Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts

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1. INTRODUCTION/HISTORY

In the past 40 years, atmospheric chemists have come to realize that halogens exert a powerful influence on the chemical composition of the troposphere and through that influence affect the fate of pollutants and may affect climate. Of particular note for climate is that halogen cycles affect methane, ozone, and particles, all of which are powerful climate forcing agents through direct and indirect radiative effects. This influence comes from the high reactivity of atomic halogen radicals (e.g., Cl, Br, I) and halogen oxides (e.g., ClO, BrO, IO, and higher oxides), known as reactive halogen species in this review. These reactive halogens are potent oxidizers for organic and inorganic compounds throughout the troposphere.

1.1. History

Although reactive halogens are important oxidizers, the hydroxyl radical (OH) was first realized to be a critical species for tropospheric photooxidation chemistry. Through studies of carbon monoxide and methane oxidation in the early 1970s, it was realized that OH radicals largely controlled the lifetime of these compounds, leading to the picture that the Earth’s atmosphere removes natural and anthropogenic pollutants primarily through OH-driven photooxidation chemistry. However, as we will show in this Review, reactive halogens have significant influences in many regions throughout the troposphere, and there is an important interplay between OH-driven and reactive-halogen-driven photooxidation mechanisms. Both OH and reactive halogen photooxidation chemistry mechanisms are tied to ozone abundance. Tropospheric primary production of OH arises from photolysis of ozone in the troposphere. Reactive halogen chemistry is important to ozone abundance. 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1.3. Purpose of this Review

The purpose of this review is to complement the recent reviews and highlight recent (e.g., the last five years, with a focus on the past few years) discoveries in tropospheric halogen chemistry. In section 2, we discuss halogen chemistry as an aspect of atmospheric radical chemistry and highlight the coupling between halogen chemistry and traditional ozone/OH photochemistry. We discuss the different dependence of halogen photochemistry on environmental parameters such as the wavelengths of light driving photochemistry, relationship to NOx pollution, and relationship to aerosol particles necessary for heterogeneous reactions. From this discussion, we highlight areas of Earth’s atmosphere that show dramatic or subtle fingerprints of tropospheric halogen chemistry. In section 3, we discuss recent advances in the field in polar regions, the marine boundary layer, in NOx-polluted regions, and regionally and globally. In section 4, we address what is known about the global impacts of tropospheric halogen chemistry, both in terms of pollutant transformations and climate. Needs for future research are discussed in section 5.

2. SYNTHESIS OF HALOGEN CHEMISTRY

2.1. Halogen Radical Reactions

In this section, we review the chemical reactions of halogen radicals and their precursors and sinks. Many prior studies and reviews have discussed these reactions, and readers are referred to those publications.23,24,27,29-32 In this discussion, we focus on examination of the halogen activation process both in terms of halogen speciation and accounting radical-producing, sustaining, and destroying reactions. In this way, we see linkages between the more commonly studied ozone photochemistry that involves cycles of HOx and NOx radicals as well as sunlight driven photolytic radical production and oxidation of hydrocarbon species as energy sources for the chemical reactions. Through this consideration, we also gain insights into primary radical production pathways versus recycling of radicals.

Figure 1 shows key chemical reactions of halogen atoms, denoted generically as “X” on this diagram. As the focus of our discussion will be on following radicals through these reactions, the diagram only lists X as a halogen species, but we note that chlorine, bromine, and iodine atoms have been shown to be important in the atmosphere and cross reactions between halogen species are critical to more detailed consideration. We discuss recent findings on these individual halogen atom types and cross reactions later in this Review but also refer readers to excellent reviews discussing detailed differences between halogen species.23,27,30,32

Radical reactions involve initiation steps, where species with all paired electrons have bonds broken homolytically to produce two radicals, propagation reactions, between a radical and a nonradical, which conserve number of radicals, and termination reactions, which combine two radicals to form nonradical products. We use the term “reactive halogen” to describe radical species such as X and XO. Halogen reservoir species are nonradicals that temporarily sequester reactive halogens; examples include X•, HOX, XNO2, andHX. Some reservoir species may associate with droplets or particulate matter and dissociate, often releasing X• anions, which we refer to as halides. Reactive halogens have short lifetimes (<seconds to minutes), typically only being present during the day, while the reservoir species are longer lived and often build at night.

2.1.1. Photolysis Rates and Actinic Spectral Regions.

Photolysis of dihalogens (X2) is a key initiation step:

\[
X_2 + \nu \rightarrow 2X
\]

A significant aspect of halogen photochemistry is that the absorption spectra of dihalogens lie in the visible to near-UV region of the spectrum, meaning that the relatively abundant photon wavelengths can drive halogen chemistry. This actinic spectral region differs from that of ozone photochemistry, which requires less abundant UV photons near 300 nm that are highly affected by overhead stratospheric ozone abundance, to drive production of OH radicals. For example, the photolysis rate of ozone to produce O1D, the precursor to OH production, is 4.5 × 10^-5 s^-1 for overhead sun (SZA = 0°), 300 DU column ozone, and 0.1 albedo, but drops below 10^-5 s^-1 when the sun goes below SZA = 60°.39 On the other hand, for overhead sun, the photolysis rates of Cl2, Br2, and I2 are 0.0022, 0.032, and 0.15 s^-1, respectively,40,41 and the attenuation of photolysis rates at lower solar elevation is much weaker than for ozone. This much faster photolysis allows halogen chemistry to be more important under lower light and higher ozone overhead slant column conditions.

Reaction 1 produces two halogen radicals, X, which are highly reactive and react with a number of competing species including ozone

\[
X + O_3 \rightarrow XO + O_2
\]

Reaction 2 reduces ozone, and cycles involving it will be seen to lead to ozone depletion. In competition with this reaction is the oxidation of hydrocarbons, which is most important for chlorine radicals, as discussed in the next section

\[
X + RH \rightarrow R• + HX
\]

In reaction 3, a halogen atom reacts with hydrocarbons, denoted generically as RH and is listed as an hydrogen abstraction reaction. Halogen radicals can also add to double bonds in organic species, which again leads to an organic radical species.

2.1.2. Relative Reactivity of Halogens to Hydrocarbons.

The decreasing bond strength from HF through HI has important impacts on the relative reactivity of halogen atoms to hydrocarbons. Fluorine atoms can react with water and abstract hydrogen to give HF, which means that fluorine cannot react in catalytic cycles and thus is different from the
The HCl bond strength is similar to that of organic CH bonds, allowing chlorine atoms to react with hydrocarbons including abundant methane, giving it a reactivity similar to or larger than that of OH, but with different patterns of relative reactivity. Therefore, for chlorine, the hydrocarbon path outcompetes the ozone depleting pathway. Bromine is less reactive to hydrocarbons and, most often, reacts with ozone or the less abundant aldehydes (e.g., formaldehyde), increasing its role in tropospheric ozone depletion. Iodine atoms are even less reactive and react primarily with ozone, leading to the formation of higher iodine oxides. Reactions 2 and 3 are both radical propagation reactions, where the number of radical species is unchanged. Tracking halogens, we see that reaction 2 maintains the radical within the halogens and their oxides, while reaction 3 converts the radical to the organic species.

Bromine and iodine, the halogen oxides (XO) photodissociate rapidly (typically on the order of minute to second time scale), which recreates X and ozone in a “null” cycle. This null cycle has no net effect on ozone destruction or production, but as these are often the fastest loss of XO, they, therefore, strongly affect the partitioning between X and XO. For typical ozone levels in the tens of picomole per mole range, the oxides dominate the atomic radical form, an effect that extends the effective lifetime of the XO = X + O family because the oxides are typically less reactive than the atomic form. The low reactivity of I is similar to that of IO, often making their ratio approximately unity. Chlorine monoxide, ClO, has a much longer photolytic lifetime, so this “null cycle” does not apply to chlorine.

The halogen oxides can react with each other with a variety of fates, which generally destroy ozone and either conserve radicals or produce dihalogens that then photolyze (in daytime) via reaction 1.

\[
\begin{align*}
\text{XO + XO} & \rightarrow \text{X}_2 + \text{O}_2 & (4) \\
\text{XO + XO} & \rightarrow \text{X} + \text{X} + \text{O}_2 & (5) \\
\text{XO + XO} & \rightarrow \text{OXO} + \text{X} & (6)
\end{align*}
\]

Only one of these, reaction 4, is depicted in Figure 1, but note that the net effect of this reaction plus photolysis (reactions 4 and 1) is equivalent to reaction 5. The last reaction forms a possible reservoir species OXO, which has many different fates that depend upon the specific halogen. The interested reader is referred to prior reviews.

### 2.1.3. Cross Halogen Reactions

Cross halogen reactions (e.g., those of XO with YO) typically have rates an order of magnitude faster than self-reactions. This increased rate means that presence of multiple reactive halogens speeds cycling of halogens and destruction of ozone. Because of the order of magnitude difference in rates, levels of other halogens at even an order of magnitude lower concentration can have serious impacts on halogen-induced chemical oxidation rates. Recent findings on this topic are discussed below, but the interested reader can also refer to prior reviews.

### 2.1.4. Halogen Recycling from Reservoirs

An important “termination” reaction involves HOX and XO

\[
\text{XO + HOX} \rightarrow \text{HOX} + \text{O}_2
\]

This reaction results in a nonradical, HOX, reservoir species that can be reactivated in two important ways. First, HOX species typically photolyze in the near UV or visible

\[
\text{HOX} + \text{hv} \rightarrow \text{X} + \text{OH}
\]

This photolysis reaction recreates two radicals, and the hydroxyl radical can react with CO or many hydrocarbon species to recreate HO\(_2\) for example

\[
\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M}
\end{align*}
\]

The cycle of reactions 2, 8, and 9 catalytically destroys ozone, while cycling one radical each of the families HO\(_2\) and XO\(_2\).

Another important fate of HOX is the heterogeneous reaction with halide anions that are held in or on condensed phases, such as aerosol particle surfaces or snow/ice surfaces

\[
\text{HOX} + \text{X}^-/\text{HX} \text{ (on surface)} \rightarrow \text{X}_2 + \text{OH}^-/\text{H}_2\text{O}
\]

This net heterogeneous reaction is pH dependent, as has been observed in the laboratory and recently in the field, as discussed in section 3.1.2. When this reaction is followed by photolysis of X\(_2\) reaction 1, it recreates two radicals. Starting from one halogen radical atom, X, and following the sequence of reactions reactions 2, 7, 10, and 1 gives the net reaction

\[
\begin{align*}
\text{X} + \text{HO}_2 + \text{X}^-/\text{HX} \text{ (on surface)} + \text{hv} & \rightarrow 2\text{X} + \text{OH}^-/\text{H}_2\text{O} \\
& (11)
\end{align*}
\]

This net reaction is often termed the “bromine explosion” when X = Br, because it produces two X radicals from one starting X radical, making it an autocatalytic cycle that builds up the pool of reactive halogen radicals. Viewed from the halogen side, this reaction sequence is indeed an explosion, but if we view it by counting radicals, we see that reaction 11 has two radicals on each side of the net chemical equation, so it is neutral with respect to production/destruction of radicals. Putting these two facts together, we see that the halogen explosion reaction sequence converts HO\(_2\) radicals to XO\(_2\) radicals through the combination of heterogeneous reactions involving halide salts and photodissociation of dihalogen gases. Last, we note that the halogen explosion sequence consumes protons and, thus, shifts the pH of surfaces in the alkaline direction.

Another group of important halogen reservoirs are the hydrogen halides, HX. These can be formed by reaction 3, or particularly in the case of the relatively weak acid HCl, stronger acids can displace HCl from chloride-containing aerosol particles (such as sea salt aerosol particles). These gas-phase hydrogen halides can react with OH via

\[
\text{OH} + \text{HX} \rightarrow \text{X} + \text{H}_2\text{O}
\]

In regions where gas phase HCl is abundant because of acid displacement reactions from sea salt, this reaction can be a significant source of atomic chlorine. This reaction conserves radicals, but converts HO\(_2\) radicals to halogen radicals.

### 2.1.5. Exchange of Halides in Aqueous Phase

The abundance of halide anions in seawater and most aqueous systems has chloride > bromide > iodide. Thus, reaction 10 often will happen with X’/HX being Cl’/HCl, which would then produce BrCl\(_{aq}\). However, dissolved dihalogens, such as BrCl\(_{aq}\), can reversibly react with halides, such as Br\(^-\), to give trihalides, in this case Br\(_3\)Cl\(^-\). This reaction is reversible, and because chloride is more stable in solution than bromide, it will most often decompose as Br\(_2\) and Cl\(^-\). These exchange reactions generally prefer to produce gas-phase species that have more heavier atoms (e.g., I > Br > Cl); however, the low aqueous abundance of iodide often limits the ability to exchange to iodine, and means that often production of Br\(_2\).
is preferred, even if $[\text{Cl}^-] > [\text{Br}^-]$. The ratio of halide ions in the condensed phase can be fairly variable, which can affect this exchange process, and these reactions are discussed further below.

2.1.6. Properties of Reactive Surfaces. Because heterogeneous chemistry depends upon the properties of the reactive surfaces, there has been a great deal of research into which surfaces are most efficient at carrying out reaction 11. Many of these are recent results and are discussed below, but a number of surface properties are clearly beneficial to these reactions. Ice surfaces are able to speed up these heterogeneous reactions, which is thought to be a combination of cryoconcentration of impurities, and also polarizability of halogen atoms that gives them a preference to reside on the surface. Recent studies of heterogeneous chemistry have shown that organic coatings can act as barriers to this type of aqueous reactivity, as has been discussed in reviews and will be discussed below. Similar effects have been observed with nocturnal nitrogen chemistry. The effect of pH and surface pH will also be discussed below.

