et al. (2004)
1613	$C_2H_5OO + HO_2 \rightarrow C_2H_5OOH$	1.12 x 10 <sup>-11</sup>	Atkinson et al. (2004)
1614	$CH_3COOO + HO_2 \rightarrow CH_3COOOH$	2.54 x 10 <sup>-11</sup>	DeMore et al. (1997)
1615	$C_2H_5OOH + OH \rightarrow C_2H_5OO$	6.0 x 10 <sup>-12</sup>	Atkinson et al. (2004)
1616	$CH_3OO + CH_3OO \rightarrow HCHO + HO_2$	3.64 x 10 <sup>-13</sup>	Lurmann et al. (1986)
1617	$CH_3OOH + OH \rightarrow HCHO + H_2O + OH$	2.54 x 10 <sup>-12</sup>	Sander and Crutzen (1996)
1618	$CH_3OOH + OH \rightarrow CH_3OO + H_2O$	6.01 x 10 <sup>-12</sup>	Sander and Crutzen (1996)

1(10	
1019	$CH_3OO + HO_2 \rightarrow CH_3OOH$
1620	$CH_3OO + NO \rightarrow HCHO + HO_2 + NO_2$
1621	$CH_{3}OO + nC_{3}H_{7}O_{2} \rightarrow HCHO + C_{3}H_{6}O + HO_{2} + HO_{2}$
1622	$CH_2OO + nC_2H_2O_2 \rightarrow C_2H_2O + CH_2OH$
1623	$CH_{0}OO + nC_{1}H_{0}O \rightarrow HCHO + nC_{1}H_{0}OH$
1674	$CH_{3}OO + HC_{3}H_{7}O_{2} \rightarrow HCHO + HC_{3}H_{7}OH$
1024	$CH_3OO + 1C_3H_7O_2 \rightarrow HCHO + CH_3COCH_3 + HO_2 + HO_2$
1025	$CH_3OO + iC_3H_7O_2 \rightarrow CH_3COCH_3 + CH_3OH$
1626	$CH_{3}OO + iC_{3}H_{7}O_{2} \rightarrow HCHO + iC_{3}H_{7}OH$
1627	$CH_{2}OO + C_{2}H_{5}OO \rightarrow CH_{2}CHO + HCHO + HO_{2} + HO_{2}$
1628	$CH_{2}OO + CH_{2}OOO \rightarrow HCHO + CH_{2}OO + HO_{2}$
1650	$C \parallel OO + NO \rightarrow C \parallel C \parallel O + HO + NO$
1620	$C_2 H_5 OO + NO - CH_3 CHO + HO_2 + NO_2$
1030	$C_2H_5OO + HO_2 \rightarrow C_2H_5OOH$
1031	$C_2H_5OO + CH_3COOO \rightarrow CH_3CHO + CH_3COO + HO_2$
1632	$iC_3H_7O_2 + HO_2 \rightarrow iPerox$
1633	$nC_{3}H_{2}O_{2} + HO_{2} \rightarrow nPerox$
1634	$HCHO + OH \rightarrow HO_2 + CO$
1635	$HCHO + HO \rightarrow HOCHO$
1626	$HCHO + HO_2 \rightarrow HOCH_2O_2$
1630	$HCHO + NO_3 \rightarrow HNO_3 + HO_2 + CO$
103/	$CH_3CHO + OH \rightarrow CH_3COOO + H_2O$
1638	$CH_3CHO + NO_3 \rightarrow HNO_3 + CH_3COOO$
1639	$CH_3COCH_3 + OH \rightarrow H_2O + CH_3COCH_2$
1640	$HOCH_2O_2 + NO \rightarrow HCOOH + HO_2 + NO_2$
1641	HOCH $O + HO \rightarrow HCOOH + HO$
16/12	HOCH O + HOCH O > HOOOH + HOOOH + HO = HO
1642	$HOUR_2O_2 + HOUR_2O_2 \rightarrow HOUH + HOUH + HO_2 + HO_2$
1043	$HCOOH + OH \rightarrow HO_2 + H_2O + CO_2$
1644	$CH_3COOO + NO \rightarrow CH_3OO + NO_2 + CO_2$
1645	$CH_3COOO + HO_2 \rightarrow CH_3COOH + O_3$
1646	$CH_2COOO + CH_2COOO \rightarrow CH_2COO + CH_2COO$
1647	
16/9	
1640	$Cl_2 + OH \rightarrow HOCI + Cl$
1049	$CI + O_3 \rightarrow CIO$
1620	$Cl + H_2 \rightarrow HCl$
1651	$Cl + HO_2 \rightarrow HCl$
1652	$Cl + HO_2 \rightarrow ClO + OH$
1653	$C_1 + H_2O_2 \rightarrow HC_1 + HO_2$
1654	$C_1 + N_0 \rightarrow C_1 + N_0$
1655	$CI + NO_3 \neq CIO + NO_2$
1055	$CI + CH_4 \rightarrow HCI + CH_3OO$
1020	$Cl + C_2H_6 \rightarrow HCl + C_2H_5OO$
1657	$Cl + C_2H_4 \rightarrow HCl + C_2H_5OO$
1658	$Cl + MEK \rightarrow HCl$
1659	$Cl + C_{2}H_{2} \rightarrow ClC_{2}CHO$
1660	$C_1 + C_2 H_2$ $\rightarrow$ $U_1 + C_2 H_2$
1661	$CI + CJI = \sum_{i=1}^{n}  CI  +  CJI  = CII = C$
1662	$CI + C_3H_8 \rightarrow HCI + iC_3H_7O_2$
1002	$Cl + C_3H_8 \rightarrow HCl + nC_3H_7O_2$
1663	$Cl + C_3H_6O \rightarrow HCl$
1664	$Cl + iC_4H_{10} \rightarrow HCl + C_4H_9$
1665	$Cl + nC_4H_{10} \rightarrow HCl + C_4H_0$
1666	$Cl + n$ Butanal $\rightarrow$ HCl + Products
1667	CI + HCHO = NHCI + HO + CO
1669	$CI + CH CHO \rightarrow HCI + CH COOO$
1000	$CI + CH_3CHO \rightarrow HCI + CH_3COOO$
100%	$Cl + CH_3COCH_3 \rightarrow HCl + CH_3COCH_2$
16/0	$Cl + CH_3OOH \rightarrow CH_3OO + HCl$
1671	$Cl + CH_3OOH \rightarrow CH_2OOH + HCl$
1672	$C1 + CHBr3 \rightarrow HC1 + Br + CBr2O$
1673	$Cl + OClO \rightarrow ClO + ClO$
1674	
1674	$Cl + CINO_3 \rightarrow Cl_2 + NO_3$
10/5	$Cl + PAN \rightarrow HCl + HCHO + NO_3$
16/6	$Cl + HNO_3 \rightarrow HCl + NO_3$
1677	$Cl + NO_2 \rightarrow ClNO_2$
1678	$Cl + HBr \rightarrow HCl + Br$
ĪĞŹŎ	$C(0 + O(^{3}P) \rightarrow C(1 + O))$
1686	$C(0 + O(1 \rightarrow C) + U_2)$
1601	$ClO + OH \rightarrow Cl + HO_2$
1001	$CIO + OH \rightarrow HCI$
1682	$ClO + HO_2 \rightarrow HOCl$
1683	$ClO + CH_3OO \rightarrow Cl + HCHO + HO_2$
1684	$ClO + CH_3COOO \rightarrow Cl + CH_3OO + CO_3$
1685	$ClO + NO \rightarrow Cl + NO_2$
1686	$CIO + NO \rightarrow CINO$
1697	$CIO + CIO_2 \neq CINO_3$
1/00/	$CIO + CIO \rightarrow Cl_2$
1088	$ClO + ClO \rightarrow Cl + Cl$

