

Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts

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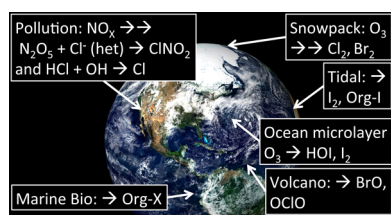
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1. INTRODUCTION/HISTORY

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,^{1–3} leading to the picture that the Earth's atmosphere removes natural and anthropogenic pollutants primarily through OH-driven photooxidation chemistry.⁴ 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 ~300–320 nm region, and cycles involving odd hydrogen radicals (known as HO_x = OH + HO₂) and nitrogen oxides (known as NO_x = NO + NO₂), sunlight, and hydrocarbons produce most tropospheric ozone.^{5,6} Reactive halogens, on the other hand, generally destroy ozone in catalytic cycles, altering the oxidation capacity of the atmosphere.

In 1974, there was a flurry of activity in the stratospheric chemistry literature considering how halogen radicals, such as chlorine atoms, could deplete ozone aloft.^{7–9} This work led to the awarding of the 1995 Nobel Prize in Chemistry to Paul Crutzen, Mario Molina and F. Sherwood Rowland for their work on stratospheric ozone depletion chemistry. However, the realization that halogens played a role in tropospheric chemistry was not yet discovered. In Cicerone's 1981¹⁰ review article, he compiled excellent information on the measurements of halogens in the troposphere, but noted that "...the major pathways of nature's halogen cycles are seen only in general terms; key transformation processes and rates are not known with any accuracy." At this time, it was known that marine aerosol particles were depleted in chloride and bromide and strongly enriched in iodide as compared to seawater ion ratios. The chloride observations were consistent with displacement of the weaker acid HCl by deposition of stronger acids such as H₂SO₄ and HNO₃, but later work would show that was not the only effect and that these observations of marine particulate ionic composition were highly influenced by photochemical processes, as discussed in section 3.2.

The first region of the troposphere where halogen chemistry was implicated was the high Arctic, where ozone depletion episodes (ODEs) were discovered in the troposphere in the midlate 1980s,^{11,12} and chemical loss of ozone by halogens, bromine in this case, was implicated by Barrie and co-workers in 1988.¹³ The presence of anomalously high particulate and

gas-phase bromine levels in the Arctic had been noted earlier, but the sources and chemistry of these bromine-containing air samples was not understood at the time.¹⁴ More important to this Review is the fact that high reactive halogen levels were found to be present, with the observable consequence being ODEs. Those reactive halogens are potent oxidizers in addition to removing ozone, which is a normal precursor of OH in photooxidation chemistry. Modeling studies¹⁵ based upon indirect measurements^{16,17} indicated that the marine boundary layer (MBL) was impacted by reactive halogens, and direct observations of elevated chlorine in coastal air were published in 1993 via mist chamber measurements¹⁸ and in 1998 via mass spectrometry.¹⁹ Subsequently, reactive halogens were detected above salt lakes and saline seas, in plumes of volcanoes, in tidal coastal areas, from the open ocean, in pollution plumes, and even in the free troposphere. Each of these specific areas will be discussed later in this review.

1.2. Earlier Reviews

The focus of the present review is on the chemistry of halogens in the troposphere. However, parallels exist between tropospheric halogen chemistry and stratospheric ozone chemistry and halogen-induced catalytic ozone loss, which was comprehensively reviewed by Solomon in 1999.²⁰ The earliest review that discusses the troposphere was that of Cicerone in 1981.¹⁰ Anthropogenic and natural sources of reactive chlorine was reviewed by Keene and co-workers.²¹ Platt, later with Hönninger, reviewed the role of halogens in the troposphere in the early 2000s.^{22,23} Finlayson-Pitts and Rossi reviewed the tropospheric chemistry of sea salt and heterogeneous reactions on those salts in 2003,^{24,25} and also in the same year, Carpenter carried out the first review of iodine chemistry in the marine boundary layer.²⁶ In 2003 and revised in 2007, von Glasow and Crutzen provided a comprehensive review of tropospheric halogen chemistry.^{27,28} Also in 2007, the role of halogens in polar boundary-layer ozone depletion was reviewed by Simpson, von Glasow, Riedel, and co-workers.²⁹ In 2012, Saiz-Lopez and co-workers³⁰ reviewed the atmospheric chemistry of iodine. In 2012, Abbatt, Thomas, and co-workers³¹ reviewed halogen heterogeneous chemistry on ice surfaces, with a focus on recent work. Most recently, in 2012, Saiz-Lopez and von Glasow provided a critical review on reactive halogens in the troposphere.³² Faxon and Allen reviewed chlorine chemistry in urban atmospheres.³³