Completing the basic reactions shown on Figure 1, we see that reaction 3 produces an organic radical, which typically then combines with O$_2$ to form an organic peroxy radical, a RO$_2$ species. These peroxy radical species are common oxidation products known in normal ozone photochemistry driven by HO$_x$ radicals. The peroxy radicals can react or rearrange in multiple steps to form HO$_2$ radicals, which then can provide the odd hydrogen radicals to drive the “halogen explosion” chemistry. Products of rearrangements of peroxy radicals, such as aldehydes like formaldehyde, HCHO, can photolyze in the near-UV region, acting as a radical amplifier. Therefore, we see that the oxidation of hydrocarbons and formation of HO$_x$ either through that oxidation or through other processes is critical to supporting halogen activation. We can also see there is a mechanism by which halogens can produce secondary HO$_x$ radicals, and if conditions are not right for the heterogeneous reaction, reaction 10, to occur, the halogen explosion will fail to increase the fraction of X radicals. Subsequent photolysis of HOX to produce X and OH radicals, coupled with losses of X, such as reaction 3, that lead to HO$_x$ radicals will then shift the reactive radical pool to the HO$_x$ family.

As we will see below, many of the places where large daytime halogen events occur tend to be low NO$_x$ environments. NO$_x$ is a key species involved in pollution-caused high ozone events, where its role is to shift the OH/HO$_2$ balance, so as to promote OH formation that more vigorously attacks hydrocarbons. In these reactions with peroxy species, NO is converted to NO$_2$ without destroying ozone, and then when the visible light absorbing NO$_2$ photolyses, ozone is produced. The halogen reactions highlighted in Figure 1 all destroy ozone except for the photolysis of XO, which can participate in an ozone-neutral null cycle as shown above. Therefore, in the absence of NO$_x$, the presence of reactive halogens destroys ozone effectively. We will discuss coupling between pollution and halogen activation in section 3.3.

Key points of this discussion are that halogen chemistry differs from normal ozone photochemistry in a number of important aspects. (1) Primary production of HO$_x$ typically is driven by ozone photolysis at wavelengths near 300 nm, while halogen photochemistry involves photolysis of X and HOX, and carbonyls at longer wavelengths that depend less upon overhead ozone and have a higher relative intensity as compared to ozone photolysis under lower light conditions. (2) Heterogeneous chemistry requiring appropriate halide-laden surfaces are necessary for halogen explosion sequences, a key difference from gas-phase ozone photooxidation chemistry. These halogen explosion sequences cause exponential increases in reactive halogen radicals, but in themselves do not change the total number of radicals; they convert other radicals to halogen radicals. (3) Oxidation of hydrocarbons by halogen attack leads to secondary HO$_x$ radical production, giving a way in which halogen radicals can be converted to odd hydrogen radicals. This two-way coupling between XO and HO$_x$ radical pools has important consequences for understanding atmospheric halogen chemistry.

2.2. Halogen Sources and Observations

This section describes the discovery of various reactive halogen sources to the atmosphere, the confirmation of these sources, and the certainty to the relevance of the sources. These sources are schematically shown in Figure 2. In cases, where a source has been established for some time, initial papers are cited below followed by reference to relevant reviews. In cases of new sources, we provide a detailed discussion in section 3. Table 1 shows the maximum observed mixing ratio of reactive halogen species and related precursor/reservoir species detected in various regions of the Earth’s atmosphere. This table is not meant to be a comprehensive listing of all observations but instead to give a range, from zero to the shown maxima for mixing ratios, in these halogen-affected regions.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Primary sources of reactive halogen species or their precursor reservoir species overlain on a MODIS image of Earth. Background image produced by the MODIS Land Group, NASA Goddard Space Flight Center, Visible Earth Project, NASA.
iodine reactive halogen species and their precursors have been observed in polar regions. Recent observations by Liao and co-workers have demonstrated high levels of molecular chlorine, Cl₂. Reactive bromine, in the form of BrO is observed to be of reactive halogen species, such as nitryl chloride, ClNO₂, providing a connection between nitrogen oxides, ClNO₂, reacting with HCl or NaCl to produce photolabile species, such as nitryl chloride, ClNO₂, providing a connection between nitrogen oxide pollution and halogen activation. Field observations in the late 2000s showed that this mechanism produced high levels of nitryl chloride in the marine boundary layer and later in the continental regions. Table 1 shows that the ClNO₂ levels go up to 3500 pmol/mol, which was detected in the polluted coastal city of Los Angeles. High levels of molecular chlorine were also detected in the same environment. Anthropogenic production of strong acids can cause acid-mediated displacement of Cl⁻ from sea-salt aerosol particles and high levels of gas-phase HCl that then can be activated to atomic chlorine via reaction 12. Detailed discussion of this heterogeneous chemistry and recent findings are discussed in section 3.3.

### 2.2.3. Open Ocean Halogen Sources

It has been known that biota, particularly in marine environments, make use of halogens and produce organohalogen species such as alkyl bromides and alkyl iodides. Many of these organohalogen species are photolabile with photolysis lifetimes from minutes to months. Organobromine species such as bromoform (CHBr₃), were initially thought to be the bromine source for Arctic ozone depletion events, but despite discovery of relatively high bromoform levels, photolysis rates were too slow to be the sole source of reactive halogens in Arctic ozone depletion episodes. Organobromine species may still be involved in reactive halogen processes by providing “seed bromine” for the bromine explosion chemistry described above or under unique conditions. Short lived organobromine gases may also provide significant sources for reactive bromine to the free troposphere, and stratosphere. Organiodine species generally have shorter photolysis lifetimes, and because iodine is a necessary nutrient, its inorganic abundance in the ocean is depleted as compared to other halides. Therefore, organiodine species are often considered to be primary sources of reactive iodine species to the atmosphere, as discussed in prior reviews. An exciting advance lies in improved understanding of how ozone reacts on the ocean surface to produce HOI and I₂ gases directly, which is discussed in section 3.2.3. This work challenges the presumption that marine biological processes are the main source of oceanic iodine emissions. Table 1 shows that significant levels of IO and I₂ are also observed in regions of the open ocean, as discussed in section 3.2.3. Reactive bromine, BrO, and precursors of reactive chlorine, Cl₂ and HOCI, are also found at significant levels in the MBL.

### 2.2.4. Tidal Stress and Release from Coastal Areas

In tidal regions, marine biota, particularly macroalgae, experience periodic stress due to being alternately submerged in saline water and exposed to air, drying, and sunlight. Many of these same organisms concentrate iodine and halogens in general, leading to the possibility of halogen release from coasts. Iodine monoxide, IO, was first detected by Alicke and co-workers, and soon after confirmed by others. The relationship of these emissions with low tide as well as production of organo halide species at low tide was observed by Carpenter and co-workers. The relationship of inorganic iodine species with low tide was confirmed by Saiz-Lopez and Plane in 2004, as well as the observations of surprisingly high molecular iodine, I₂. Table 1 shows that in the marine boundary layer (MBL), high levels of IO and I₂ are observed in tidal areas as a result of stress on marine biota. The reviews by Carpenter and Saiz-Lopez and co-workers contain excellent information on these topics, and the most recent findings in this area are discussed in section 3.2.

### 2.2.5. Volcanoes, Salt Lakes, and Lake Beds

Some unique geographic regions appear to have particularly intense tropospheric halogen chemistry. However, the uniqueness of these locations may limit the regional and global impacts of these sources.

#### Table 1. Maximum Mixing Ratios (pmol/mol) in Various Regions

| species       | polar | MBL | polluted | free troposphere |
|---------------|-------|-----|----------|------------------|
| ClO           | <30–125 Fohlér52 | 35 Lawler54 | 200 Riedel55 |
| OClO          | 24 Fohlér52 | 400 Liao53 | 3500 Mielke57b |
| Cl₂           | 6 Buys56 | 170 Lawler54 | 1.5 Prados-Roman50 |
| BrCl          | 35 Liao58 (NH) | 6 Read59 | 13 Buys56 (SH) |
| ClNO₂         | 46 Liao58 (NH) | 19 Finley61 | 45 Buys56 (SH) |
| HOBr          | 26 Liao58 (NH) | 2 Read59 | 0.4 Puentedura63 |
| IO            | 3 Mahajan62 (NH) | 0.6 Dix65 | 20 Saiz-Lopez64 (SH) |
| I₂            | 0.1 Dix65 | 1.7 Lawler66 | 0.6 Dix65 |
| I₂ (tidal)    | 0.1 Dix65 | 300 Huang68 | 0.6 Dix65 |
| I₂ (tidal)    | 0.1 Dix65 | 50 Commane67 | 0.6 Dix65 |

*Only the last name of the first author for the reference is listed for space considerations. Northern and Southern Hemisphere data are designated by NH and SH, respectively. As discussed below, tidal and open ocean areas differ in iodine emissions, so the table separates these locations. These mixing ratios represent selected values from recent literature and are not a comprehensive listing but are meant to roughly indicate the range of levels in these regions. The reviews of Saiz-Lopez and von Glasow and Saiz-Lopez and co-workers present comprehensive lists of observations published before 2012, and recent observations appear in this review and in this table. More recent observations at coastal and continental sites are described in section 3.3.1.*
Saline lakes like the Dead Sea,91 and the Great Salt Lake,92 as well as dry salt plains,93 all appear to produce high levels of halogen oxides. These reactive halogen emissions have recently been linked to mercury chemistry.94,95 The recent review by Saiz-Lopez and von Glasow32 covers these topics in detail. Although not shown on the table, the important chlorine reservoir, OCIO has very recently been measured in a volcanic plume.96

2.2.6. Free Tropospheric Observations. Many exciting recent advances in the study of reactive halogens and their precursors have been enabled by airborne instrumentation, which has allowed researchers to measure reactive halogens in the free troposphere, where they can affect upper tropospheric ozone and thus affect climate. Table 1 shows a number of these recent measurements. Initial measurements with airborne DOAS spectroscopy allowed Prados-Roman and co-workers60 to detect vertical profiles of BrO and show that that significant levels exist near the tropopause. Mountain-top observations of IO63 showed that free tropospheric IO occurs above the subtropical Atlantic Ocean. Recent airborne DOAS observations of IO over the Pacific Ocean65 also show that a significant fraction of the IO column lies above the marine boundary layer. These observations are further discussed in Section 3.4.

3. RECENT ADVANCES IN TROPOSPHERIC HALOGEN CHEMISTRY

3.1. Polar regions

3.1.1. Background. The polar regions were the first region in which the role of halogens in the troposphere was proven. As discussed in the introduction, Barrie and co-workers13 discovered that filterable bromine was present during Arctic boundary-layer ozone depletion events and argued that halogens caused the depletion. Differential optical absorption spectroscopy (DOAS) confirmed the presence of reactive halogens by the detection of BrO first at Alert, Canada, in 1994 by Hausmann and Platt.97 Boundary layer halogen events were soon after detected in other regions of the Arctic98,99 and Antarctica.100 The fingerprint of reactive chlorine atoms was seen in the patterns of hydrocarbon oxidation by Jobson and co-workers in 1994.101 Reactive iodine (IO) was detected by DOAS in the nonpolar marine boundary layer64 before its detection in the Antarctic boundary layer.64 Most Arctic attempts to detect IO have been below detection limits (typically ~1 pmol/mol),82,98,102 although one detection has been reported.82 Satellite-based spectrometers have detected global BrO vertical column densities (VCDs) and found that enhanced BrO VCDs are ubiquitous across the Arctic and Antarctic Sea Ice regions,103–105 although some of this enhancement appears to be stratospheric in origin, as discussed below. Iodine monoxide in the Antarctic was also detected from space-borne spectrometers.74,106 Recent polar field campaigns, satellite-derived analysis, and modeling have expanded our understanding of these halogen events, and in the section below, we discuss advances in each area with a focus on recent publications.

3.1.2. Recent Discoveries. A critical question in polar halogen chemistry is what types of surfaces provide the halides for heterogeneous production of photolabile halogen gases. Snowpack, open water, ice forms such as frost flowers, and aerosol particles have all been proposed as candidates for principal reactive surfaces, as discussed below and in past reviews (references 29 and 31). Foster and co-workers in 2001 found that snowpack produces Br2 and BrCl, even under twilight conditions.107 Recently, Pratt and co-workers43 used chemical ionization mass spectroscopy (CIMS) to measure production of molecular bromine in outdoor snow-chamber experiments, where snow and ice samples from various environments were tested for their ability to produce bromine. Figure 3 shows that bromine was produced when the snow was exposed to natural sunlight, and that production of bromine increased upon addition of ozone gas. They show that the snow types that produce Br2 most efficiently were characterized by lower pH, and higher bromide to chloride ratios.43 They interpret their results as indicating that reactions in a quasi-brine layer108 of snow/ice in which reagents are cryoconcentrated at lower pH and higher bromide to chloride ratios were responsible for samples having greater bromine production. Laboratory studies have also found lower pH speeds heterogeneous halogen activation,31,42 also as discussed below. It is important to note that CIMS inlets can convert between bromine species, such as Neuman and co-workers109 found that HOBr is efficiently converted to Br2 on Teflon inlet surfaces, although the most recent inlets are designed to minimize these problems. Liao and co-workers53 discovered high levels, up to 400 pmol/mol, of molecular chlorine, Cl2, in ambient air at Barrow, Alaska. By correlation analysis, they find that small amounts of Cl2 are produced during the night, and that the daytime production is dependent on sunlight amount and ambient ozone levels.53 Modeling indicates that the production rate of chlorine gas peaks with sunlight intensity at noon.53 They argue based upon lack of correlation of Cl2...
levels with aerosol particle properties and the existence of sufficient reservoir of chloride in snowpack, that the snowpack is responsible for this production.53

In an attempt to simulate snowpack production of dihalogen gases, Wren and co-workers110 exposed laboratory salt-doped snow to ozone, irradiation, and “seed” halogens and observed production of dihalogen gases. Figure 4 shows the result of one of these experiments. Note the similarity between these laboratory simulations and the field observations shown in Figure 3. Wren and co-workers110 explored dependence of this halogen activation upon pH, surface area, ozone, and photolytic wavelength. An interesting finding was that lower pH was necessary for halogen production as shown in Figure 4, with decreased dihalogen formation at prefreezing pH 4.3, and below detection limits dihalogen production at prefreezing pH 5.9. This acidity requirement is in agreement with field observations, but the absolute pH levels are significantly more acidic than most ambient melted snow samples. A better understanding of the effective pH of the surface of snow is required to resolve these questions.