$1.01 \ge 10^{-11}$	Atkinson et al. (2004)
$8.76 \times 10^{-12}$	Atkinson et al $(2004)$
6.70 x 10	
6.70 x 10 <sup>13</sup>	Lightfoot et al. (1992)
2.3 x 10 <sup>-13</sup>	Lightfoot et al. (1992)
$2.3 \times 10^{-13}$	Lightfoot et al (1992)
1.2 10 <sup>-14</sup>	$L_{1}^{-1}$
1.2 x 10	Lightfoot et al. (1992)
4.1 x 10 <sup>-15</sup>	Lightfoot et al. (1992)
$4.1 \times 10^{-15}$	Lightfoot et al. (1992)
4.1 X 10	
$2.0 \times 10^{-15}$	Kirchner and Stockwell (1996)
$1.58 \times 10^{-11}$	Kirchner and Stockwell (1996)
$9.69 \times 10^{-12}$	Lurmonn et al. (1096)
8.08 × 10	Luimann et al. (1980)
$9.23 \times 10^{-12}$	Atkinson et al. (2004)
$4.0 \ge 10^{-12}$	Michalowski et al. (2000)
$0.22 \times 10^{-12}$	Michalowski at al. (2000)
9.25 X 10	Witchalowski et al. (2000)
9.23 x 10 <sup>-12</sup>	Michalowski et al. (2000)
9.3 x 10 <sup>-12</sup>	Atkinson et al. (2004)
$7.53 \times 10^{-14}$	Sander et al (2006)
7.55 X 10	$D_{1} = \frac{1}{2000}$
5.8 x 10 <sup>10</sup>	DeMore et al. (1997)
1.98 x 10 <sup>-11</sup>	Atkinson et al. (2004)
$1.4 \times 10^{-15}$	DeMore et al $(1997)$
1.27 10-13	
1.3/X 10	Atkinson et al. (2004)
8.68 x 10 <sup>-12</sup>	Lurmann et al. (1986)
$2.0 \times 10^{-12}$	Lurmann et al (1986)
1.0 x 10 <sup>-13</sup>	
1.0 X 10	Lurmann et al. (1986)
4.0 x 10 <sup>-15</sup>	DeMore et al. (1997)
2.4 x 10 <sup>-11</sup>	Atkinson et al. (2004)
$1.87 \times 10^{-11}$	Kirchner and Stockwell (1996)
$2.5 \times 10^{-11}$	Kirahnar and Staakwall (1006)
2.3 X 10	Kirchiller allu Stockwell (1990)
$2.85 \times 10^{-14}$	Atkinson et al. (2004)
$1.02 \ge 10^{-11}$	Atkinson et al. (2004)
$3.5 \times 10^{-15}$	Atkinson et al $(2004)$
2.57 - 10-11	$S_{\rm em} d_{\rm em} = t_{\rm eff} (2001)$
5.57 X 10	Sander et al. (2006)
$6.68 \ge 10^{-12}$	Sander et al. (2006)
2.11 x 10 <sup>-13</sup>	Atkinson et al. (2004)
2.4 x 10 <sup>-11</sup>	Atkinson et al. (2004)
$3.99 \times 10^{-14}$	Sander et al. (2006)
5.36 x 10 <sup>-11</sup>	Sander et al. (2006)
1.0 10 <sup>-10</sup>	$\begin{array}{c} \text{Sander et al.} (2000) \\ \text{Atlains an at al.} (2004) \end{array}$
1.0 X 10	Atkinson et al. (2004)
4.21 x 10 <sup>-11</sup>	Atkinson et al. (2004)
2.5 x 10 <sup>-10</sup>	Atkinson et al. (2004)
2.7 x 10 <sup>-10</sup>	Keil and Shepson (2006)
1 65 x 10 <sup>-10</sup>	DeMore et al (1997)
$1.65 \times 10^{-10}$	DeMore et al. $(1997)$
1.1 10 <sup>-10</sup>	
1.1 X 10	wallington et al. (1988)
$1.3 \times 10^{10}$	Hooshiyar and Niki (1995)
2.15 x 10 <sup>-10</sup>	Tyndall et al. (1997)
$1.1 \ge 10^{-10}$	Michalowski et al. (2000)
7 18 x 10 <sup>-11</sup>	Sander et al $(2003)$
$8.08 \times 10^{-11}$	Atkinson et al. (2004)
0.00 X 10	Atkinson et al. (2004)
1.39 x 10	Atkinson et al. (2004)
$2.36 \ge 10^{-11}$	Atkinson et al. (2004)
3.54 x 10 <sup>-11</sup>	Atkinson et al. (2004)
$2.9 \times 10^{-13}$ (at 298 K)	Kamboures et al $(2002)$
$6.25 \times 10^{-11}$	Atlainson at al. (2002)
0.55 X 10	Atkinson et al. (2004)
1.12 x 10	Sander et al. (2006)
$1.0 \ge 10^{-14}$	Tsalkani et al. (1988)
1.0 x 10 <sup>-16</sup>	Wine et al. (1988)
1.43 x 10 <sup>-12</sup> (at 298 K)	Ravishankara et al. (1988)
$4.48 \times 10^{-12}$	Nicovich and Wine (2004)
1. TO A 10	Attring $\rightarrow$
1.0 X 10	Atkinson et al. (2004)
2.45 x 10 <sup>-11</sup>	Atkinson et al. (2004)
2.37 x 10 <sup>-13</sup>	Sander et al. (2006)
8.67 x 10 <sup>-12</sup>	Atkinson et al. (2004)
2.08 x 10 <sup>-12</sup>	Sander et al. (2006)
$2.03 \times 10^{-12}$	Michalowski et al. (2000)
$2.04 \times 10^{-11}$	Atkinson et al. (2004)
$2.07 \times 10^{-12}$	Atkinson et al. $(2004)$
/.1 X 10	Atkinson et al. (2004)
1.64 x 10 <sup>-15</sup>	Atkinson et al. (2004)
1.54 x 10 <sup>-15</sup>	Atkinson et al. (2004)