Although not directly addressing tropospheric halogen chemistry, it is useful to discuss some related topics that have had recent reviews. Unlike ozone/OH photochemistry, which is dominated by gas-phase reactions, heterogeneous reactions between gas-phase species and halides on surfaces are centrally important to halogen chemistry. Abbatt, Lee, and Thornton recently reviewed heterogeneous chemistry on tropospheric aerosol particles.³⁴ Chang and co-workers reviewed heterogeneous chemistry of dinitrogen pentoxide, N₂O₅.³⁵ Brown and Stutz reviewed nighttime radical chemistry, which similarly covers some aspects of nitrogen oxide driven halogen activation.³⁶ Both of these reviews cover topics important for pollution-related halogen activation (see section 3.3). Ice surfaces are particularly effective at halogen activation, and photochemistry on ice was reviewed by Grannas and co-workers in 2007,³⁷ and recently by Bartels-Rausch and co-workers.³⁸

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 NO_x 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 NO_x-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 HO_x and NO_x 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

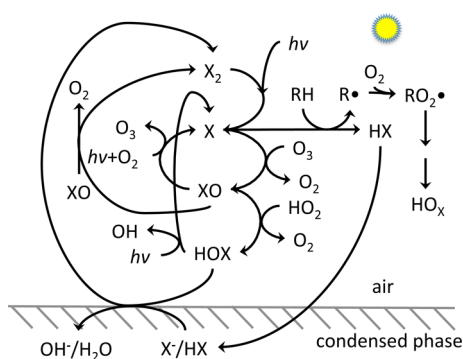


Figure 1. Simplified reaction diagram for halogen atoms, represented as “X” in this diagram, key chemical reaction pathways. Note that many species on this diagram are radicals, but for simplicity, only organic radicals and organic peroxy radicals, denoted by R• and RO₂•, are explicitly shown with an unpaired electron.

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 X₂, HOX, XNO₂, and HX. 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:



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 $4.5 \times 10^{-5} \text{ s}^{-1}$ 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



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



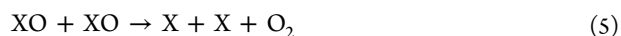
In reaction 3, a halogen atom reacts with hydrocarbons, denoted generically as RH and is listed as an hydrogen abstraction reaction. Halogen radicals can also add to double bonds in organic species, which again leads to an organic radical species.

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

other halogens. 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.²³ 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 scale⁴¹), 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 $XO_x = X + XO$ 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,²³ 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.



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.³²

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.³² 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.^{28,32}

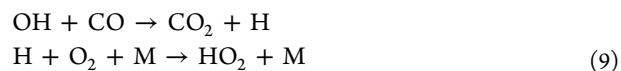
2.1.4. Halogen Recycling from Reservoirs. An important “termination” reaction involves HO₂ and XO



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

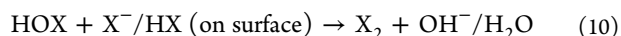


This photolysis reaction recreates two radicals, and the hydroxyl radical can react with CO or many hydrocarbon species to recreate HO₂, for example

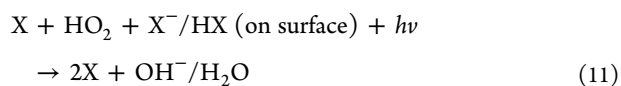


The cycle of reactions 2, 8, and 9 catalytically destroys ozone, while cycling one radical each of the families HO_x and XO_x.