Advances in mass spectrometric observations have allowed for observations of more inorganic bromine species, advancing our knowledge of their cycling and confirming mechanisms discussed above. HOBr, BrO, and Br2 were simultaneously measured during the OASIS field campaign in spring 2009, and for lower wind speeds (<6 m s$^{-1}$), observed and predicted HOBr levels from a photochemical box model constrained by HO2 and BrO observations and including heterogeneous uptake of HOBr were well correlated ($R^2 = 0.57$).58 At higher wind speeds (>6 m s$^{-1}$), predicted HOBr levels exceeded observations, and high BrO levels were observed, consistent with production of reactive bromine on blowing snow.58 During the same campaign, CIMS and long-path DOAS (LP-DOAS) observations of BrO were highly correlated, particularly for moderate wind speeds (between 3 and 8 m s$^{-1}$) and low NO conditions, where spatial inhomogeneities in the horizontal distribution of BrO would be expected to be smaller.111 Multiple axis DOAS spectroscopy (MAX-DOAS), analyzed by optimal estimation techniques, correlated with LP-DOAS BrO observations ($R = 0.78$), although MAX-DOAS observations at high surface extinction (>0.5 km$^{-1}$) showed deviation as would be expected for poor visibility and were excluded from the correlation.112 High BrO mixing ratios were observed in the presence of high optical extinction near the surface, again consistent with blowing snow being a surface on which halogen production can take place.112 The observations of these chlorine and bromine species during the OASIS campaign were used to compute steady-state Br and Cl radical atom concentrations and investigate the oxidation of atmospheric mercury. Bromine radicals, Br, and BrO had the greatest contribution to mercury decay.113 During the ARCPAC airborne campaign, Pommier and co-workers114 found two instances of elevated BrO in the Arctic free troposphere that could not be linked to a surface or stratospheric source but rather were linked to Siberian biomass burning. The exact source mechanism is unclear, but production of free-tropospheric halogens is important for ozone radiative forcing, as discussed in section 4.1. Observations of Br2, BrCl, and BrO in coastal West Antarctica showed higher levels of halogens in sea-ice influenced air than continental airmasses and a diurnal profile of BrO similar to chemical model predictions.56 In coastal East Antarctica, a novel mode-locked cavity enhanced absorption spectrometer failed to detect BrO and detected very low IO levels (<0.15 pmol mol$^{-1}$).115 The difference between the East and West of Antarctica was interpreted in terms of differing sea ice/continental influence, with greater sea ice influence leading to higher halogen levels.115 Molecular iodine, I2, was reported from a ship in the Antarctic Weddell Sea, but models could not reconcile the high levels of I2 with lower levels of IO also detected.116 Further study of the apparent asymmetry of iodine chemistry between the Arctic and Antarctic could help resolve this outstanding question.

Jones and co-workers observed high BrO vertical column densities in correlation with a high wind event in coastal Antarctica and proposed that blowing saline snow, in addition to surface snowpack, can be a significant source of reactive halogens.117 In-situ observations during the OASIS campaign found high levels of BrO during high wind58 and low visibility112 conditions, consistent with this hypothesis. However, significant levels of BrO are observed at lower wind speeds, possibly from snowpack sources. Satellite-based spectrometers, such as the Global Ozone Monitoring Experiment (GOME) and successors (GOME-2), SCIAMACHY
(Scanning Imaging Absorption Spectrometer for Atmospheric Chartography), Ozone Monitoring Instrument (OMI), measure global distributions of the total column density of BrO, providing an opportunity to observe global reactive bromine distributions. Early work considered the stratospheric portion of BrO to have only zonal variability, and thus “hotspots” of total column BrO were associated with boundary layer halogen activation events. However, airborne observations of BrO and O₃ showed that boundary-layer events were sometimes at locations not associated with satellite-detected BrO enhanced columns, and that some enhanced BrO columns were associated with regions of low tropopause height, indicating stratospheric origin to the enhancement. Theys and co-workers developed a global stratospheric BrO climatology based upon the BASCOE stratospheric model, and showed that stratospheric BrO covaries with stratospheric ozone and is affected by stratospheric NO₂ by repartitioning of the Br family. This climatology and related methods have been used to separate stratospheric and tropospheric BrO column densities. Aircraft-based observations of BrO found that tropospheric BrO associated with enhanced VCD can be distributed over a range of altitudes and are not necessarily constrained to the boundary layer. Measurements from autonomous buoys deployed on the sea ice showed that transport mechanisms dominate the variability in ozone as opposed to in situ halogen-induced loss rates. Observations of the typical heights of ozone depletion in the range from ~400 to 800 m above the surface indicate the region of halogen activation. These ozone observations indicated that ozone-depleted air masses are transported to Barrow with the primary source region of ozone depleted air being the frozen Arctic Ocean.

### 3.1.3. Polar Radical Sources

As discussed earlier, primary production of radical species is necessary for halogen chemistry. Therefore, sources of radicals in polar regions need to be better understood. Nitrous acid, HONO, a photolabile precursor of hydroxyl radicals was measured using the long path absorption photometer (LOPAP) technique during the OASIS campaign and found to be up to 500 pmol/mol in locally polluted plumes, but <10 pmol/mol in “clean” airmasses more typical of the Arctic. Photochemical production of HONO on snow as proposed to be the source of these high HONO levels. Formaldehyde, HCHO, is a key precursor of HO₂ radicals through its photolysis, which produces two HO₂ radicals. Typically, formaldehyde is formed by oxidation of organic gases but it is also formed by radical chemistry in the snowpack. Formaldehyde can also be a large sink for bromine atoms through the reaction of HCHO + Br. Note that this reaction repartitions halogens to decrease halogen levels but conserves radicals because the HCO radical goes on to produce HO₂. Formaldehyde was recently measured and found at levels up to 1 nmol/mol, and bidirectional exchange between the atmosphere and the snowpack were observed. Low levels of HCHO, around 40 pmol/mol, were measured during a severe ozone depletion episode, as is consistent with its reaction with Br atoms. Other small carbonyls, such as acetaldehyde, CH₃CHO, have been observed to be produced from snowpack, and may be radical sources that can feed halogen radical chemistry.

### 3.1.4. Modeling of Polar Halogen Chemistry

A number of groups have modeled coupled HOₓ, NOₓ, and halogen chemistry in polar regions using zero-dimensional box modeling constrained by radical measurements. Bloss and co-workers simulated Antarctic boundary layer observations and found good replication of mean levels and diurnal cycles of observed HOₓ, NOₓ and halogen oxides. These simulations indicated that photolysis and reaction of Br with HCHO, along with ozone photolysis followed by reaction with water were the principal sources of HOₓ radicals. In this Antarctic study, iodine chemistry was explicitly included and the model was able to simulate iodine monoxide levels similar to observations. A similar zero-dimensional box model was applied at Summit Greenland, again constrained by radical measurements, found generally good agreement with observations that were improved by including bromine chemistry, although the agreement was not quantitative. Caö and co-workers recently carried out an extensive sensitivity modeling study on halogen release and ozone depletion chemistry. Three reaction schemes were used. First, only bromine chemistry was included then NOₓ was added and finally chlorine chemistry was included. Heterogeneous chemistry was considered to be influenced by aerodynamic resistance, reactive surface area, and boundary layer height parameters. In the presence of significant reactive surface area, bromine explosions were found to occur after a few days induction period and with ozone depletion time scales of 1–2 days. The inclusion of chlorine in this modeling study had a minor influence in ozone depletion as compared to bromine and NOₓ. However, no snowpack source of chlorine was included in the model, as has been indicated by the study of Liao and co-workers. As has been discussed earlier, many studies indicate that snow and ice surfaces on the ground or frozen polar oceans are key sources of halides for heterogeneous production of reactive halogens. In addition, surfaces of aerosol particles can provide these surfaces aloft. Therefore, groups have investigated one or higher dimensional models where the vertical transport of halogens is modeled, as well as the competition between reactions at the snow/ice surface and reactions on particles aloft. Thomas and co-workers coupled the 1-D chemical/transport model MISTR with a 1-D snow model to investigate the role of snowpack as a source of NOₓ and reactive bromine over the Greenland Ice Sheet. The model successfully simulated observed halogen and NOₓ levels and found that the presence of snowpack emissions increases the oxidation capacity significantly and increases daytime OH concentrations. Toyota and co-workers performed 3-D model simulations using GEM-AQ over the Arctic basin. The model was able to reproduce temporal and spatial behavior of ozone depletions observed at coastal sites and spatial distributions of BrO VCDs observed by satellite-borne instruments. More recently, Toyota and co-workers developed a 1-D model with explicit snowpack chemistry that coupled bromine, ozone, and mercury chemistry in the air and snowpack. This study investigated the role of snowpack production of halogens and transport of reactive halogens and found that enhanced vertical mixing led to higher BrO CVD due to increased vertical extent of snowpack influence on the atmosphere. Figure 5 shows the BrO CVD as a function of time and wind speed. The same model was applied to understand mercury oxidation and speciation. In that modeling study, the amount of mercury deposition increases with the thickness of the boundary layer and corresponds to the column amount of BrO.
oxidize the mercury. The modeling studies\textsuperscript{143,144} indicate that boundary layer, where halogens can remove the ozone and aloft. This mixing brings down more mercury and ozone to the cover, elevates these gaseous abundances by down mixing from convection from sea-ice leads, which are cracks in the sea ice.

Recent advances in both mass spectrometric and optical instrumentation have enabled new observations of halogen chemistry. Moore and co-workers\textsuperscript{145} examined ozone and mercury levels and found that vertical mixing induced by storms.\textsuperscript{117,122} Arctic\textsuperscript{118,123,124} and Antarctic work\textsuperscript{146} indicated that significant amounts of BrO exists above the convective boundary layer. What is less clear and has been the subject of many studies in the last few decades is the mechanism and efficiency of their release from sea salt aerosol, any transformations in the atmosphere and the relevance for the chemistry of the marine atmosphere of these halogens. Furthermore, it is known that organic and inorganic halogen-containing gases are being produced in the oceans and at the ocean’s surface and are being released into the atmosphere. In this section, recent progress in this field is summarized with a focus on the literature not covered in Saiz-Lopez and von Glasow, 2012.\textsuperscript{52} This discussion excludes the polar marine boundary layer which has been covered extensively above in section 3.1.

3.2. Marine Boundary Layer

More than 70% of the Earth’s surface is covered by oceans. Globally, sea spray aerosol released from the oceans is together with dust the largest natural source of aerosol particles. It is therefore obvious that large amounts of chloride and bromide, which are contained in seawater, are present in the marine boundary layer (MBL). What is less clear and has been the subject of many studies in the last few decades is the mechanism and efficiency of their release from sea salt aerosol, any transformations in the atmosphere and the relevance for the chemistry of the marine atmosphere of these halogens. Furthermore, it is known that organic and inorganic halogen-containing gases are being produced in the oceans and at the ocean’s surface and are being released into the atmosphere. In this section, recent progress in this field is summarized with a focus on the literature not covered in Saiz-Lopez and von Glasow, 2012.\textsuperscript{52} This discussion excludes the polar marine boundary layer which has been covered extensively above in section 3.1.

3.2.1. MBL Reactive Chlorine and Bromine. Chloride is the most abundant halide in the marine boundary layer and is released from sea salt aerosol as HCl by acid displacement and photochemically as reactive radicals or their precursors (see section 2.1). Recent very exciting discoveries around ClNO\textsubscript{2} in polluted coastal regions and other areas with high NO\textsubscript{x} loadings are discussed in section 3.3.

Reactive chlorine species, such as HOCl and Cl\textsubscript{2}, have been measured at Cape Verde,\textsuperscript{54,148} an island in the central Atlantic Ocean, but numerical models struggle to reproduce these observations.\textsuperscript{54,149} The models predict that most non-HCl chlorine that is released from sea salt aerosol is released as BrCl whereas the measurements show no detectable BrCl. This clearly shows that our understanding of the main halide compound in the MBL is incomplete.