1689	$ClO + ClO \rightarrow Cl + OclO$	1.40 x 10 <sup>-15</sup>	Atkinson et al. (2004)
1690	$OclO + OH \rightarrow HOCl$	1.13 x 10 <sup>-11</sup>	Atkinson et al. (2004)
1691	$OclO + NO \rightarrow ClO + H_2O$	$1.51 \ge 10^{-13}$	Atkinson et al. (2004)
1692	$HOC1 + OH \rightarrow ClO + H_2O$	$4.0 \times 10^{-13}$	Sander et al. (2006)
1693	$HCl + OH \rightarrow Cl + H_2O$	$6.84 \times 10^{-13}$	Atkinson et al. (2004)
1694	$CINO_3 + OH \rightarrow HOCI + NO_3$	$3.17 \times 10^{-13}$	Atkinson et al. $(2004)$
1695	$HOCI + O(P) \rightarrow CIO + OH$	1.7 x 10	Atkinson et al. (2004)
1697	$Br + O_2 \rightarrow BrO$	6 75 x 10 <sup>-13</sup>	Atkinson et al. (2004)
1698	$Br_2 + OH \rightarrow HOBr$	$5.0 \times 10^{-11}$	Atkinson et al. (2004)
1699	$Br + HO_2 \rightarrow HBr$	$1.25 \times 10^{-12}$	Atkinson et al. (2004)
1700	$Br + C_2H_2 \rightarrow BrCH_2CHO$	$3.7 \times 10^{-14}$	Atkinson et al. (2004)
1701	$Br + C_2H_4 \rightarrow HBr + C_2H_5OO$	1.3 x 10 <sup>-13</sup>	Atkinson et al. (2004)
1702	$Br + C_3H_6 \rightarrow HBr + C_3H_5$	$1.60 \ge 10^{-12}$	Atkinson et al. (2004)
1703	$Br + HCHO \rightarrow HBr + CO + HO_2$	$6.75 \ge 10^{-13}$	Sander et al. (2006)
1704	$Br + CH_3CHO \rightarrow HBr + CH_3COOO$	$2.8 \times 10^{-12}$	Atkinson et al. (2004)
1705	$Br + C_3H_6O \rightarrow HBr$	$9.7 \times 10^{-12}$	Wallington et al. (1989)
1700	Br + nButanal $\rightarrow$ HBr	9.7 x $10^{-12}$	Michalowski et al. (2000)
1708	$Br + CH_3OOH \rightarrow HBr + CH_3OO$	$4.03 \times 10^{13}$	Mallard et al. $(1993)$
1700	$BI + NO_2 \rightarrow BINO_2$ $Br + NO_2 \rightarrow DrONO_2$	$9.41 \times 10$ 5.22 × 10 <sup>-12</sup>	Atkinson et al. (2004)
1710	$Br + BrNO \rightarrow Br + NO$	$3.55 \times 10^{-11}$	Orlando and Tyndall (1997)
1711	$Br + BrNO_3 \rightarrow Br_2 + NO_3$ Br + BrNO_2 $\rightarrow Br_2 + NO_2$	$5 \times 10^{-11}$	Orlando et al $(2000)$
1712	$Br + BrONO \rightarrow Br_2 + NO_2$	$1 \times 10^{-12}$	Orlando et al. $(2000)$
1713	BrONO $\rightarrow$ Br + NO <sub>2</sub>	0.02	Orlando et al. (2000)
1714	$BrONO \rightarrow BrNO_2$	0.014	Orlando et al. (2000)
1715	$Br + OClO \rightarrow BrO + ClO$	$1.43 \ge 10^{-13}$	Atkinson et al. (2004)
1716	$BrO + O(^{3}P) \rightarrow Br$	4.8 x 10 <sup>-11</sup>	Atkinson et al. (2004)
1717	$BrO + OH \rightarrow Br + HO_2$	$4.93 \times 10^{-11}$	Atkinson et al. (2004)
1718	$BrO + HO_2 \rightarrow HOBr$	$3.38 \times 10^{-11}$	Atkinson et al. (2004)
1/19	$BrO + CH_3OO \rightarrow HOBr + CH_2OO$	$4.1 \times 10^{-12}$	Aranda et al. (1997)
1720	$BrO + CH_3OO \rightarrow Br + HCHO + HO_2$	$1.6 \times 10^{-12}$	Aranda et al. (1997)
1722	$BrO + CH_3COOO \rightarrow Br + CH_3COO$	$1.7 \times 10^{-2}$	Michalowski et al. (2000)
1773	$BrO + NO \rightarrow Br + NO$	$2.48 \times 10^{-11}$	Atkinson et al. (2004)