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



This net heterogeneous reaction is pH dependent, as has been observed in the laboratory⁴² and recently in the field,⁴³ as discussed in section 3.1.2. When this reaction is followed by photolysis of X₂, 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



This net reaction is often termed the “bromine explosion”⁴⁴ 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_x radicals to XO_x 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



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.⁴⁵ This reaction conserves radicals, but converts HO_x 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 Br₂Cl⁻. This reaction is reversible, and because chloride is more stable in solution than bromide, it will most often decompose as Br₂ 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 Br₂

is preferred, even if $[Cl^-] > [Br^-]$. 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,^{31,38} and also polarizability of halogen atoms that gives them a preference to reside on the surface.²⁴ Recent studies of heterogeneous chemistry have shown that organic coatings can act as barriers to this type of aqueous reactivity,^{46,47} as has been discussed in reviews^{34,35,48} and will be discussed below. Similar effects have been observed with nocturnal nitrogen chemistry.^{34,35} 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_x 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.^{49–51} 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 HO_x 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.⁵⁰

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 photolyzes, 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_2 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_x 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

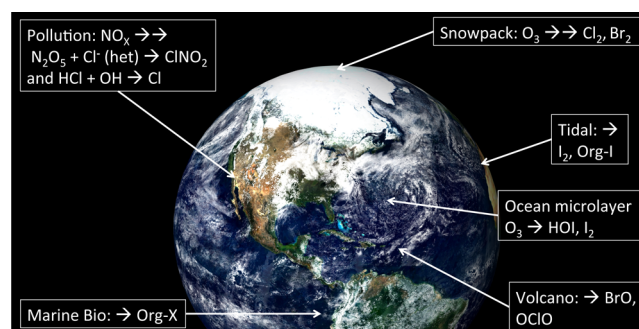


Figure 2. Primary sources of reactive halogen species or their precursor reservoir species overlain on a MODIS image of Earth. Background image produced by the MODIS Land Group, NASA Goddard Space Flight Center, Visible Earth Project, NASA.

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.

2.2.1. Heterogeneous Chemistry. Heterogeneous chemistry, as has been discussed in section 2.1, has been established as a key process for halogen chemistry. Heterogeneous recycling of halogen reservoirs back into reactive halogen species that lead to the Antarctic Ozone Hole in the stratosphere, as reviewed by Solomon,²⁰ established the importance of surfaces in that environment. The identification that similar chemistry occurred in the troposphere, followed the discovery of Arctic boundary-layer ozone depletion events in the troposphere, where chemical modeling^{15,69–71} including heterogeneous chemistry was able to reproduce ozone depletion episodes.²⁹ Schroeder and co-workers in 1998⁷² found that gas phase mercury was depleted in correlation with Arctic boundary-layer ozone. Later, reactive halogens were implicated as the oxidant for mercury, as is discussed in a recent review⁷³ and below. Observations from Antarctica showed that both polar regions experience boundary-layer halogen chemistry and ozone loss. Table 1 shows that chlorine, bromine, and

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

species	polar	MBL	polluted	free troposphere
ClO	<30–125 Pöhler ⁵²			
OCIO	24 Pöhler ⁵²			
Cl ₂	400 Liao ⁵³	35 Lawler ⁵⁴	200 Riedel ⁵⁵	
BrCl	6 Buys ⁵⁶			
ClNO ₂			3500 Mielke ^{57b}	
HOCl		170 Lawler ⁵⁴		
BrO	35 Liao ⁵⁸ (NH)	6 Read ⁵⁹		1.5 Prados-Roman ⁶⁰
	13 Buys ⁵⁶ (SH)			
Br ₂	46 Liao ⁵⁸ (NH)		19 Finley ⁶¹	
	45 Buys ⁵⁶ (SH)			
HOBr	26 Liao ⁵⁸ (NH)			
IO	3 Mahajan ⁶² (NH)	2 Read ⁵⁹		0.4 Puentedura ⁶³
	20 Saiz-Lopez ⁶⁴ (SH)	0.6 Dix ⁶⁵		0.1 Dix ⁶⁵
I ₂		1.7 Lawler ⁶⁶	8 Finley ⁶¹	
IO (tidal)		50 Commane ⁶⁷		
I ₂ (tidal)		300 Huang ⁶⁸		

^aOnly 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 Glasow³⁰ and Saiz-Lopez and co-workers³⁰ present comprehensive lists of observations published before 2012, and recent observations appear in this review and in this table. ^bMore recent observations at coastal and continental sites are described in section 3.3.1.

iodine reactive halogen species and their precursors have been observed in polar regions. Recent observations by Liao and co-workers⁵³ have demonstrated high levels of molecular chlorine, Cl₂. Reactive bromine, in the form of BrO is observed to be of similar magnitude to its precursors, Br₂ and HOBr, and at similar levels in both polar regions. Reactive iodine, detected as IO appears to show a hemispheric difference, with lower levels detected in the Arctic than in the Antarctic. Similar heterogeneous halogen activation chemistry was proposed to occur in the warmer marine boundary layer outside the Arctic, although reactive halogen levels are lower and thus ozone depletion outside the Arctic is less dramatic. Heterogeneous recycling is also important in the free troposphere and in NO_x-pollution-related halogen chemistry.