In polar regions, reactive bromine in the form of BrO is routinely detected, but outside polar regions, there are only a few reports of BrO that exceed detection limits. We are only aware of published detection of BrO two times in nonpolar coastal areas\textsuperscript{150,151} during 2 cruises in the North Atlantic\textsuperscript{152,153} and at Cape Verde.\textsuperscript{59,154} The Cape Verde observations are regarded as representative of the MBL surrounding the island and not influenced by coastal effects. Recent NO\textsubscript{3}^{-}\textsuperscript{1}
isotope analyses from Cape Verde\textsuperscript{155} suggest that BrNO$_3$ contributes 20 ± 10\% to NO$_3^-$ formation, implying the presence of BrO. The lack of open ocean detection of BrO at locations other than the tropical North Atlantic (around Cape Verde) and a small part of the West-Pacific is very surprising especially given that it has been known for decades that marine aerosol particles are substantially depleted in bromide,\textsuperscript{156} and that bromide would have been expected to be liberated photochemically to produce reactive halogens rather than simple acid displacement as happens with chloride.

Photochemical models were initially used to interpret the first measurements of Cl atom precursors (Cl$_2$ and HOCl) in early and recent studies.\textsuperscript{19,54,157,158} From those initial measurements of reactive chlorine precursors, models were used to estimate the source strength needed to reproduce the observations, and to assess the atmospheric implications of the resulting Cl atom concentrations. Early pioneering work by Hov\textsuperscript{159} employed a photochemical model to investigate the effects of chlorine emissions from chemical industries, on the formation of photochemical oxidants in southern Telemark, Norway. The 1D model MISTRA\textsuperscript{157} was later used to highlight the importance of recirculation of polluted air masses over the marine atmosphere as an additional source of chlorine from sea-salt aerosols. This model was also used to simulate the results from experimental measurements of Cl$_2$ and HOCl performed over the ocean at the Cape Verde islands.\textsuperscript{149} These model results showed that Cl atoms accounted for 5.4--11.6\% of the total methane oxidation at this tropical Atlantic site.

Detailed multiphase models\textsuperscript{149,160--162} (see section 3.4) suggest BrO mixing ratios should be present well above detection limits, so it remains unclear why so little BrO is present in the MBL other than the few locations mentioned above. The global study by Long and co-workers\textsuperscript{162} successfully reproduces some of the measured Br$^-$ deficits in aerosol particles but still seems to underestimate BrO mixing ratios. Sommariva and co-workers\textsuperscript{149} discuss potential reasons for this surprising mismatch between models and field data.

### 3.2.2. Organobromine Sources

So-called very short-lived (VSL, lifetime of less than 6 months) substances have been identified as playing a key role in supplying bromine to the stratosphere.\textsuperscript{163} Due to their short lifetimes of a few weeks to a few months, compounds, such as CHBr$_3$ and CH$_2$Br$_2$, also constitute a source for bromine in the troposphere, and are thus relevant to this review article. Ground based, shipboard, and airborne measurements during the recent TRANSBROM and SHIVA campaigns and related model simulations showed that contrary to earlier suggestions (e.g., Pyle and co-workers\textsuperscript{164}), the Western Pacific and Maritime Continent do not constitute a “hot spot” for brominated VSL emission and transport into the upper troposphere/lower stratosphere (UTLS).\textsuperscript{165--170}

During measurements of sea-air fluxes of bromocarbons in the North Atlantic, a link with marine biological precursors was confirmed.\textsuperscript{171} It was also suggested that the height of the MBL plays a role in determining sea-to-air fluxes of CHBr$_3$ as variations in this height lead to changes in the atmospheric CHBr$_3$ mixing ratios,\textsuperscript{171,172} and potentially also to changes in the magnitude of the sea-air concentration gradient, which determines the flux. A very good discussion of the main currently used global emission inventories for bromocarbons is given by Ashfold and co-workers.\textsuperscript{167} Hossaini and co-workers\textsuperscript{173} evaluated these various inventories comparing the resulting concentrations in a global model with available field data and concluded that large uncertainties still exist even though CHBr$_3$ in the free troposphere can be reproduced reasonably well. Compared to short-lived organobromine species, less is known about fluxes of organochlorine species. However, most organic Cl species are longer lived and contribute to stratospheric Cl predominantly rather than tropospheric halogens that are the focus of this review. Organic chlorine species should be further investigated for their roles in both the troposphere and stratosphere.

### 3.2.3. MBL Iodine

Unlike bromide and chloride, which are abundant in the oceans and not significantly depleted by marine biological processes, oceanic iodide is at low levels because of its consumption as a nutrient by biological systems, as well as possible inorganic processes. Therefore, the sources for reactive iodine in the MBL are very different from chlorine and bromide. For iodine, sea salt aerosol particles represent a sink rather than a source\textsuperscript{16} and virtually all inorganic iodine that is present in the MBL originates from decomposition of natural iodocarbons such as CH$_3$I and CH$_2$I$_2$ and the inorganic precursors HOI and I$_2$.\textsuperscript{30} The reactions involved in ozone-
mediated iodide release via HOI are shown in reactions 13 and 14.

\[
\begin{align*}
H^+ + I^- + O_3 &\rightarrow HOI + O_2 \quad (13) \\
H^+ + HOI + I^- &\leftrightarrow I_2 + H_2O \quad (14)
\end{align*}
\]

Recent laboratory studies quantifying these reactions coupled with modeling has been successful at predicting field IO observations. Model calculations of IO and its organic precursors have also been successful recently. Although the quantitative success of this mechanism is a recent development, the idea of HOI and I2 being released from the ocean surface goes back to Garland and Curtis in 1981.

In the MBL, two regions show distinctly different sources and amounts of IO. First, in coastal regions, tidal exposure of macroalgae leads to large fluxes of iodine precursors, formation of IO and new particles. Second, in the open ocean, tidal exposure of marine biota is absent, thus more modest fluxes of iodine atom precursors occur and resulting IO mixing ratios occur. As the atmosphere processes these gas-phase species to oxidized, ionic iodide species, iodine accumulates in marine aerosol particles. On various cruises iodide, iodate and organic iodine have been identified, but the reaction pathways leading to the differences in speciation which vary with location and time are not yet fully understood.

Iodine oxide in the remote MBL has been observed at Tenerife, Tasmania, Cape Verde, the West-Pacific, and East-Pacific. At these locations, comparisons of model results with field data suggest that organic iodine precursors are insufficient to explain the observed levels of IO. pointing at the importance of I2 and especially HOI as a source for reactive iodine from the reaction of O3 on the ocean’s surface. At Cape Verde, I2 was measured recently showing an increase in its mixing ratio at sunset, a leveling off around midnight and rapid decrease at sunrise. However, the nocturnal leveling off was only observed on about half of the reported days. Model calculations suggested that I2 and iodocarbons were insufficient to explain observed IO levels, implying the relevance of the sea-air exchange of HOI.

Prados-Roman and co-workers compiled data from a global circumnavigation and other field campaigns to produce the global map of IO shown in Figure 6. Measurements on a cruise in the East Pacific by Mahajan and co-workers showed maximum IO mixing ratios of 1.2 pmol/mol. They observed a positive correlation with sea surface temperature and salinity but a negative correlation with organic matter in the surface ocean, chlorophyll, and atmospheric ozone. A seasonal relationship of IO with the sea surface temperature was also observed by Gómez Martín and co-workers at Galapagos and by Prados-Roman and co-workers. A correlation with sea surface temperature might be the result of iodide in surface water showing a reasonable correlation with the sea surface temperature, which would hint at the above-discussed reaction of ozone with iodide in the sea surface layer as source for reactive iodine (HOI and I2). Interestingly, the analysis of CHI trends at five Pacific sites by Yokouchi and co-workers showed variations with a period of 11 years, which the authors related to the Pacific Decadal Oscillation and might imply a sea surface temperature dependence of CHI fluxes. Prados-Roman and co-workers also performed global model calculations which showed that these abiotic precursors contribute about 75% to IO in the MBL. They observed a strong geographical pattern of the relative contribution of organic versus inorganic precursors to IO.

Wang and co-workers present year-long mercury speciation measurements at the Galapagos islands and report low elemental mercury concentrations throughout but higher than expected amounts of oxidized mercury around midday suggesting a photochemical sink. Their calculations suggest that neither BrO, O3 or OH can lead to the observed values of oxidized mercury and suggest that iodine atoms or potentially HO2 or NO2 might play an important role in stabilizing intermediate mercury compounds, such as HgBr.

3.2.4. Laboratory Studies of MBL Halogen Activation Reactions. The observations described above point to the importance of Reactions 13 and 14 in producing HOI and I2 from ocean surfaces. An important aspect of this reaction is that the presence of the sea surface microlayer modifies the reactivity of either the ocean’s surface or that of sea salt aerosol particles produced by bubble breaking. Therefore, a number of recent laboratory studies have investigated the role of organics in modifying ozone-oxidation of iodide on proxies of ocean surfaces. Reeser and Donaldson studied the effect of octanol on the heterogeneous reaction of I2 with ozone and found that octanol slightly increased the total amount of I2 produced, but diminished the partitioning of this iodine to the air, instead retaining it in the organic layer. Hayase and co-workers studied the effects of various aqueous organic species on iodide oxidation by ozone and found differing effects from different organics, with anionic phenolates suppressing iodine activation. Later work from this group found that fulvic acids enhanced I2 production, but a number of other similar humic-like substances did not affect these reactions. Sill and Carpenter found that marine-origin DOC suppressed the production of I2 by roughly a factor of 2 in laboratory samples with reactivity ratios between I2 to DOC similar to natural seawater. Pillar and co-workers studied the reaction of iodide with ozone in aerosolized solutions as a function of iodide concentration and observed production of HOI and I2 in agreement with solution studies. Sakamoto and co-workers found that Fe2+ ions increased ozone-oxidation of iodide solutions, an effect that they interpreted as due to pH buffering. Overall, these laboratory studies help to quantify effects of organics and pH and assist in understanding the processes controlling I2 and HOI production via ozone reactions in the marine boundary layer.

As discussed in sections 2.1.4 and 2.2.1, heterogeneous reactions of halides with hypohalous acids (HOX species) is an important process for activating and maintaining reactive halogen levels. A number of laboratory investigations have addressed this heterogeneous process under tropospheric conditions. Recently, Roberts and co-workers reevaluated HOBr reactive uptake and reaction with HBr/HCl as a general acid-assisted reaction. This model is able to reproduce laboratory observations, and inclusion of this type of models in chemical transport models may improve understanding of the role of pH on halogen activation.

3.2.5. Summary of Recent Findings in the MBL. Marine boundary layer chlorine cycling remains poorly understood. Recent HOCl and Cl2 observations have been made at Cape Verde, but they are in contrast to some models that suggest the prevalence of compounds, such as BrCl. Models do suggest that the measurement imply >5% of methane oxidation occurring through Cl regionally.
In contrast to polar regions, only a very limited number of measurements of BrO in the marine boundary layer have shown levels above instrumental detection limits. Measurements at Cape Verde do show low levels of BrO and are regarded as representative. Several lines of evidence suggest the importance of BrO, such as measurements of oxygen isotopes in particulate nitrate and the Br depletion in sea salt. Models generally predict considerably more BrO than observed, indicating the need for much better mechanistic understanding of Br MBL chemistry. Organic bromine is a source of MBL Br and has been recently linked with ocean biological activity.

Recent laboratory studies suggest the importance of heterogeneous uptake of ozone to iodide containing substrates as a source of HOI and I$_2$. This work is supported by recent measurements and associated modeling of iodine species in marine environments, which indicate that heterogeneous uptake of O$_3$ may be an important source for atmospheric I compounds relative to the more conventional emission and oxidation of organo-iodine species. Iodine species are present at high concentrations in some coastal areas, but I$_2$ has been shown recently to be widespread at low levels across the world’s oceans.

3.3. NO$_3$ Pollution-Related Halogen Chemistry

For decades, there has been significant interest in reactive halogen chemistry occurring in polluted regions. In part, the motivation is to understand sources of oxidants that contribute to the formation of secondary pollutants, such as ozone and particle mass in populated regions, as well as the lifetime of primary pollutants such as hydrocarbons and their oxidation products. As noted in previous sections and other literature reviews, the mechanisms of halogen activation and recycling are strongly influenced by anthropogenic pollutants. The high concentrations of HNO$_3$ and H$_2$SO$_4$ in polluted regions can promote the acidity dependent autocatalytic release of bromine and chlorine via HOBr and HOCl reactions with aerosol chloride or bromide (see section 2.1). But, the efficiency of the autocatalytic mechanisms is degraded by the presence of both high nitric oxide, NO, which suppresses HO$_2$ formation, and hydrocarbons and their oxidation products, which serve as strong sinks of halogen atoms that terminate reactive halogen cycling.

Research over the past decade has demonstrated that activation readily occurs within polluted urban areas, both coastal and inland, especially the activation driven by N$_2$O$_5$ heterogeneous chemistry to form nitryl halides. To date, there is no in situ evidence for enhanced bromine or iodine activation by this mechanism in urban areas, though laboratory studies and modeling would suggest it should occur. Below, we briefly review halogen cycling and activation in polluted regions, focusing on recent work, which has mostly centered on the role of nighttime production of ClONO$_2$ by N$_2$O$_5$ and its impacts on hydrocarbon oxidation, ozone production and the lifetime of methane. Over the past five years, relatively little advancement has occurred in our understanding of daytime halogen recycling chemistry in polluted regions, and thus we provide suggestions on areas for future research in this regard in section 5.