1774	$BrO + NO_2 \rightarrow BrNO_2$	$1.53 \times 10^{-11}$	Atkinson et al. $(2004)$
1725	$BrO + BrO \rightarrow Br + Br$	$2.82 \times 10^{-12}$	Sander et al. $(2004)$
1726	$BrO + BrO \rightarrow Br_2$	$9.3 \times 10^{-13}$	Sander et al. (2006)
1727	$BrO + HBr \rightarrow HOBr + Br$	$2.1 \times 10^{-14}$	Hansen et al. (1999)
1728	$HBr + OH \rightarrow Br + H_2O$	1.26 x 10 <sup>-11</sup>	Sander et al. (2006)
1729	$CH_3Br + OH \rightarrow H_2O + Br$	1.27 x 10 <sup>-14</sup>	Atkinson et al. (2004)
1730	$\mathrm{CHBr}_3 + \mathrm{OH} \xrightarrow{} \mathrm{H}_2\mathrm{O} + \mathrm{Br}$	$1.2 \ge 10^{-13}$	Atkinson et al. (2004)
1/31			~
1/32	$Cl + BrCl \leftrightarrow Br + Cl_2$	f: $1.5 \times 10^{-11}$ r: $1.1 \times 10^{-13}$	Clyne and Cruse (1972)
1737	$CI + Br_2 \leftarrow \rightarrow BrCI + Br$	f: $1.2 \times 10^{-12}$ r: $3.3 \times 10^{-12}$	Clyne and Cruse (19/2)
1735	$BrO + CIO \rightarrow BrCl$	$1.04 \times 10^{-12}$	Atkinson et al. (2004)
1736	$BrO + ClO \rightarrow Br + OclO$	$9.06 \times 10^{-12}$	Atkinson et al. (2004)
1737	$HOBr + OH \rightarrow BrO + H_2O$	$5.0 \times 10^{-13}$	Kukui et al. (1996)
1738	$HOBr + Cl \rightarrow BrCl + OH$	$8.0 \times 10^{-11}$	Kukui et al. (1996)
1739	$HOBr + O(^{3}P) \rightarrow BrO + OH$	2.12 x 10 <sup>-11</sup>	Atkinson et al. (2004)
1740			
1741	$I_2 + O(^{3}P) \rightarrow IO + I$	1.25 x 10 <sup>-10</sup> (at 298 K)	Atkinson et al. (2004)
1742	$IO + O(^{3}P) \rightarrow I$	$1.4 \ge 10^{-10}$ (at 298 K)	Atkinson et al. (2004)
1743	$I + HO_2 \rightarrow HI$	$1.85 \times 10^{-13}$	Atkinson et al. (2004)
1744	$I + O_3 \rightarrow IO$	$7.39 \times 10^{-13}$	Atkinson et al. (2004)
1743	$1 + NO \rightarrow INO$	$3.48 \times 10^{-13}$ (at 298 K)	Atkinson et al. $(2004)$
1740	$I + NO_2 \rightarrow INO_2$ $I + NO_2 \rightarrow IO_1 + NO_2$	$5.76 \times 10^{-10}$ (at 298 K)	Atkinson et al. (2004)
1748	$I + NO_3 \rightarrow IO + NO_3$ $I_1 + NO_2 \rightarrow I + IONO_2$	$1.0 \times 10^{-12}$ (at 298 K)	Atkinson et al. (2004)
1749	$HI + OH \rightarrow I + H_{2}O$	$9.43 \times 10^{-11}$	Atkinson et al. $(2004)$
1750	$I_2 + OH \rightarrow HOI + I$	$2.1 \times 10^{-10}$	Atkinson et al. (2004)
ī751	$IO + NO_3 \rightarrow OIO + NO_2$	9.0 x 10 <sup>-12</sup> (at 298 K)	Atkinson et al. (2004)
1752	$IO + HO_2 \rightarrow HOI$	8.4 x 10 <sup>-11</sup> (at 298 K)	Atkinson et al. (2004)
1753	$IO + ClO \rightarrow Icl$	$3.16 \times 10^{-12}$	Turnipseed et al. (1997)
1754	$IO + CIO \rightarrow I + CI$	$3.95 \times 10^{-12}$	Turnipseed et al. (1997)
1/25	$IO + CIO \rightarrow I + OcIO$	8.69 x 10 <sup>-12</sup>	Turnipseed et al. (1997)
1/20	$IO + BrO \rightarrow Br + OIO$	9.36 x 10 <sup>-11</sup>	Rowley et al. (2001)
1/3/	$IO + BrO \rightarrow Ibr$	$4.32 \times 10^{-11}$	Rowley et al. (2001)
1/38	$IO + BrO \rightarrow Br + I$	7.2 x 10 <sup>-12</sup>	Rowley et al. (2001)