2.2.2. Pollution-Mediated Halogen Release. Tolbert and co-workers⁷⁴ and Finlayson Pitts and co-workers around 1990^{75,76} showed that the nocturnal NO_x reservoir species, N₂O₅, reacted 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 first that this mechanism produced high levels of nitryl chloride in the marine boundary layer⁷⁷ and later in the continental regions.^{78,79} Table 1 shows that the ClNO₂ levels go up to 3500 pmol/mol,⁵⁷ which was detected in the polluted coastal city of Los Angeles. High levels

of molecular chlorine⁸⁰ 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 HCl⁴⁵ 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.⁸¹ Organobromine species such as bromoform (CHBr₃), were initially thought to be the bromine source for Arctic ozone depletion events,¹³ but despite discovery of relatively high bromoform levels,⁸² photolysis rates were too slow to be the sole source of reactive halogens in Arctic ozone depletion episodes.⁸³ 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.⁸⁴ Short lived organobromine gases may also provide significant sources for reactive bromine to the free troposphere, and stratosphere.⁸¹ 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.^{26,30} An exciting advance lies in improved understanding of how ozone reacts on the ocean surface to produce HOI and I₂ gases directly,⁸⁵ 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 HOCl, 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,⁸⁶ and soon after confirmed by others.⁸⁷ 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.⁸⁸ The relationship of inorganic iodine species with low tide was confirmed by Saiz-Lopez and Plane in 2004,⁸⁹ 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 Carpenter²⁶ and Saiz-Lopez and co-workers³² 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. Bobrowski and co-workers in 2003⁹⁰ discovered extremely high levels of bromine monoxide in a volcanic plume.

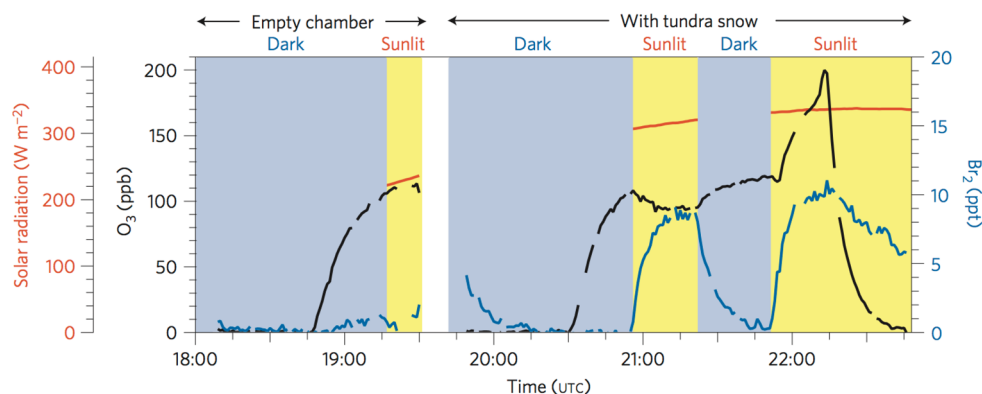


Figure 3. Br₂ production during a snow chamber experiments on 27 March 2012. Tundra snow is exposed to ambient radiation and varying ozone levels, and produced Br₂ is monitored. Reprinted with permission from Pratt and co-workers (2013).⁴³ Copyright 2013 Nature Publishing Group.

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, OClO 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 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 Arctic^{98,99} 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 layer⁸⁶ before its detection in the Antarctic boundary layer.⁶⁴ Most Arctic attempts to detect IO have been below detection limits (typically ~1 pmol/mol),^{52,98,102} although one detection has been reported.⁶² 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.^{64,106} 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