3.3.1. Activation Mechanisms. In polluted regions, all activation mechanisms previously discussed (see sections 2.1 and 2.2) are possible. Dihalogen Cl$_2$, Br$_2$, and I$_2$ all have been observed in polluted coastal air, albeit at fairly different mixing ratios: low pmol/mol for Br$_2$ and I$_2$ and up to 200 pmol/mol for Cl$_2$, as shown in Table 1. Interestingly, BrCl has only sporadically been detected, or not detected at all outside of polar regions. While substantial mixing ratios of Cl$_2$ have been detected in polluted coastal regions, or pollution impacted remote regions, the mechanisms by which the Cl$_2$ is produced remain uncertain. Additionally, instrumental methods for detection of Cl$_2$ are challenging, opening the possibility of large measurement uncertainties. Possible chemical sources of Cl$_2$ include light activated reactions, multiphase chemistry of nitryl halides, or reactions of BrCl and HOCI at rates that are different than current mechanisms predict. The autocatalytic mechanisms involving hypohalous acids, presented in section 2.1.4, are expected to be suppressed or key reservoirs substantially altered in polluted air relative to remote regions, as discussed in the next section. It is also clear that some industrial processes and power generation lead to direct emissions of Cl$_2$ but these point sources can usually be distinguished from regional sources of Cl$_2$, which seem to have diurnal patterns that depend upon location. There is no consensus on the most important sources of dihalogen in polluted regions, as such further research efforts are required and these issues are discussed in section 5.

Of particular interest for pollution-induced halogen activation is the production of nitryl halides (XNO$_2$, where X = Cl, Br, I), such as ClINO$_2$ (reactions 15−19), which is now considered to be a major halogen activation process in polluted regions. At night, nitrogen oxide radicals are oxidized by O$_3$ to NO$_2$, which can react with NO$_3$ to form N$_2$O$_5$. N$_2$O$_5$ can then react with halide-containing particles or on halide surfaces to produce XNO$_2$. The activation of halogens by N$_2$O$_5$ is therefore tied to NO$_x$ sources, ozone concentrations, the homogeneous reactivity of NO$_3$ and availability of halide-containing aerosol particles; all of which vary with season and location. Photolysis of XNO$_2$ is slower than dihalogen, but fast enough to contribute significantly to the morning radical budget. The low sunlight intensity at sunrise means that the morningtime production of chlorine radicals is spread over ∼3−5 h, even though the noontime photolysis rate is often less than an hour. XNO$_2$ formation and photolysis also affect the reactive nitrogen budget and partitioning with indirect impacts on oxidants.

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_3 + \text{NO}_2 & \rightarrow \text{N}_2\text{O}_5 \\
\text{N}_2\text{O}_5 + X^- & \rightarrow \text{product} \rightarrow \text{XNO}_2 + \text{NO}_3 \\
\text{XNO}_2 + \text{hv} & \rightarrow \text{X} + \text{NO}_2
\end{align*}
\]
chloride attack of the NO$_2^-$ intermediate is a factor of $\sim$500 more efficient than that of water. Thus, nitryl halide production by N$_2$O$_5$ competes with N$_2$O$_5$ hydrolysis down to <0.1% halide solute mass fractions.\textsuperscript{217} Figure 8 shows that CINO$_2$ product yield per N$_2$O$_5$ reaction on chloride containing media approaches unity for chloride contents of fresh sea spray, but remains greater than 10% for trace chloride contents. Given that the N$_2$O$_5$ reaction probability on most aqueous aerosol particles (the exception being nitrate containing particles)\textsuperscript{215} is fairly insensitive to the presence or absence of halide ions, the rate limiting step for nitryl halide formation is presumably the solvation and ionization of N$_2$O$_5$, and not nucleophilic attack.

To date, there have been no reported in situ observations of BrNO$_2$ nor INO$_2$. The reactivity and or solubility of BrNO$_2$ and INO$_2$ are likely much greater than CINO$_2$, such that once produced they either react away to other halogen products or remain in the condensed phase. This latter suggestion is supported by recent work studying N$_2$O$_5$ reactive uptake to halide-doped ices and bromide salts, where Br$_2$ not BrNO$_2$ was always the dominant product.\textsuperscript{219} Similar findings of enhanced multiphase reactivity of BrNO$_2$ were obtained in studies of uptake to aqueous solutions.\textsuperscript{219} Thus, CINO$_2$ is likely to be the dominant nitryl halide observed because of its lower solubility and reactivity and thus greater accumulation in the nighttime air. N$_2$O$_5$ may activate the more trace halides (Br$^-$ and I$^-$) to completion but in the form of other molecular halogens (e.g., Br$_2$, BrCl, I$_2$, ICl, IBr, etc.). Roberts and co-workers\textsuperscript{220} showed that at highly acidic pH (pH <2), N$_2$O$_5$ can directly oxidize chloride to Cl$_2$, which may be responsible for production of molecular chlorine on acidic aerosol particles.

The significant nitryl chloride yield even at low chloride concentrations helps to explain the detection of CINO$_2$ several hundreds of kilometers inland from sea spray sources such as near Denver in the U.S., Calgary in Canada, Umtah Basin of the U.S., and Frankfurt in Germany,\textsuperscript{51,55,57,78,79,209,221} and the significant concentrations produced in polluted coastal regions. Osthooff and co-workers\textsuperscript{77} and Thornton and co-workers\textsuperscript{78} estimated that 3–20 Tg/year of Cl atoms could be produced by this mechanism alone on a global basis. If all of these chlorine atoms reacted with methane, that process would account for a significant part of the global methane loss budget. However, while it is unlikely that all chlorine atoms in polluted regions react with methane,\textsuperscript{211} there are secondary impacts of CINO$_2$ production on the abundance and sources of OH, which would further enhance the methane loss rate in regions with significant CINO$_2$. Thus, the budget and spatial distribution of CINO$_2$ production are important to constrain in order to develop accurate estimates of methane removal.

A key scientific question with respect to CINO$_2$ distributions is not so much related to the mechanism of CINO$_2$ formation, but more so whether chloride is present to promote such chemistry in polluted regions, and if so, what the sources and aerosol partitioning of the labile chloride are, especially well inland. A recent global modeling study, described in detail in section 3.4.1, illustrated that with an updated chloride emission inventory that included only sea spray and biomass burning sources, widespread production of CINO$_2$ is predicted well inland of the polluted coastal regions\textsuperscript{222} (see Figure 9 below). The model predicted that with just these sources mean daytime maximum CINO$_2$ mixing ratios reached >0.5 nmol/mol throughout regions of the eastern U.S. and China, as well as in regions of Europe, accounting for ~15% of reactive nitrogen, generally consistent with observational based estimates.\textsuperscript{76} Peak CINO$_2$ mixing ratios from the model were generally lower than observations, suggesting differences between modeled and actual vertical mixing in the nocturnal atmosphere and/or additional chloride sources such as from power generation, as are found in recent inventories.\textsuperscript{73} Vertical profiles of CINO$_2$ measured outside of Denver, CO, provide evidence for a source of chloride and CINO$_2$ production within coal-fired power plant plumes.\textsuperscript{211} The magnitude of such a source compared to sea spray transport and biomass burning remains uncertain, in part, to a lack of measurements of chloride and CINO$_2$ within isolated power plant plumes.

**Figure 7.** Nighttime observations of NO$_2$ polluted air containing N$_2$O$_5$ and produced reactive halogen precursor, nitryl chloride, CINO$_2$, measured at the Scripps Institution of Oceanography Pier. Reprinted with permission from Kim and co-workers (2014).\textsuperscript{212} Copyright 2014 National Academy of Sciences.

**Figure 8.** Conversion efficiency for production of CINO$_2$ from N$_2$O$_5$ from laboratory measurements along with models. Panel b shows ranges of particulate chloride composition from the TexAQS-GoMACCS 2006 field campaign. Reprinted with permission from Roberts and co-workers (2009).\textsuperscript{217} Copyright 2009 American Geophysical Union.

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The literature demonstrating high levels of ClNO₂ far from the coast has grown in recent years. Mielke and co-workers observed nighttime ClNO₂ maxima of 80–250 pmol/mol at the continental site of Calgary, Alberta, Canada, 800 km from the nearest ocean in late April. Phillips and co-workers found ClNO₂ mixing ratios up to 800 pmol/mol at a mountaintop site in southwestern Germany, about 400 km from the nearest coastal regions. Edwards and co-workers in 2012 observed median levels of ClNO₂ above 400 pmol/mol and peaks above 800 pmol/mol during wintertime in the oil and gas producing Uintah Basin of Utah, again hundreds of kilometers from coastal regions. In 2013, the same group observed ClNO₂ levels, with peaks ~500 pmol/mol, and significant wintertime ozone production leading to violations of the National Ambient Air Quality Standards.

In coastal regions, high mixing ratios of ClNO₂ and Cl₂ were detected in recent studies. Riedel and co-workers observed nighttime ClNO₂ maxima commonly over 500 pmol/mol and up to 2100 pmol/mol during May/June from a shipboard platform in the Santa Monica Bay at times when sampling the Los Angeles urban pollution plume during the CalNex campaign. Wagner and co-workers considered the sea breeze/land breeze circulation pattern in the Los Angeles basin and modeled the role of in situ production versus transport of nitril chloride. They found that on most nights the majority of ClNO₂ is produced in the basin over land and transported offshore by the land breeze. More variable levels of activation of Cl₂ with peak levels up to 200 pmol/mol were observed. Mielke and co-workers observed ClNO₂ at the polluted near-coastal site of Pasadena, California every night during the same campaign, with a median mixing ratio of 800 pmol/mol. At sunrise, the median ClNO₂ abundance constituted more than 20% of non-NOₓ reactive nitrogen oxides. As shown in Figure 7, ClNO₂ was observed in the marine boundary layer near San Diego, California. This study used a fast-response detector and the eddy-covariance technique to measure the deposition flux of both N₂O₅ and ClNO₂ and found that both species deposit to the ocean rapidly under the relatively windy conditions (mean windspeed 9 m s⁻¹) of this night’s data, indicating that elevated mixing ratios seen in the studies mentioned above are sustained primarily on aerosol particles rather than the ocean surface layer. Vertical profile measurements of ClNO₂ by Young and co-workers during the CalNex campaign over the Los Angeles basin showed no average dependence upon height in the boundary layer and residual layer, indicating that reactions on aerosol
particles are the most important sources of CINO2. Crisp and co-workers224 made measurements off the California coast and found a very good correlation of HCl with non-NOx reactive nitrogen, NOx = NOy − NOx. They found strong chloride depletion in aerosol particles off the coast of Northern California but surprisingly they detected chloride enrichment in 25% of the particles sampled off Southern California pointing at large, possibly anthropogenic, sources of nonsea salt chlorine in Southern California.

In addition to nitril halides, reactive nitrogen can also activate nitrosyl halides (XNO). In particular, nitrosyl chloride (CINO) was proposed to be a Cl atom source in polluted air.225 Using a regional 3-D chemical transport model, Raff and co-workers225 predict that CINO mixing ratios in polluted marine areas could reach parts per billion mixing ratios or higher, that is, similar to CINO2 concentrations detected in such regions. However, these theoretical and laboratory studies have yet to be confirmed by field measurements of CINO in ambient air. A possible explanation is that hydrolysis of CINO at moderate and high relative humidity (RH > 20%) is likely sufficiently rapid to prevent the buildup of appreciable atmospheric concentrations of CINO.226 Further attempts to quantify CINO in ambient air are certainly warranted.

3.3.2. Halogen Recycling in Polluted Regions. Following the autocatalytic mechanism (see section 2.1), in remote regions during daytime, a halogen atom (X) will often react with ozone to form the corresponding halogen oxide (XO), or in the case of atomic chlorine, approximately half react with O3 and half with CH4.55 The XO then typically react with HO2 to form the hypohalous acid (HOX), which either photolyzes or partitions to aerosol where it undergoes condensed-phase reactions to form dihalogens at low pH. The dihalogens then react with NO (reaction 21) to reform NO2 under the autocatalytic mechanism (see section 2.1), in remote regions during daytime relative to remote regions. But, nitric oxide is lost at night, decreasing ozone levels. However, when formation of CINO2 happens via reaction of aerosol-particle-accommodated NOx with Cl, a reservoir is formed that photolyses (reaction 19) in the morning, releasing NO2 and the potent oxidizer, chlorine radical atoms. Riedel and co-workers228 found that the peak producer of chlorine atomic radicals was the morningtime photolysis of CINO2, with peak production of Cl exceeding that of OH + HCl (reaction 12). Using the MCM model with added halogen chemistry reactions, Riedel and co-workers228 find that CINO2 increases the total integrated daytime radical source by 17%, which leads to a similar enhancement in integrated ozone production of 15%. The modeled effect on acyl peroxy nitrates (APN) was more than 100%. Therefore, the impact of nighttime formation of CINO2 extends out to late afternoon. Another complexity noted in this study228 is the effect of CINO2 in extending the lifetime of NOx by preventing nocturnal loss via NOx hydrolysis yet secondary OH produced after morning photolysis of CINO2 reduces the lifetime of daytime NOx lifetime via OH + NO2 (+ M). Osthoff and co-workers77 also presented an MCM model of the effect of CINO2 photolysis on ozone production in Houston, TX, showing that inclusion of measured CINO2 levels increased afternoon ozone by 6−9 nmol/mol. These results were qualitatively consistent with previous modeling studies of the influence of Cl sources on ozone production in both Los Angeles260 and Houston231 that showed considerable sensitivity of ozone to Cl atom sources, but that did not explicitly consider CINO2 as a Cl atom source. Hydrocarbon clocks involving sets of three VOCs, two of which have similar OH rate constants but different Cl rate constants, and two of which have the opposite, have been used to demonstrate the importance of Cl oxidation in remote, polar regions with low NOx.101,207 Young and co-workers50 showed that in higher NOx environments characteristic of urban areas, where CINO2 may be a large radical source, the secondary recycling of OH subsequent to the initial Cl atom production obscures the effect of Cl atoms on these hydrocarbon clocks, such that they do not reflect the influence of Cl even in simulations where CINO2 photolysis is the sole primary radical source. At the continental site in the Uintah Basin, Edwards and

nitrates, XONO2 from three-body reaction of XO with NO2. Relatively little experimental data exists to constrain estimates of reactivity in aerosol particles having compositions typical of polluted regions. However, after reaction with NO, XONO2 formation is the next most important fate for XO radicals in polluted regions. Given the slow photolysis of XONO2 in the lower troposphere, about 30 times slower than NO2, XONO2 is subject only to thermal decomposition at rates similar to acyl peroxy nitrates, wet and dry deposition, or uptake to aerosol particles. Dieber and co-workers229 showed that XONO2 reacted rapidly on aqueous halide solutions to form dihalogens instead of hydrolysis (which, for X = Br, would produce HOBr and HNO3), as may have been expected and has been included in models.136 If this process can be verified and the reaction probabilities quantified as a function of halide content in aerosol particles representative of urban areas, then the potential for halogen recycling in polluted regions would be much better constrained.