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**Table 2.** Photochemical reactions.  $J_{\text{max}}$  values for 25 March are shown as an example. J1816 coefficients are expressed in units of s<sup>-1</sup>.

1817				
1818	Reaction	J <sub>max</sub> 25 March	Lifetime	Source
1819	$O_3 \rightarrow O_2 + O(^1D)$	3.9 x 10 <sup>-6</sup>	3.0 days	calculated from OASIS data
1820	$NO_2 \rightarrow NO + O(^3P)$	8.6 x 10 <sup>-3</sup>	1.9 min	calculated from OASIS data
1821	$H_2O_2 \rightarrow OH + OH$	3.4 x 10 <sup>-6</sup>	3.4 days	calculated from OASIS data
1822	$NO_3 \rightarrow NO + O_2$	4.5 x 10 <sup>-2</sup>	22 s	Michalowski et al. [2000]
1823	$N_2O_5 \rightarrow NO_2 + NO_3$	1.5 x 10 <sup>-5</sup>	18 h	calculated from OASIS data
1824	HONO $\rightarrow$ OH + NO	1.8 x 10 <sup>-3</sup>	9.2 min	calculated from OASIS data
1825	$HNO_3 \rightarrow NO_2 + OH$	1.5 x 10 <sup>-7</sup>	79 days	calculated from OASIS data
1826	$HNO_4 \rightarrow NO_2 + HO_2$	7.3 x 10 <sup>-7</sup>	16 days	calculated from OASIS data
1827	HCHO $\rightarrow$ HO <sub>2</sub> + HO <sub>2</sub> + CO	1.5 x 10 <sup>-5</sup>	19 h	calculated from OASIS data
1828	$HCHO \rightarrow CO + H_2$	3.1 x 10 <sup>-5</sup>	8.8 h	calculated from OASIS data
1829	$CH_3CHO \rightarrow CH_3OO + HO_2 + CO$	1.1 x 10 <sup>-6</sup>	11 days	calculated from OASIS data
1830	$CH_3OOH \rightarrow HCHO + HO_2 + OH$	3.2 x 10 <sup>-6</sup>	3.7 days	calculated from OASIS data
1831	$C3H6O \rightarrow HO2 + C2H5OO + CO$	1.4 x 10 <sup>-6</sup>	8.3 days	calculated from OASIS data
1832	$PAN \rightarrow CH_3COOO + NO_2$	1.7 x 10 <sup>-7</sup>	66 days	calculated from OASIS data
1833	$OclO \rightarrow O(^{3}P) + ClO$	0.12	8.1 s	estimate from Pöhler et al. (2010)
1834	$Cl_2 \rightarrow Cl + Cl$	2.1 x 10 <sup>-3</sup>	8.1 min	calculated from OASIS data
1835	$ClO \rightarrow Cl + O(^{3}P)$	2.4 x 10 <sup>-5</sup>	11 h	calculated from OASIS data
1836	$HOCI \rightarrow OH + CI$	1.4 x 10 <sup>-4</sup>	2 h	estimate from Lehrer et al. (2004)
1837	$CINO_3 \rightarrow Cl + NO_3$	2.9 x 10 <sup>-5</sup>	9.5 h	calculated from OASIS data
1838	$CINO_3 \rightarrow CIO + NO_2$	3.4 x 10 <sup>-6</sup>	3.4 days	calculated from OASIS data
1839	$BrNO_3 \rightarrow Br + NO_3$	2.1 x 10 <sup>-4</sup>	1.3 h	calculated from OASIS data
1840	$BrNO_3 \rightarrow BrO + NO_2$	1.2 x 10 <sup>-3</sup>	14.2 min	calculated from OASIS data
1841	$BrO \rightarrow Br + O(^{3}P)$	$3.0 \ge 10^{-2}$	33 s	calculated from OASIS data
1842	$Br_2 \rightarrow Br + Br$	$4.4 \times 10^{-2}$	23 s	calculated from OASIS data
1843	$HOBr \rightarrow Br + OH$	2.3 x 10 <sup>-3</sup>	7.2 min	calculated from OASIS data
1844	$BrNO_2 \rightarrow Br + NO_2$	$1.5 \times 10^{-4}$	1.8 h	estimate from Lehrer et al. (2004)
1845	$CINO_2 \rightarrow Cl + NO_2$	4.4 x 10 <sup>-5</sup>	6.3 h	estimate from Ganske et al. (1992)
1849	$BrCl \rightarrow Br + Cl$	1.26 x 10 <sup>-2</sup>	1.3 min	calculated from OASIS data
184/	$I_2 \rightarrow I + I$	0.15	6.7 s	calculated from Calvert and Lindberg (2004)
1848	$ICl \rightarrow I + Cl$	2.21 x 10 <sup>-2</sup>	45 s	calculated from Calvert and Lindberg (2004)
1849	$IBr \rightarrow I + Br$	$6.83 \times 10^{-2}$	14.6 s	calculated from Calvert and Lindberg (2004)
1820	$INO_2 \rightarrow I + NO_2$	2.23 x 10 <sup>-3</sup>	7.5 min	calculated from Calvert and Lindberg (2004)
	$INO \rightarrow I + NO$	8.34 x 10 <sup>-2</sup>	12 s	calculated from Calvert and Lindberg (2004)
1822	$IONO_2 \rightarrow IO + NO_2$	7.13 x 10 <sup>-4</sup>	23.4 min	calculated from Calvert and Lindberg (2004)
1823	$IONO_2 \rightarrow I + NO_3$	2.91 x 10 <sup>-4</sup>	57.3 min	calculated from Calvert and Lindberg (2004)
1824	$IOOI \rightarrow I + I$	$1.50 \times 10^{-2}$	66.7 s	calculated from Calvert and Lindberg (2004)
1822	$1001 \rightarrow 10 + 10$	$1.50 \times 10^{-2}$	66.7 s	calculated from Calvert and Lindberg (2004)
1820	$HOI \rightarrow I + OH$	5.09 x 10 <sup>-5</sup>	3.3 min	calculated from Calvert and Lindberg (2004)
	$IO \rightarrow I + O(^{\circ}P)$	0.18	5.6 s	calculated from Calvert and Lindberg (2004)
1828	$OIO \rightarrow IO + O(^{\circ}P)$	$1.52 \times 10^{-3}$	11 min	calculated from Calvert and Lindberg (2004)
1839	010 → 1	3.26 x 10 <sup>-2</sup>	30.7 s	calculated from Calvert and Lindberg (2004)