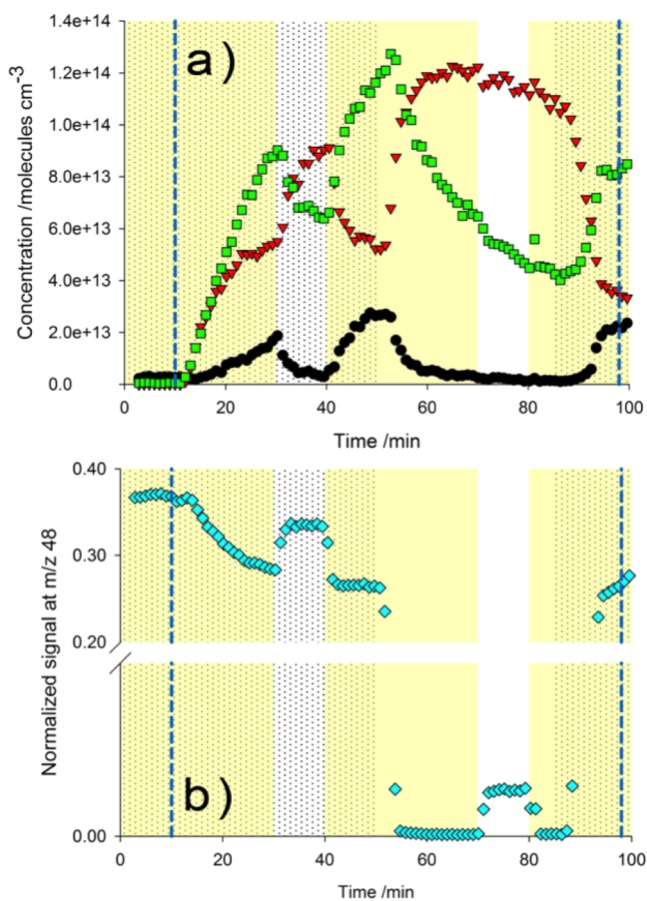


Figure 4. Evolution of dihalogen gases from laboratory experiments simulating polar halogen activation by irradiating salt-doped ice particles with or without coexposure to ozone gas. Panel a shows dihalogens (Br₂ in red, Cl₂ in black, and BrCl in green). Panel b shows ozone, and yellow areas indicate times when the sample was irradiated. The dotted shading visible on top of the yellow indicates when the ozone generator was switched on (dotted = ozone on, no dots = ozone off). Reprinted with permission from Wren and co-workers (2013).¹¹⁰ Copyright Wren and co-workers 2013. CC Attribution 3.0 License.

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.¹¹⁸ 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_y family.¹¹⁹ This climatology and related methods have been used to separate stratospheric and tropospheric BrO column densities.^{120–124} These methods have generally shown a good correlation with ground-based measurements.¹²² 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.¹²⁴ 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.¹²⁵ 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.¹²⁶ 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.^{126,127}

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.¹²⁸ Photochemical production of HONO on snow as proposed to be the source of these high HONO levels.¹²⁸ Formaldehyde, HCHO, is a key precursor of HO_x 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.¹²⁹ 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.¹³⁰ 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.¹³⁰ Other small carbonyls, such as acetaldehyde, CH₃CHO, have been observed to be produced from snowpack,^{131,132} 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 HO_x, NO_x, and halogen chemistry in polar regions using zero-dimensional box

modeling constrained by radical measurements.^{58,133–136} Bloss and co-workers¹³⁴ simulated Antarctic boundary layer observations and found good replication of mean levels and diurnal cycles of observed HO_x, NO_x 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 HO_x radicals.¹³⁴ In this Antarctic study, iodine chemistry was explicitly included and the model was able to simulate iodine monoxide levels similar to observations.⁶⁴ 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.¹³⁵ Cao and co-workers¹³⁶ 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 NO_x 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.¹³⁶ The inclusion of chlorine in this modeling study had a minor influence in ozone depletion as compared to bromine and NO_x.¹³⁶ However, no snowpack source of chlorine was included in the model, as has been indicated by the study of Liao and co-workers.⁵³

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.^{121,137–143} Thomas and co-workers^{141,142} coupled the 1-D chemical/transport model MISTRA with a 1-D snow model to investigate the role of snowpack as a source of NO_x and reactive bromine over the Greenland Ice Sheet. The model successfully simulated observed halogen and NO_x levels and found that the presence of snowpack emissions increases the oxidation capacity significantly and increases daytime OH concentrations.^{141,142} Toyota and co-workers¹²¹ 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.¹²¹ More recently, Toyota and co-workers^{143,144} 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 vertical transport of reactive halogens and found that enhanced vertical mixing led to higher BrO VCD due to increased vertical extent of snowpack influence on the atmosphere.¹⁴³ Figure 5 shows the BrO VCD as a function of time and wind speed. The same model was applied to understand mercury oxidation and speciation.¹⁴⁴ 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.¹⁴⁴