3.3.3. Interactions with Oxidants and Reactive Nitrogen. Formation of nitril chloride by reactions 15−19 has a complex interplay with ozone. The nocturnal production of O3 consumes significant amounts of ozone at night, and to the extent that heterogeneous hydrolysis of N2O5 occurs, both ozone and NOx are lost at night, decreasing ozone levels. However, when formation of CINO2 happens via reaction of aerosol-particle-accommodated NOx with Cl, a reservoir is formed that photolyses (reaction 19) in the morning, releasing NO2 and the potent oxidizer, chlorine radical atoms. Riedel and co-workers228 found that the peak producer of chlorine atomic radicals was the morningtime photolysis of CINO2, with peak production of Cl exceeding that of OH + HCl (reaction 12). Using the MCM model with added halogen chemistry reactions, Riedel and co-workers228 find that CINO2 increases the total integrated daytime radical source by 17%, which leads to a similar enhancement in integrated ozone production of 15%. The modeled effect on acyl peroxy nitrates (APN) was more than 100%. Therefore, the impact of nighttime formation of CINO2 extends out to late afternoon. Another complexity noted in this study228 is the effect of CINO2 in extending the lifetime of NOx by preventing nocturnal loss via NOx hydrolysis yet secondary OH produced after morning photolysis of CINO2 reduces the lifetime of daytime NOx lifetime via OH + NO2 (+ M). Osthoff and co-workers77 also presented an MCM model of the effect of CINO2 photolysis on ozone production in Houston, TX, showing that inclusion of measured CINO2 levels increased afternoon ozone by 6−9 nmol/mol. These results were qualitatively consistent with previous modeling studies of the influence of Cl sources on ozone production in both Los Angeles260 and Houston231 that showed considerable sensitivity of ozone to Cl atom sources, but that did not explicitly consider CINO2 as a Cl atom source. Hydrocarbon clocks involving sets of three VOCs, two of which have similar OH rate constants but different Cl rate constants, and two of which have the opposite, have been used to demonstrate the importance of Cl oxidation in remote, polar regions with low NOx.101,207 Young and co-workers50 showed that in higher NOx environments characteristic of urban areas, where CINO2 may be a large radical source, the secondary recycling of OH subsequent to the initial Cl atom production obscures the effect of Cl atoms on these hydrocarbon clocks, such that they do not reflect the influence of Cl even in simulations where CINO2 photolysis is the sole primary radical source. At the continental site in the Uintah Basin, Edwards and
co-workers found that wintertime high ozone events had radical budgets dominated by photolysis of carbonyl species that were products of VOC oxidation by primary and secondary radicals. Nitril chloride photolysis did contribute to morning-time primary radical sources, but constituted only about 6% of total primary radical source and 1% of total radicals. This work points out the large effect of carbonyl species that come from oxidation of VOC in amplifying radical production in multiday pollution episodes. Because chlorine radicals and hydroxyl radicals differ in their rates and preference for oxidation of VOC species, production of carbonyls may depend upon the relative abundance of chlorine and HO radicals. These studies point out the multifaceted nature of halogen activation and “normal” ozone photochemistry and the need for further study of the interaction between pollution and halogen activation for ozone and other air quality issues.

3.3.4. Summary of Recent Findings in the Polluted Regions. There are numerous observations of Cl2 in polluted air, but not of other dihalogens. Sources of these compounds, either from emissions or chemistry, remain highly uncertain. By contrast, recent observations suggest very large ambient mixing ratios of CINO2, derived from a well-known mechanism involving nighttime heterogeneous uptake of N2O5 to chloride-containing aerosol particles or surfaces. This mechanism can in principle also activate Br and I, but the corresponding halides have yet to be observed in ambient air and may undergo additional heterogeneous chemistry to produce dihalogens. The database for ambient CINO2 observations is growing, and demonstrates this compound to be widespread, occurring at appreciable levels even in continental environments. The observations imply a substantial global atomic Cl source from CINO2 photolysis. Chemical transport models that incorporate recent parametrizations of CINO2 from N2O5 uptake to chloride substrates are consistent with the widespread occurrence of CINO2. Nitril halide (XNO) production has also been suggested from laboratory and modeling studies of heterogeneous NO3 chemistry, but these compounds have yet to be observed in ambient air and may be unstable against further heterogeneous reactions.

Cycling of halogen radicals in polluted regions is predicted to differ substantially from that in remote areas, especially polar regions. Atomic chlorine and bromine react preferentially with hydrocarbons rather than methane or ozone, suppressing formation of XO. Subsequent reaction of XO that does form is dominated by reactions with NO and NO2 rather than by heterogeneous recycling mechanisms that can lead to halogen explosions in polar areas.

Nitril chloride, CINO2, production and photolysis certainly influences ozone production in regionally polluted environments. The Cl atom can be a large radical source, especially during the morning, and can increase total daytime radical production by up to 17%. The NO2 recycled through this mechanism provides a morning NO2 source that will also influence ozone production, though the exact influence will depend on the specific sensitivity of ozone to NO2 in a given area.

3.4. Regional and Global Halogen Chemistry

The latest developments in global modeling of halogen chemistry aim to characterize the inorganic bromine (Br) and iodine (I) burdens, and partitioning, in both the troposphere and the stratosphere, since their impact on global atmospheric oxidizing capacity, ozone budget, and its associated radiative forcing remains an open question. Recent global modeling studies have focused on bromine chemistry, and to a much lesser extent on iodine, while the published works about chlorine chemistry are mainly local studies using photochemical and 1-D box models (described in section 3.3) and, more recently, regional models to explain measurements of Cl atoms precursors (Cl2, CINO2, or HOCl) and their implications on ozone levels. Over the past decade, most global halogen chemistry models have focused on estimating ocean emissions of very short-lived halocarbons (VSL) and the transport of these VSL species, and their breakdown products, to the stratosphere. However, this review focuses on tropospheric halogen chemistry, and several models have assessed the role of reactive bromine chemistry on tropospheric ozone, primarily over the marine atmosphere. More recently first estimates of the enhanced effect of combined bromine and iodine chemistries on tropospheric ozone, and its associated radiative impact, have been reported.

3.4.1. Regional Modeling of NO2-Related Halogen Chemistry. As discussed in section 3.3.3, NO2-induced halogen activation via CINO2 affects ozone, particularly near coasts. On a regional scale, Sarwar and Bhave combined gas-phase chlorine chemistry with the Carbon Bond Mechanism in the Community Multiscale Air Quality model (CMAQ), to study the impact of chlorine chemistry on ozone levels over the Eastern United States. The model incorporated anthropogenic emissions of Cl2 and HOCl, and natural sources from sea-salt aerosols. Heterogeneous reactions involving chloride in aerosols and gas-phase species were modeled in CMAQ as the source of chlorine from aerosols. The results from this study suggested that O3 concentrations in most areas of the eastern United States were not affected by chlorine emissions. Only in the Houston and New York—New Jersey areas the daily maximum 1-h O3 concentrations were considerably affected by up to 12 and 6 nmol/mol, respectively, compared to a typical values of ozone mixing ratios in these regions of 40–80 nmol/mol. Simon and co-workers incorporated CINO2 production into their CAMx model of ozone formation in southeast Texas. Although they found only a modest influence on regional ozone, with peak increases in 1 h ozone on the order of 1–1.5 nmol/mol, they demonstrated that N2O5 uptake and CINO2 photolysis was by far the largest source of atomic Cl in the region, in contrast to previous results implicating industrial and residential sources. They identified key uncertainties in the yield of CINO2 from N2O5 uptake and in the vertical distribution of CINO2 at sunrise. More recently, Sarwar and co-workers updated the chlorine activation mechanism, including the treatment of heterogeneous hydrolysis of N2O5 to include CINO2 as product and improved emissions inventories. This updated version of the CMAQ model, with a comprehensive inventory of chlorine and reactive nitrogen emissions, has been employed to evaluate the impact of heterogeneous nitril chloride production on the United States air quality. The results from this work show that the production of CINO2 slightly increases the monthly 8 h ozone mean by up to 1–2 nmol/mol. They also reported an episode, albeit isolated, of considerable ozone enhancements of up to 13 nmol/mol. The authors expanded the scope of their study recently to assess the atmospheric role of CINO2 chemistry in the whole Northern Hemisphere. Figure 9 shows CINO2 modeled mixing ratios from this most recent study. This hemispheric modeling approach indicates a general decrease in the nitrate levels and an increase in ozone, as a consequence of
the production of ClNO₂. The largest increase in O₃ levels was found in China with an increase of more than 7.0 nmol/mol in winter, while the increase in the rest of the northern hemisphere was on average within the range of 1–6 nmol/mol. During summer the increase is only 0.2–1.6 nmol/mol. Their results further suggest total nitrate reductions of 0.3–0.5 μg m⁻³ during the winter season over China, India, Western Europe and Western USA, with peak reductions of 2.0–3.0 μg m⁻³ in regions of China. This study also indicates that ClNO₂ could be generated on the surface of biomass burning plumes, as much of the ClNO₂ predicted to occur over China is generated by chloride from biomass burning plumes.

### 3.4.2. Model Estimates of Ocean Very Short-Lived Bromocarbon Emissions and Contribution to Bromine in the Stratosphere

Over the last two decades, there has been a growing interest in VSL bromocarbons that are emitted from the oceans and are transported to the stratosphere where they can deplete ozone. This interest was sparked by stratospheric BrO observations, which indicated that a missing source of reactive bromine, other than that from long-lived bromine carriers such as CH₃Br and halons, is necessary to account for BrO levels in the stratosphere. Several modeling groups have studied the contribution of VSL bromocarbons to the Br⁻ budget in the stratosphere, which confirm the importance of natural ocean emissions of these species for the total stratospheric bromine burden. The most recent estimate by the World Meteorological Organization provides with a range between 2 and 8 pmol/mol for the contribution of VSL halocarbons to the stratospheric bromine loading.

The first studies highlighting the importance of the contribution of VSL bromocarbons to the Br⁻ budget in the stratosphere were those by Dvortsov and co-workers and Nielsen and Douglass. They reported mixing ratios of 1.1 pmol/mol over the equator and 1.8 pmol/mol at mid latitudes, respectively, for the contribution of CHBr₃ to Br⁻ using uniformly distributed sources of bromofluorocarbons. Dvortsov and co-workers used the Model of Atmospheric Transport and Chemistry (MATCH), the off-line version of NCAR Community Climate Model version 3 (CCM3), while Nielsen and Douglass used the Parameterized Chemistry and Transport Model (PCTM). Warwick and co-workers used the p-TOMCAT model with bromofluorocarbon emissions concentrated in the tropics and coastal regions to reproduce the latitudinal distribution of a suite of CHBr₃ measurements throughout the troposphere, and calculated values of 6–7 pmol/mol of inorganic bromine in the upper troposphere as a result of the tropospheric processing of VSL bromocarbons.

This early model study also included contributions from other short-lived brominated organics such as CH₂Br₂, CH₂BrCl, CHBr₂Cl, and CHBrCl₂.

Kerkweg and co-workers included the Warwick and co-workers VSL emissions inventory in the ECHAMS/MESSy model to simulate bromine chemistry in the troposphere and stratosphere. They modeled that the main tropospheric loss process for CH₂Br₂ and CH₂ClBr is reaction with OH, while for CHBr₃, CHClBr₂ and CHClBr two main loss pathways are photolysis. In the stratosphere the dominant decomposition process is photolysis. Aschmann and co-workers modeled the transport of VSL species into the UTLS using the Sinnhuber and co-workers chemical transport model and assessed its contribution to the simulation of stratospheric ozone observations. These authors reported a contribution of bromoform to stratospheric bromine of 1.6–3 pmol/mol. They also concluded that the most effective region for VSL transport into the stratosphere is the Western Pacific, where 55% of the injected bromine to the stratosphere comes from bromoform.

In the recent work of Hessaini and co-workers, the TOMCAT 3D CTM was combined with the existing ocean emission inventories (see also section 3.2.2) of CHBr₃ and CH₂Br₂ to evaluate their tropospheric distribution and resulting stratospheric bromine injection. They reported a range of bromine injection to the stratosphere of ~4.0–8.0 pmol/mol depending on the emission inventory, and quantitatively evaluated the different emissions by comparing the model results with available ground-based and aircraft observations from recent field campaigns. Four different emission schemes were used in this evaluation exercise. The Warwick and co-workers top-down emission inventory used in this work is based on scenarios 3 and 5 of the original inventory, updated according to Pyle and co-workers, with emission fluxes concentrated in uniform strips over tropical and extratropical oceans. The top-down inventory of Liang and co-workers is based on a baseline scenario from Warwick and co-workers adjusted in both magnitude and location to match a variety of observations in the mid troposphere. Ordoñez and co-workers followed the top-down approach to develop an emission inventory that includes a time-dependent emission parametrization based on biogenic chlorophyll-a distributions. Finally, the Ziska and co-workers inventory is a bottom-up estimation in which global emission maps are calculated from marine and atmospheric surface halocarbon concentration maps.