**Table 3.** Mass transfer reactions. All rate constants are expressed in units of  $s^{-1}$ .

1876			1
1877	Reaction	<i>k</i> (forward)	k (reverse)
1879	Particles	× /	
1880	$HCl_{(2)} \rightarrow H^+_{(2)} + Cl_{(2)}$	$2.58 \times 10^{-3}$	
1881	$HBr_{(g)} \rightarrow H^{+}_{(p)} + Br_{(p)}$	$1.80 \times 10^{-3}$	
1882	$HOC_{(m)} \rightarrow HOC_{(m)}$	$2.16 \times 10^{-3}$	
1883	$HOBr(g) \rightarrow HOBr(p)$	$1.26 \times 10^{-3}$	
1884	$HOI_{(g)} \rightarrow HOI_{(p)}$	$5.42 \times 10^{-4}$	
1885	$OH_{(g)} \rightarrow OH_{(p)}$	$3.26 \ge 10^{-5}$	
1886	$O_{3(g)} \leftarrow \rightarrow O_{3(p)}$	6.54 x 10 <sup>-6</sup>	$8.76 \ge 10^5$
1887	$\operatorname{Cl}_{2(\mathfrak{g})} \longleftrightarrow \operatorname{Cl}_{2(\mathfrak{g})}$	2.69 x 10 <sup>-5</sup>	$2.96 \times 10^7$
1888	$\operatorname{Br}_{2(g)} \longleftrightarrow \operatorname{Br}_{2(p)}$	1.78 x 10 <sup>-5</sup>	$2.97 \times 10^8$
1889	$\operatorname{BrCl}_{(g)} \longleftrightarrow \operatorname{BrCl}_{(p)}$	$6.60 \ge 10^{-4}$	$1.91 \times 10^{10}$
1890	$\operatorname{Icl}_{(p)} \xrightarrow{(p)} \operatorname{Icl}_{(g)}$	$2.83 \times 10^{10}$	
1891	$Ibr_{(p)} \rightarrow Ibr_{(g)}$	5.53 x 10 <sup>9</sup>	
1892	$HNO_{3(g)} \rightarrow HNO_{3(p)}$	5.50 x 10 <sup>-4</sup>	
1893	$N_2O_{5(g)} \rightarrow N_2O_{5(p)}$	$1.08 \ge 10^{-4}$	
1894	$HONO_{(g)} \rightarrow HONO_{(p)}$	$1.63 \ge 10^{-4}$	
1895	$PAN_{(g)} \rightarrow PAN_{(p)}$	2.05 x 10 <sup>-5</sup>	
1896	$HNO_{4(g)} \rightarrow HNO_{4(p)}$	4.89 x 10 <sup>-4</sup>	
1897	$\text{CINO}_{2(p)} \rightarrow \text{CINO}_{2(g)}$	$9.44 \ge 10^3$	
1898	$BrNO_{2(p)} \rightarrow BrNO_{2(g)}$	$4.94 \ge 10^4$	
1899			
1900	Snow		
1901	$HBr_{(g)} \rightarrow H^+_{(s)} + Br_{(s)}$	$1.67 \ge 10^{-5}$	
1902	$HCl_{(g)} \rightarrow H^+_{(s)} + Cl^{(s)}$	$1.67 \ge 10^{-5}$	
1903	$HOBr_{(g)} \rightarrow HOBr_{(s)}$	$1.67 \ge 10^{-5}$	
1904	$HOCl_{(g)} \rightarrow HOCl_{(s)}$	$1.67 \ge 10^{-5}$	
1905	$HOI_{(g)} \rightarrow HOI_{(s)}$	1.67 x 10 <sup>-5</sup>	
1906	$OH_{(g)} \rightarrow OH_{(s)}$	1.67 x 10 <sup>-6</sup>	
1907	$O_{3(g)} \rightarrow O_{3(s)}$	1.67 x 10 <sup>-6</sup>	2
1908	$Cl_{2(g)} \leftrightarrow Cl_{2(s)}$	$8.0 \times 10^{-6}$	$7.71 \times 10^{-2}$
1909	$\operatorname{Br}_{2(g)} \longleftrightarrow \operatorname{Br}_{2(s)}$	$1.0 \times 10^{-3}$	$7.71 \times 10^{-2}$
1910	$\operatorname{BrCl}_{(g)} \longleftrightarrow \operatorname{BrCl}_{(s)}$	$1.25 \times 10^{-5}$	7.71 x 10 <sup>-2</sup>
1911	$Icl_{(s)} \rightarrow Icl_{(g)}$	$7.71 \times 10^{-2}$	
1912	$Ibr_{(s)} \rightarrow Ibr_{(g)}$	$7.71 \times 10^{-2}$	
1913	$HNO_{3(g)} \rightarrow HNO_{3(s)}$	$1.67 \times 10^{-5}$	
1914	$N_2O_{5(g)} \rightarrow N_2O_{5(s)}$	$1.67 \times 10^{-5}$	
1915	$HONO_{(g)} \rightarrow HONO_{(s)}$	$1.67 \times 10^{-5}$	
1910	$PAN_{(g)} \rightarrow PAN_{(s)}$	$1.67 \times 10^{-5}$	
191/	$HNO_{4(g)} \rightarrow HNO_{4(s)}$	$1.67 \times 10^{-2}$	
1918	$CINO_{2(s)} \rightarrow CINO_{2(g)}$	$7.71 \times 10^{-2}$	
1919	$BrNO_{2(s)} \rightarrow BrNO_{2(g)}$	/./1 x 10 <sup>-2</sup>	

Table 4. Aqueous-phase reactions in the model. All aqueous reaction rate constants are converted to units consistent to the gas-phase

reactions to be read by the modeling program.

\* Third order rate constant, expressed in units of  $cm^6 \cdot molecule^{-2} \cdot s^{-1}$ † Second order rate constant, expressed in units of  $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ 