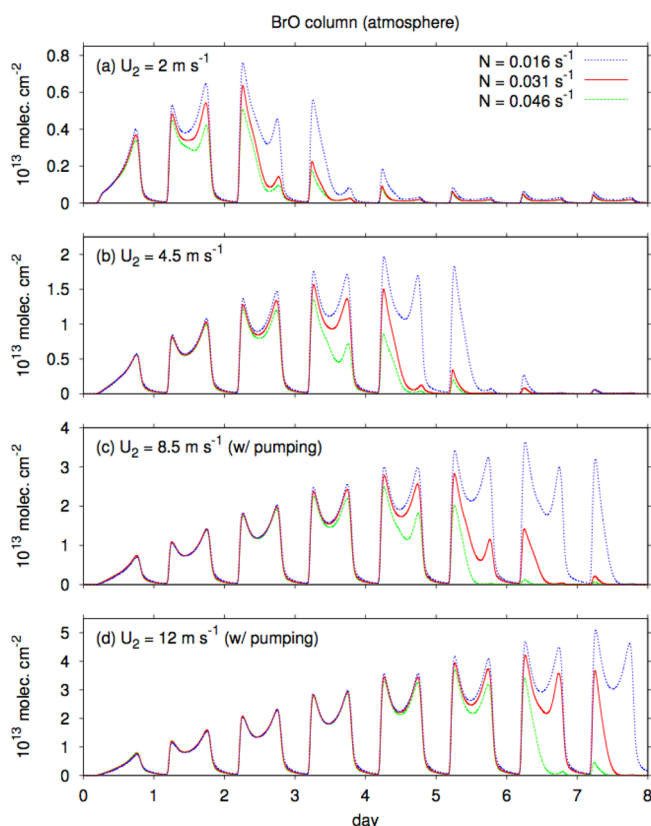


Figure 5. Simulated column amounts of BrO in the atmosphere versus time from the 1-D model of Toyota and co-workers (2014).¹⁴³ The panels show different assumptions for turbulence in the atmospheric boundary layer based upon windspeed, U_2 , and various values of the Brunt–Väisälä frequency, N . Note that the BrO column scale on each panel is different, and the higher windspeeds show much higher VCDs. Reprinted with permission from Toyota and co-workers (2014).¹⁴³ Copyright Toyota and co-workers 2014. CC Attribution 3.0 License.

3.1.5. Vertical Structure/Mixing. As has been discussed in the context of modeling studies above, the role of vertical mixing appears to have strong influences on polar halogen chemistry. Moore and co-workers¹⁴⁵ examined ozone and mercury levels and found that vertical mixing induced by convection from sea-ice leads, which are cracks in the sea ice cover, elevates these gaseous abundances by down mixing from aloft. This mixing brings down more mercury and ozone to the boundary layer, where halogens can remove the ozone and oxidize the mercury. The modeling studies^{143,144} indicate that increased vertical mixing extends the region of halogen chemistry, increasing the modeled BrO VCD, and the amount of mercury deposition. High winds and atmospheric frontal passages are also causes for increased vertical transport, which may be relevant to higher BrO VCDs observed by satellite-based spectrometers associated with storms.^{117,122} Arctic^{118,123,124} and Antarctic work¹⁴⁶ indicated that significant amounts of BrO exists above the convective boundary layer. Recently, Peterson and co-workers¹⁴⁷ found that higher vertical column densities of BrO in the troposphere were associated with less meteorologically stable conditions where vertical mixing of snowpack-surface-sourced halogens could be moved into a deeper boundary layer.

3.1.6. Summary of Recent Findings in Polar Regions. Recent advances in both mass spectrometric and optical instrumentation have enabled new observations of halogen

radicals and reservoirs. These studies point to an improved understanding of heterogeneous halogen activation process in polar regions, though more work is clearly required to develop a consistent picture. Surface, airborne and satellite measurements of BrO are significantly improving the understanding of the horizontal and vertical distribution of this compound in polar regions.

Recent work has also investigated the potential sources of HO_x radicals in polar regions, highlighting the role of both HONO and formaldehyde photolysis. Snowpack reactions have been demonstrated to produce reactive halogens, possibly fueled by production of radicals in the snowpack.