Hessaini and co-workers used the TOMCAT/SLIMCAT model with a chemical scheme for the degradation of bromoform and dibromomethane. They reported that these two species contribute ~2.4 pmol/mol of inorganic bromine to the lower stratosphere with source gas (i.e., VSL bromocarbons) injection being the dominant fraction of VSL bromine injected to the stratosphere. This estimation was improved by the same group recently using the same model including the contribution of other species, such as CH₂Br₂, CH₂BrCl, CH₂BrCl₂, CHBrCl₂, CH₂BrCl, and CH₂Br₂Cl, concluding that 4.9–5.2 pmol/mol is the contribution from the sum of these VSL to the stratospheric bromine budget, with ~76% arising from bromoform and dibromomethane. Aschmann and Sinnhuber used the B3DCTM global model also reported that VSLs injection to the stratosphere contributes 4.5–6 pmol/mol to the Br⁻ loading. The contribution of bromoform and dibromomethane to the stratospheric bromine, as well as its sensitivity to convection strength was recently investigated by Liang and co-workers using the NASA Goddard 3-D Chemistry Climate Model (GEOSCCM). They reported a contribution of ~8 pmol/mol to total bromine in the tropical tropopause layer (TTL). The tropical Indian Ocean, the tropical Western Pacific, and the Pacific coast of Mexico are the zones suggested by this model exercise to have the most active upward transport of VSL species.

The first implementation of combined bromine and iodine oceanic sources from VSL in a global chemistry-climate model was done by Ordoñez and co-workers and Saiz-Lopez and co-workers. The authors incorporated a comprehensive bromine and iodine chemistry scheme in the CAM-Chem model, and developed an inventory for ocean emissions of the bromocarbons CHBr₃, CH₂Br₂, CH₂BrCl, CHBrCl₂, and CHBrCl₃, and the iodocarbons CH₂ICl, CH₂IBr, and CH₂I₂.
This configuration and emissions inventory in CAM-Chem was later employed together with an improved heterogeneous reactions scheme for HBr, HOBr and BrONOO3 on ice particles and aerosol particle surfaces, to study the reactive bromine partitioning in the TTL. In this work, the authors report a stratospheric injection of 5 pmol/mol of total bromine due to VSL species. The authors find a larger contribution from inorganic bromine (product gas VSL = PGvsl ~3 pmol/mol) than that from source gas VSL (SGvsl ~2 pmol/mol), contrary to previous work. This difference in the organic and inorganic fractions of bromine injection to the stratosphere highlights the need to further explore the gaseous and heterogeneous chemistry of reactive bromine across the TTL.

Some recent studies have modeled the future evolution of source gas injection of Br to the stratosphere. This injection is expected to increase in the future as suggested in the studies of Dessens and co-workers and Hossaini and co-workers. Dessens and co-workers used the SLIMCAT model to simulate projected changes in the general circulation of the troposphere. They found that the modeled changes cause an increase of ~10% of the bromine loading in the stratosphere because of the contribution of short-lived brominated species, leading to a decrease of ~8% of ozone in the tropopause region. Hossaini and co-workers reported an increased injection of 2.0–2.7 pmol/mol for the brominated SGvsl over the tropical West Pacific, from 2000 year to 2100, using the IPCC RCPs 4.5 and 8.5 scenarios as input in the United Kingdom Chemistry and Aerosols (UKCA) CCM. The authors suggest that the stratospheric injection of SGvsl will probably increase as a consequence of climate change due to projections of more efficient convection in 2100. These two studies highlight the importance of having accurate and validated VSL inventories in order to assess the impact of atmospheric VLS under a changing climate.

Finally, an accurate estimate of Br loading in both troposphere and stratosphere requires global models to implement realistic inventories of bromine emissions distribution, both in source region and flux strength. Currently, although very significant progress has been made, bromine emission inventories are still poorly constrained by air–sea exchange process information and thus represent a considerable limitation in global modeling of bromine chemistry. Further experimental studies about the biogeochemical control of halocarbons production in the seawater and its emission to the atmosphere are necessary for a more realistic representation of global VSL halocarbon distributions and atmospheric impacts.

3.4.3. Iodine Loading in the Free Troposphere and Stratosphere. An important recent development regarding upper atmospheric iodine chemistry are observations of reactive iodine in the free troposphere, where it has the potential to influence ozone and ozone’s radiative forcing. Puentedura and co-workers measured IO from the Izaña subtropical observatory at an altitude of 2370 m, well above the top of the marine boundary layer, and thus representative of the free troposphere. The detection of IO appeared every day from May to August with a relative standard deviation of 33%. Radiative transfer calculations indicated that IO levels were on the order of 0.2–0.4 pmol/mol. The near constant observation of IO along with the lack of correlation with the diurnal cycling of upslope breeze indicated that these IO levels were representative of the regional open-ocean free troposphere instead of a result of marine boundary layer ventilation. Dix and co-workers detected IO via airborne multiple-axis DOAS spectroscopy onboard a high altitude plane flying up to 9.5 km in both deep convective outflow regions and aged free tropospheric airmasses. Mixing ratios varied from ~0.5 pmol/mol in the MBL to ~0.1 pmol/mol in the free troposphere. Two-thirds of the total column was observed to be above the marine boundary layer. Modeling calculations indicated that the observed IO accounts for 20% of the overall tropospheric ozone loss rate in the free troposphere. Further research is needed to verify these observations and to understand iodine sources to the upper atmosphere and heterogeneous recycling mechanisms that may help maintaining these levels.

Concerning the budget of inorganic iodine (I) in the stratosphere, only two reports have been used to estimate upper limits combining balloon-borne solar occultation DOAS measurements and photochemical modeling. The most recent report estimates I in 0.09–0.16 (+0.10/−0.04) pmol/mol in the tropical lower stratosphere and 0.14–0.35 (+0.20/−0.08) pmol/mol in the tropical upper troposphere.

3.4.4. Summary of Recent Findings via Modeling. Regional and hemispheric models support the influence of recently discovered CINO3 on ozone, showing mean influences of up to 7 nmol/mol in China in the wintertime, and significant but lesser influences elsewhere. Influences on peak ozone in polluted regions are likely to be more variable.

Model studies of very short-lived (VSL) Br emissions and chemistry from the world’s oceans have been motivated by the suggestion that these Br compounds are required to understand stratospheric BrO loading and its associated impact on stratospheric ozone. CH3Br has been suggested as the most important of these compounds, with smaller contributions from other bromoorganic species. The Western Pacific, tropical Indian Ocean and the Pacific coast of Mexico have been identified as regions with where VSL emissions are efficiently transported to the stratosphere. Models generally reproduce most or all of the 2–8 pmol/mol contribution to of VSLs to stratospheric Br, suggested as needed by the WMO to explain stratospheric Br loading. Of particular importance is the potential change in VSL emissions in a warming climate. This possibility highlights the need for accurate emission inventories for these compounds.

Recent observations have also suggested the presence of IO in the upper troposphere. Because IO is a potent ozone destroying gas, these observations point to the need for understanding upper atmospheric iodine sources.

4. IMPACTS OF HALOGEN CHEMISTRY

4.1. Impacts of Halogen Chemistry on Ozone and the Oxidizing Capacity of the Troposphere

von Glasow and co-workers used the MATCH-MPIC 3D chemical transport model and organic bromine gases as the main source of reactive bromine to quantify the effect of bromine chemistry on tropospheric ozone. They calculated a bromine-induced ozone column reduction of 12–18% in the tropical troposphere region. Sea-salt aerosol sources of reactive bromine species were included by means of a simplification parameterization for heterogeneous recycling of bromine. Yang and co-workers reported a tropospheric ozone column reduction of a 4–6% due to bromine chemistry in the same domain, using the p-TOMCAT model with sea-salt aerosols and organic bromine as sources. Parrella and co-workers included a bromine chemistry scheme in the GEOS-Chem...
model and modeled the implications for ozone and mercury in the present and preindustrial times. The sources of bromine were sea-salt aerosol, organic bromine and transport from the stratosphere. They reported a 6.5% decrease in tropospheric ozone because of bromine chemistry. As shown in Figure 10, the simulations reproduce many seasonal and latitudinal features observed by GOME-2 satellite BrO observations. Specifically, the seasonal shape with greater BrO during winter and increase in BrO poleward are present in both simulations and observations. However, GEOS-Chem underestimates the GOME-2 observations by about 30%, which could be explained by errors in observations or may possibly indicate underestimated bromine emissions or insufficient halogen recycling in the simulations. Saiz-Lopez and co-workers used the halogen chemistry scheme and VSL inventory implemented in CAM-Chem, and estimated a contribution of 10% for annually averaged tropospheric ozone depletion (with values ranging from 6 to 20%). The differences in the estimated impact of halogens on tropospheric ozone between the early and more recent studies may be due to the different bromine loadings in the models. For instance, von Glasow and co-workers included 30 pmol/mol Br from a generic organic sources, compared to 13 pmol/mol of Br, in addition to iodine sources, in the tropical troposphere simulated by Saiz-Lopez and co-workers.

The recent work by Saiz-Lopez and co-workers included the first time in a global model (CAM-Chem) the parametrization of MacDonald and co-workers to account for the open ocean ozone oxidation of iodide to I$_2$ and HOI (see Section 3.2.3). In this work a global modeling experiment is performed to estimate lower and upper limits of inorganic iodine burden, partitioning the impact of iodine chemistry in the ozone loss in the troposphere. They proposed the existence of a "tropical ring of atomic iodine", with values from 0.2 to 0.8 pmol/mol extending from 30°S to 30°N peaking at a height between 11 and 14 km. Fernandez and co-workers suggested the existence of a similar ring of atomic bromine circling the tropics, in a modeling study in which the bromine loading injected to the stratosphere and the geographical distribution and partitioning of bromine was calculated. The features of the atomic halogen rings arise from the low ozone and temperature conditions during the sunlit tropical upper troposphere, which make the atomic bromine the dominant inorganic species. This injection of inorganic bromine to the stratosphere would make the stratospheric ozone layer more sensitive to biogeochemical changes in the oceans, and once again point to the need of including accurate halogen chemistry schemes in global climate models. As discussed in section 3.2.3 and shown in Figure 6, Prados-Roman and co-workers used the same configuration of CAM-Chem to estimate the geographical distribution and contribution of organic (25%) and inorganic sources gases (75%) to the loading of IO in the global MBL.

The effects of halogen chemistry on the methane, NMHCs, DMS and the atmospheric oxidants O$_3$, HO$_x$, NO$_x$ were studied by Long and co-workers using size-resolved multiphase coupled chemistry-global climate model (NCAR Community Atmosphere Model (CAM) version 3.6.33). In this modeling work, sea-salt aerosol is the only source of bromine and chlorine, although the calculated bromine values were higher than previously reported in field or modeling studies. All these studies demonstrate that oceanic halogen sources and chemistry need to be incorporated in climate simulations to reproduce the ozone budget and its climate impact properly.

The impact of halogen chemistry on oxidation of elemental mercury has also been the focus of several modeling works, including the above-mentioned study by Parrella and co-workers. Holmes and co-workers used the p-TOMCAT configuration of a prior study to estimate the lifetime of tropospheric elemental mercury (Hg$^0$) against the oxidation by atomic bromine. The estimated lifetime of 0.5–1.7 year suggest that this oxidation pathway could be an important sink for Hg$^0$, mainly in places like the free troposphere. The feasibility of atomic bromine as an alternative Hg$^0$ global oxidant was demonstrated using the global 3D model GEOS-Chem. The topic of mercury deposition to the polar regions is discussed in section 4.2.

Using the GEOS-Chem model, Parrella and co-workers found a 6.5% decrease in tropospheric ozone in present day and also the same tropospheric ozone decrease because of halogen chemistry in preindustrial times, indicating minimal climate forcing by changes to global halogen chemistry. However, their simulations indicated preindustrial ozone was much lower than present day because of changes in NO$_x$ and other emissions. This ozone change leads in the GEOS-Chem simulations to 40% higher levels of atomic Br concentrations in the preindustrial simulations. Considering Br radical-driven oxidation of Hg$^0$, this change in Br levels causes a Hg$^0$ lifetime of 4 months in preindustrial simulations as compared to 7 months in present day.

Saiz-Lopez and co-workers estimated the contribution of bromine, chlorine, and iodine chemistry to ozone loss and also the associated radiative impact in the tropical marine troposphere. The authors calculated that the inclusion of halogen sources and chemistry in the CAM-Chem global model reduces by 10% the annually averaged tropospheric ozone...
column, which accounts for a change of $-0.10 \text{ Wm}^{-2}$ in the radiative flux at the tropical tropopause. This suggests that the negative contribution of halogen-driven ozone loss to the longwave radiative flux is significant, constituting about 30% of the positive contribution to the top-of-the-atmosphere radiation flux due to ozone absorption in the infrared.