‡ First order rate constant, expressed in units of s<sup>-1</sup> 

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1931	Reaction	k (actual)	k (particle)	k(snow)	Reference
1932	$Cl^- + HOBr + H^+ \rightarrow BrCl *$	1.55 x 10 <sup>-32</sup>	5.17 x 10 <sup>-21</sup>	9.30 x 10 <sup>-26</sup>	Wang et al.(1994)
1933	$Br^{-} + HOCl + H^{+} \rightarrow BrCl *$	3.59 x 10 <sup>-36</sup>	$1.2 \ge 10^{-24}$	2.15 x 10 <sup>-29</sup>	Sander et al. (1997)
1934	$Br^{-} + HOBr + H^{+} \rightarrow Br_{2} *$	4.41 x 10 <sup>-32</sup>	1.47 x 10 <sup>-20</sup>	2.64 x 10 <sup>-25</sup>	Beckwith et al. (1996)
1935	$Cl^{-} + HOCl + H^{+} \rightarrow Cl_{2} *$	6.07 x 10 <sup>-38</sup>	2.02 x 10 <sup>-26</sup>	3.63 x 10 <sup>-31</sup>	Wang and Margerum (1994)
1936	$Cl^- + HOI + H^+ \rightarrow ICl *$	8.01 x 10 <sup>-32</sup>	2.67 x 10 <sup>-20</sup>	4.80 x 10 <sup>-25</sup>	Wang et al. (1989)
1937	$Br^- + HOI + H^+ \rightarrow IBr *$	9.12 x 10 <sup>-30</sup>	$3.04 \times 10^{-18}$	5.46 x 10 <sup>-23</sup>	Troy et al. (1991)
1938	$BrCl + Cl^{-} \rightarrow BrCl_{2}^{-} \dagger$	$1 \times 10^{-11}$	3.3	5.99 x 10 <sup>-5</sup>	Michalowski et al. (2000)
1939	$BrCl_2 \rightarrow BrCl + Cl^2 \ddagger$	1.58 x 10 <sup>9</sup>	1.58 x 10 <sup>9</sup>	1.58 x 10 <sup>9</sup>	Michalowski et al. (2000)
1940	$BrCl + Br \rightarrow Br_2Cl \dagger$	$1 \times 10^{-11}$	3.3	5.99 x 10 <sup>-5</sup>	Michalowski et al. (2000)
1941	$Br_2Cl^- \rightarrow BrCl + Br^- \ddagger$	$3.34 \ge 10^5$	$3.34 \times 10^5$	$3.34 \times 10^5$	Wang et al.(1994); Michalowski et al. (2000)
1942	$Cl_2 + Br \rightarrow BrCl_2 \dagger$	1.28 x 10 <sup>-11</sup>	4.27	7.66 x 10 <sup>-5</sup>	Wang et al.(1994); Michalowski et al. (2000)
1943	$BrCl_2 \rightarrow Cl_2 + Br^{\dagger} \ddagger$	$6.94 \times 10^2$	$6.94 \times 10^2$	$6.94 \times 10^2$	Wang et al.(1994); Michalowski et al. (2000)
1944	$O_3 + Br^- \rightarrow HOBr \dagger$	1.35 x 10 <sup>-20</sup>	4.5 x 10 <sup>-9</sup>	8.08 x 10 <sup>-14</sup>	Oum et al. (1998); Michalowski et al. (2000)
1945	OH + Cl⁻ → HOCl †	1.35 x 10 <sup>-20</sup>	4.5 x 10 <sup>-9</sup>	8.08 x 10 <sup>-14</sup>	assumed same as $O_3 + Br^-$
1946	$N_2O_5 + Cl^- \rightarrow ClNO_2 \dagger$	1.66 x 10 <sup>-12</sup>	5.5 x 10 <sup>-1</sup>	9.94 x 10 <sup>-5</sup>	assume diffusion limited
1947	$\text{ClNO}_2 + \text{H}^+ + \text{Cl}^- \rightarrow \text{Cl}_2 \dagger$	1.66 x 10 <sup>-14</sup>	$5.5 \ge 10^{-3}$	9.94 x 10 <sup>-8</sup>	estimated from Roberts et al. (2008)
1948	$N_2O_5 + Br \rightarrow BrNO_2 \dagger$	1.66 x 10 <sup>-12</sup>	$5.5 \ge 10^{-1}$	9.94 x 10 <sup>-5</sup>	assume diffusion limited
1949	$BrNO_2 + H^+ + Br^- \rightarrow Br_2 \dagger$	7.31 x 10 <sup>-17</sup>	2.44 x 10 <sup>-5</sup>	4.38 x 10 <sup>-10</sup>	estimated from Schweitzer et al. (1998)

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**Table 5.** Summary of the ambient measurements from OASIS that were used to constramodel and the instrumental method used.

	Measured Species	Method	Reference
	O <sub>3</sub> , NO, NO <sub>2</sub>	Chemiluminescence	Ridley et al. (1992), Ryerson et al. (2000)
	CO	IR Absorption CO Analyzer	
	Cl <sub>2</sub> , Br <sub>2</sub> , BrO, HOBr	Chemical Ionization Mass Spectrometry (CIMS)	Liao et al. (2011, 2012, 2014)
	ClO	Chemical Reaction GC-ECD	Stephens et al. (2012)
	НСНО	Tunable Diode Laser Absorption	Fried et al. (1997),
		Spectroscopy	Lancaster et al. (2000)
	HONO	Long-path Absorption Photometer	Villena et al. (2011)
	CH <sub>3</sub> CHO, CH <sub>3</sub> COCH <sub>3</sub> , MEK,	Online fast GC-MS	Apel et al. (2010)
	$n-C_4H_{10}$ , $i-C_4H_{10}$		
	$C_2H_2$ , $C_2H_4$ , $C_2H_6$ , $C_3H_8$ , $C_3H_6$ , <i>n</i> - $C_4H_{10}$ , <i>i</i> - $C_4H_{10}$	Canister samples, offline GC-MS	Russo et al. (2010)
1964 1965			
1966			
1967			
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**Table 6.** Fraction of ozone depleted by each halogen calculated for mid-day of 29 March via
Equation 4. "Br and Cl" is the base model.

	Model Conditions	$\Delta O_3$ (ppbv)	Total O <sub>3</sub> Production (ppbv)	Sum O <sub>3</sub> Loss Terms <i>(ppbv)</i>	% of O <sub>3</sub> Loss by Br	% of O <sub>3</sub> Loss by Cl	% of O <sub>3</sub> Loss by I
-	No Halogens	0.05	0.07	0.01			
	Br Only	-2.57	0.46	2.24	98.6		
	Cl Only	0.39	0.89	0.36		81.9	
	Low I Only	-0.12	0.07	0.16			92.1
	High I Only	-2.39	0.09	1.68			99.1
	Br and Cl (Base)	-4.09	0.86	4.15	87.1	11.5	
	Br and Low I	-3.36	0.46	2.94	86.9		11.9
	Br and High I	-7.17	0.45	6.08	64.4		35.0
	Br, Cl, and Low I	-4.91	0.85	4.95	80.2	9.72	8.94
	Br, Cl, and High I	-8.43	0.83	7.92	64.5	5.99	28.8
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<del>)</del> 6							
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Table 7. Fraction of ozone depleted by bromine and chlorine calculated for mid-day of 29 March
 via Equation 4 for modeling scenarios performed by varying Cl<sub>2</sub> mole ratios.

Model Conditions	$\Delta O_3$ (ppbv)	Total O <sub>3</sub> Production (ppbv)	Sum O <sub>3</sub> Loss Terms (ppbv)	% of O <sub>3</sub> Loss by Br	% of O <sub>3</sub> Loss by Cl
25 pptv Cl <sub>2</sub>	-3.15	0.62	2.87	94.1	4.30
50 pptv Cl <sub>2</sub>	-3.60	0.74	3.46	90.6	7.80
100 pptv Cl <sub>2</sub>	-4.36	0.92	4.55	85.3	13.5
200 pptv Cl <sub>2</sub>	-5.66	1.13	6.55	78.1	21.0
400 pptv Cl <sub>2</sub>	-7.96	1.20	10.05	70.4	29.1

2017 Table 8. Ozone depletion rates in ppbv/h calculated by Equation 3 and the corresponding
2018 timescale for ozone depletion from 35 ppbv to 5 ppbv for mid-day of day 29 March for eight

2019 different modeling scenarios with different combinations of halogen radicals present. "Br and Cl"

is the base model.

Model Conditions	Ozone Depletion Rate (ppbv/h)	Depletion Timescale (35 ppbv to 5 ppbv)
Br Only	1.85	16.2 h
Low Iodine Only	0.09	13.9 days
High Iodine Only	1.72	17.4 h
Br and Low Iodine	2.42	12.4 h
Br and High Iodine	5.16	5.81 h
Br and Cl (Base)	2.94	10.2 h
Br, Cl, and Low Iodine	3.54	8.47 h
Br, Cl and High Iodine	6.07	4.94 h

Table 9. Ozone depletion rates in ppbv/h calculated by Equation 3 and the corresponding timescale for ozone depletion from 35 ppbv to 5 ppbv for mid-day of 29 March for five different modeling scenarios performed by varying Cl<sub>2</sub> mole ratios. 

Model Conditions	Ozone Depletion Rate (ppbv/h)	Depletion Timescale (35 ppbv to 5 ppbv)	
25 pptv Cl <sub>2</sub>	2.27	13.2 h	
50 pptv Cl <sub>2</sub>	2.59	11.6 h	
100 pptv Cl <sub>2</sub>	3.14	9.55 h	
200 pptv Cl <sub>2</sub>	4.08	7.35 h	
400 pptv Cl <sub>2</sub>	5.73	5.24 h	

Table 10. Partitioning of the HO<sub>x</sub>, BrO<sub>x</sub>, ClO<sub>x</sub>, and IO<sub>x</sub> radical partners for mid-day of 29 March for a variety of modeling scenarios performed by including or excluding different halogen

- species.

Model Conditions	[HO <sub>2</sub> ]\[OH] Ratio	[BrO]\[Br] Ratio	[ClO]\[Cl] Ratio	[IO]\[I] Ratio
No Halogens	115			
Br Only	63.0	7.65		
Cl Only	229		293	
Low Iodine Only	99.4			2.60
High Iodine Only	62.5			2.30
Br and Cl (Base)	104	5.66	247	
Br and Low Iodine	60.8	7.34		1.96
Br and High Iodine	53.1	6.12		1.76
Br, Cl, and Low Iodine	98.7	5.48	244	1.74
Br, Cl, and High Iodine	81.0	4.68	230	1.57



Fig. 1. Ambient measurements of O<sub>3</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, NO<sub>2</sub>, NO, CO, VOCs, and OVOCs that are
incorporated into the model. Mixing ratios for the NMHCs that were collected as canister
samples were interpolated between samples. Available canister sample data points are indicated
on their respective plot. The photolysis rate coefficient (*J*) is shown for NO<sub>2</sub> as an example in
Panel A. Time is expressed in Alaska Standard Time.



**Fig. 2.** Modeled (black) compared to observed (red) time-series for BrO, HOBr, ClO, OH, and HO<sub>2</sub>. Modeled Br and Cl (black) are compared to steady-state approximations as calculated in Stephens et al. (2012) (red). All concentrations are shown in molecules  $\cdot$  cm<sup>-3</sup> on the left axis and

as mole ratios in pptv on the right axis. Radiation is shown as the cyan trace as a reference.Time is expressed in Alaska Standard Time.

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Fig. 3. (A) Time series of in situ HONO observations (red data) and modeled HONO including an additional flux (black trace) and without an added flux (blue data). (B) Time series of observed NO (black trace) and NO<sub>2</sub> (red trace) that has been re-scaled to a smaller range on the y-axis to show the relatively higher NO<sub>x</sub> mole ratios on 29 and 30 March.

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Fig. 4. Simulated time-series of IO shown for the "Low Iodine" (solid line) and "High Iodine" (dashed line) scenarios. The "Low Iodine" scenario and the "High Iodine" scenario correspond to a daytime average of 0.025 pptv and 0.5 pptv I<sub>2</sub>, respectively. Time is expressed in Alaska Standard Time.

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Fig. 6. A) Time-varying fraction of Br (blue), Cl (red), and I (green) atoms that react with O<sub>3</sub> across the 7 days of the simulation. B) Time-series of observed ozone mole ratios, with radiation is shown as the cyan trace as a reference. Time is expressed in Alaska Standard Time.





**Fig. 7.** Time-varying rates (in molecules  $cm^{-3} \cdot s^{-1}$ ) of the important Br atom sinks during ODEs (O<sub>3</sub> < 5 ppbv). The inset pie chart represents the fractional importance of each sink calculated as the median value across the three days shown. Time is expressed in Alaska Standard Time.



Fig. 8. Rates of reaction for the most important Cl atom reaction partners during ODE days (Panel A;  $O_3 > 5ppbv$ ) and non-ODE days (Panel B). The corresponding pie charts represent the fractional importance of each sink, calculated as median values across the days shown. HO<sub>x</sub> is defined as the sum of OH and HO<sub>2</sub>, NO<sub>y</sub> is the sum of all nitrogen oxide compounds, VOCs includes all non-functionalized alkanes, alkenes, and acetylene, OVOCs includes all non-radical organic compounds with an oxygen (carbonyls, ketones, carboxylic acids), and halogens includes

2117 all inorganic halogenated species.

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Fig. 9. Comparison of modeled HO<sub>2</sub> (Panel A) and RO<sub>2</sub> (Panel B) from four different modeling scenarios: Base (Br and Cl present; black trace), Br Only (blue trace), Cl Only (red trace), and Base + High Iodine (green trace). RO<sub>2</sub> is defined here as the sum of the methyl through butyl forms of alkyl peroxy radicals. Time is expressed in Alaska Standard Time.



**Fig. 10.** Comparison of HO<sub>x</sub> production rates (in molecules  $\cdot$  cm<sup>-3</sup> · s<sup>-1</sup>) for five primary pathways: OH production from HONO photolysis (orange trace), OH production from O<sub>3</sub> photolysis and subsequent reaction with H<sub>2</sub>O (black trace), HO<sub>2</sub> production from HCHO photolysis (green trace), HO<sub>2</sub> production from Br + HCHO reaction (blue trace), and HO<sub>2</sub> production from Cl + HCHO reaction (red trace). The corresponding pie charts represent the fractional importance of each source for a select ODE day (27 March;  $O_3 > 5$  ppbv) and a select non-ODE day (30 March) calculated as the median value across each day. Time is expressed in Alaska Standard Time.