The influence of anthropogenic emissions that have altered \( \text{O}_3 \) levels on the natural cycle of iodine in the oceans was studied by Prados-Roman and co-workers.\(^{262}\) Figure 11 shows the calculated anthropogenic influence on the natural iodine cycle from this work, demonstrating large impacts of pollution on iodine cycling. The same configuration of CAM-Chem of Saiz-Lopez and co-workers\(^{259}\) was employed to quantify the oceanic global emissions of inorganic iodine, according to empirical parametrizations\(^{85,176}\) and to estimate the change in these emissions since preindustrial times (1850), when tropospheric ozone was lower. The results from this work show that the enhancement of ozone caused by anthropogenic emissions of ozone precursors has doubled the oceanic inorganic iodine (HO\(_I\) and I\(_2\)) emissions, as a consequence of the reaction between ozone and iodide at the surface level. Therefore, the authors propose the existence of a negative geochemical feedback loop between the anthropogenically influenced \( \text{O}_3 \) levels and oceanic inorganic iodine emissions. The anthropogenic enhancement of \( \text{O}_3 \) levels may have led to an increase in the inorganic iodine emissions. These reactive iodine emissions cause a reduction in the ozone lifetime, which might have partially compensated the anthropogenic increase in ozone and its associated warming effects in the troposphere. This work emphasizes the need for improved understanding of ocean-atmosphere interactions and their effects and feedbacks on ozone.

### 4.2. Polar Impacts of Halogen Chemistry

Within polar regions, a large seasonal shift happens between “normal” \( \text{HO}_x \)-dominated summertime photochemistry and springtime, meaning from return of sunlight after polar night through snowmelt, when halogen dominate oxidation processes. This change causes ozone depletion events that further slow the production of HO\(_x\) by normal photolysis of \( \text{O}_3 \) followed by reaction with water vapor. Because halogens oxidize hydrocarbons faster and with relative rates that differ from OH, this change in oxidizer affects the fate of hydrocarbon pollution. Gilman and co-workers\(^{207}\) found that the ratio of acetylene to benzene, which is a marker of chlorine and bromine oxidation, was very highly correlated (\( R = 0.98 \)) to ozone for samples collected north of 68° north. This recent work highlights the dominance of halogens for oxidation in the Arctic springtime. Recent work that has combined measurements of other radicals (e.g., HO\(_x\)) with halogens\(^{53,134,135}\) has demonstrated that partitioning of other radicals is modified by the presence of halogen radicals, also affecting the fate of other pollutants.

Mercury is also oxidized much more rapidly by halogens than under normal photochemical conditions, and atomic bromine has been implicated as the key oxidizer.\(^{113,260,261}\) Mercury dynamics are complex, however, and it is known that some of the mercury deposited to snowpack is reduced photochemically to elemental mercury, which then reemits to the gas phase,\(^{263,264}\) which reduces the snowpack mercury burden and leads to elevated Hg\(^0\) levels in summertime. Similar photoreduction of mercury occurs in the Arctic Ocean, and based upon the seasonal timing of snowmelt and riverine discharge into the Arctic Ocean, Fisher and co-workers\(^{265}\) proposed that river discharge dominates snowpack processes in delivering mercury to the Arctic Ocean. In a subsequent work also using the GEOS-Chem model, Fisher and co-workers\(^{266}\) simulated intrannual variability of mercury at Arctic sites and found that this variability was dominated by sea ice meltwater flux of Hg previously deposited to sea ice. Moore and co-workers\(^{267}\) found that vertical mixing caused by sea ice leads in springtime brought higher levels of mercury down to the surface, where it is more likely to encounter reactive halogens and be oxidized. These studies show that mercury dynamics are complex and more work needs to be done on halogen/mercury interactions, mercury photoemission, and riverine emissions to predict a future state of mercury in the Arctic Ocean region. Additionally, further biogeochemical transformations of mer-

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**Figure 11.** Modeled anthropogenic influence on oceanic iodine source as a percentage change from preindustrial times to current conditions. Reprinted with permission from Prados-Roman and co-workers.\(^{262}\) Copyright Prados-Roman and co-workers 2015. CC Attribution 3.0 License.
cury that lead to formation of the highly neurotoxic methyl mercury species need to be further studied to examine ecological effects of mercury in the food web.

4.3. Marine Boundary Layer Halogen Impacts

Halogen activation in the marine boundary layer produces reactive halogen gases that generally deplete ozone in that layer. Although tropospheric ozone is a greenhouse gas, marine boundary layer (MBL) ozone is at a temperature close to the Earth’s surface, so radiation trapping by MBL ozone is small and the effect of halogens on ozone radiative forcing is probably not significant. However, MBL ozone loss greatly alters photochemistry in this region, with many impacts on other compounds since O$_3$ is a main driver of the atmospheric oxidation capacity. As discussed in section 4.1, tropospheric ozone at higher altitudes, where temperatures are colder have a larger, and possibly significant climate impact. Iodine gases that are present in the MBL can nucleate particle formation, which may have climate impacts through direct and indirect effects.

4.4. Polluted Region Impacts of Halogen Chemistry

The coupling between halogen chemistry and NO$_x$ chemistry is complex and multifaceted. It is clear that nocturnal production of N$_2$O$_5$ and its heterogeneous reaction with particulate chloride forms ClONO$_2$, which photolyses in the early morning, producing an early start to daytime radical production as well as liberation of NO$_x$. That early start to daytime radical chemistry can lead to increased ozone production in the day. On the other hand, nocturnal reactions of nitrogen oxides can also decrease ozone and NO$_x$ through heterogeneous hydrolysis of N$_2$O$_5$ competing with daytime ozone production. The study of the effects of NO$_x$ on halogen radical activation has only recently begun, but likely NO$_x$ exerts strong controls on the possibility to liberate halogens. Recent studies have also pointed out that production of daytime halogen radicals (e.g., from photolysis of ClONO$_2$) often leads to production of hydrocarbon radicals that then typically form secondary HO$_x$ radicals or photolabile carbonyl species that act to amplify radical production. This two-way coupling between halogen radical and HO$_x$ radical chemistry points out the need for both intensive field studies with many species being measured simultaneously and modeling with full chemical coupling between these interacting species.

5. NEEDS FOR FUTURE RESEARCH

The advances in our understanding of tropospheric halogen chemistry in the past few years have pointed out their role in the global oxidation capacity and impacts on fate of pollutants, effects on tropospheric ozone and production of particles and thus radiative forcing. Some areas that recent work has pointed to that clearly need further investigation are highlighted in the following: (1) The free troposphere is a region where halogen oxides have recently been measured. Because of cold temperatures in that area, tropospheric ozone’s radiative impact is largest in the free troposphere. Thus, we need further measurements and modeling of reactive halogens, their precursors, and surfaces that assist recycling of halogens in that altitude region. (2) Heterogeneous reactions between halides on surfaces and halogen gases are critical for activation of halogen radicals, but our understanding of those surfaces and environmental controls on the surface properties remain elusive. Therefore, further field and laboratory investigations need to be carried out. (3) Investigations of organic aerosol composition show that a significant fraction of organic aerosol is secondary in nature, meaning it is produced by photo-oxidation of more volatile precursors. The role of halogens in oxidizing organic gases, producing secondary HO$_x$ and photolabile carbonyl species, and modifying secondary organic aerosol species needs investigation. (4) In many regions that are important for the global oxidation capacity (e.g., the marine boundary layer and the free troposphere), very few measurements of reactive halogens and their precursors are available and often the abundances are close to the detection limits of current instrumentation. Therefore, more measurements with improved detection limits and alternative techniques are required to build up a picture of reactive halogen abundances globally. (5) The Arctic region is undergoing unprecedented climate changes, with high rates of warming and loss of summer sea ice leading to different wintertime sea ice properties including salinity. However, our understanding of halogen activation chemistry in relationship to Arctic environmental conditions still needs development to make predictions of how Arctic climate changes will affect halogen chemistry. (6) As we discuss above, halogen radical chemistry is coupled to HO$_x$ and NO$_x$ cycles in complex feedback cycles. Observations of these coupled cycles in the laboratory, field, and modeling of them is necessary to improve our understanding of tropospheric halogen chemistry and its impacts. Production of carbonyl and other photolabile radical amplifier species by both halogen and HO$_x$ photochemistry needs further investigation. (7) Many of the regions where halogen activation occurs have hindered vertical mixing because of inversion layers that may occur at night or over cold surfaces such as sea ice or in the Marine Boundary Layer. This effect complicates understanding of halogen chemistry and requires 1-D (vertical) or higher dimensional modeling as well as improved measurements both of chemicals and mixing aloft. Experimental and modeling approaches are needed to address mixing and the relative role of reactions at the Earth’s surface as compared to reactions on particles aloft. (8) Recent modeling studies have indicated significant impacts of ClONO$_2$ production and subsequent photochemistry. However, those models are sensitive to particulate chloride spatial distributions and seasonality, which needs better understanding. Additionally, the vertical and long-range transport of ClONO$_2$ and precursors needs further investigation. (9) Field measurements have clearly shown production of CINO$_2$, but other XNO$_2$ species have not been measured, and the search for these species and/or reasons for their lack of observations needs study. The chemistry of how these species produce dihalogens (e.g., Cl$_2$.Br$_2$, I$_2$ and/or interhalogen species) needs further investigation. (10) Satellite-based instrumentation has made many important advances in detection of halogen oxides and determination of their spatial distribution, particularly in more remote locations. We need to continue these global measurements and enhance our analysis methods to separate halogen oxide vertical column density into stratospheric, free tropospheric, and boundary layer abundances. Long-term planning is needed to ensure future satellite missions will satisfy the research community’s needs.

6. CONCLUSIONS

In this Review, we have discussed four areas where recent advances have been made in our understanding of tropospheric halogen chemistry. The underlying chemistry was discussed to point out the role of heterogeneous reactions between halide-
laden surfaces and halogen or NOx gases in production of photolabile precursor species. Many of these precursors photolyze at longer wavelengths than typical HOx precursors, allowing halogen chemistry to occur in twilight or in polar regions. The reactions that liberate halogen precursors often consume other radicals such as HO2, and thus sources of radicals is a key question for both halogen and all photochemistry. Both halogens and HOx oxidize hydrocarbon species, producing secondary organic radicals and subsequently HOx radicals. This two-way coupling between halogen and HOx radical photochemistry is evident in recent studies. In polar regions, recent observations have shown production of high levels of molecular chlorine53 and dependence of halogen activation on acidity, both in the field43 and with similar results in laboratory.110 In the marine boundary layer, laboratory and modeling advances have improved our understanding of inorganic chemistry involving ozone oxidation of iodide as a source of HOI and I2. In NOx-polluted regions, we have expanded our observational evidence of the role of nocturnal NO2 chemistry in halogen activation55,57,79 as well as advanced our understanding of production of secondary radicals from morningtime chemistry.50 At the regional and global scales, recent modeling efforts are beginning to identify impacts of NOx-pollution produced CINO222 and impacts of free tropospheric halogen-induced ozone changes.162,250,258

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Notes

The authors declare no competing financial interest.

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Steven Brown received his B.A. in Chemistry from Dartmouth College in 1989. He then received a Ph. D. in physical chemistry at the University of Wisconsin-Madison and came to the National Oceanic and Atmospheric Administration (NOAA) Laboratories in Boulder, Colorado in 1997. He is currently a Research Chemist at NOAA and serves as an adjunct professor at the University of Colorado. He studies the chemistry and impacts of nitrogen oxides in the Earth’s atmosphere, with an emphasis on field measurements of tropospheric nitrogen oxides, particularly those that occur in the dark (nighttime chemistry). His other main research interest has been the development of high sensitivity optical instrumentation for laboratory and field studies of atmospheric trace gases and aerosol particles.

Alfonso Saiz-Lopez studied Chemistry in Ciudad Real, Spain. In 2006, he received his Ph.D. degree in Atmospheric Physical Chemistry at the University of East Anglia, focused on absorption spectroscopy for atmospheric measurement and marine boundary layer halogen chemistry. After a brief postdoctoral stay at the University of Leeds, he was a NASA Postdoctoral Scholar at the Jet Propulsion Laboratory and Research Associate at the Harvard-Smithsonian Center for Astrophysics. Since 2009, he is a Senior Research Scientist at the Spanish National Research Council (CSIC) and an Affiliate Scientist at the NCAR. The work of his group focuses on atmospheric halogen chemistry and its effect on climate.
Joel Thornton obtained his B.A. in Chemistry from Dartmouth College in 1996. He obtained his Ph.D. in Chemistry from University of California, Berkeley in 2002. Following a postdoctoral appointment at University of Toronto, he entered the faculty at the University of Washington in 2004. He is currently an Associate Professor in the Department of Atmospheric Sciences at University of Washington, with an affiliate appointment in Chemistry. Research in his group utilizes state-of-the-art analytical techniques based on mass spectrometry and spectroscopy to study the physical chemistry of atmospheric phenomena, such as halogen chemistry, pollution chemistry, and aerosol particle formation/modification.

Roland von Glasow studied atmospheric physics at the University of Mainz, Germany; he then completed his Ph.D. on atmospheric chemistry at the Max-Planck-Institute (MPI) in Mainz, Germany, in 2001. He continued research as a postdoctoral fellow at MPI and then at the Scripps Institution of Oceanography, San Diego. He led a research group at the University of Heidelberg, Germany, for three years before moving to the University of East Anglia, U.K., in 2007, where he was promoted to Professor in 2012. He and his group develop and apply numerical models to study chemical and physical processes in the troposphere with a focus on reactive halogen chemistry. Regions of this investigation include the marine boundary layer, the polar regions, volcanic plumes, and the free troposphere.

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