Model comparisons to these observations serve as a test mechanistic understanding the underlying process chemistry. Box models generally perform better when heterogeneous halogen sources are included, though they do not always produce quantitative agreement with observations. The role of vertical structure and mixing has been identified as an important parameter, as demonstrated by several 1-D models of polar halogen chemistry.

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, 2012.³² 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_2 in polluted coastal regions and other areas with high NO_x loadings are discussed in section 3.3.

Reactive chlorine species, such as HOCl and Cl_2 , have been measured at Cape Verde,^{54,148} an island in the central Atlantic Ocean, but numerical models struggle to reproduce these observations.^{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,^{150,151} during 2 cruises in the North Atlantic^{152,153} and at Cape Verde.^{59,154} The Cape Verde observations are regarded as of representative of the MBL surrounding the island and not influenced by coastal effects. Recent NO_3^-

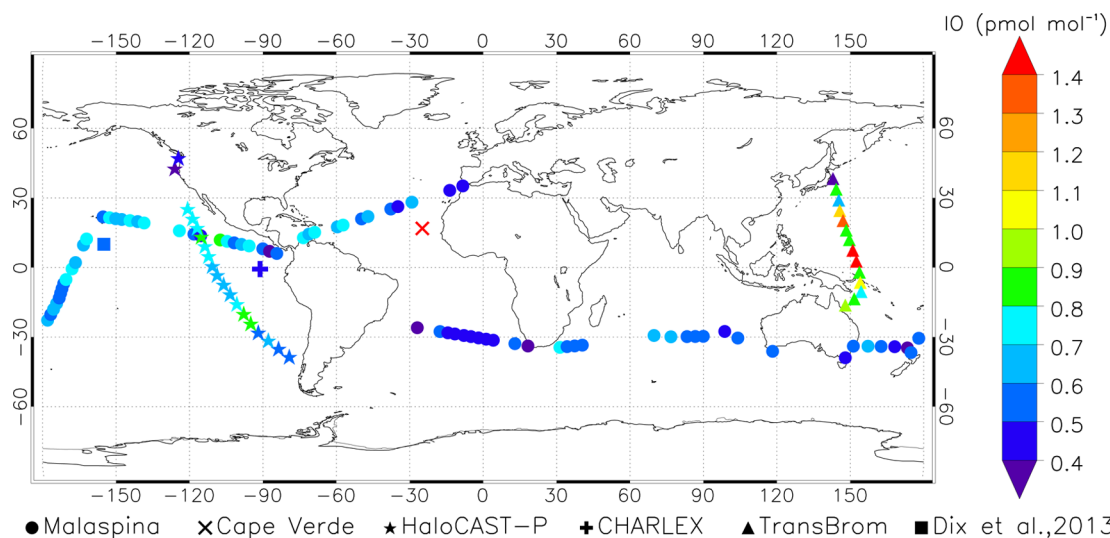


Figure 6. Marine boundary layer iodine monoxide (IO) observations from ship cruise and coastal station observations in pmol/mol. Reprinted with permission from Prados-Roman and co-workers (2015).¹⁹⁴ Copyright Prados-Roman and co-workers 2015. CC Attribution 3.0 License.

isotope analyses from Cape Verde¹⁵⁵ suggest that BrNO_3 contributes $20 \pm 10\%$ 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,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.^{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 Hov¹⁵⁹ 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 MISTRA¹⁵⁷ 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.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^{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-workers¹⁶² successfully reproduces some of the measured Br^- deficits in aerosol particles but still seems to overestimate BrO mixing ratios. Sommariva and co-workers¹⁴⁹ discuss potential reasons for this surprising mismatch between models and field data.

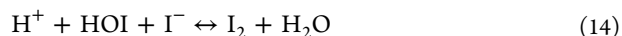
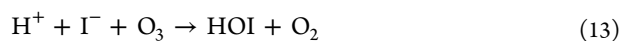
3.2.2. Organobromine Sources. So-called very short-lived (VSL, lifetime of less than 6 months) substances have been identified as playing a key role in supplying bromine to the stratosphere.¹⁶³ Due to their short lifetimes of a few weeks to a

few months, compounds, such as CHBr_3 and CH_2Br_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-workers¹⁶⁴), 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).^{165–170}

During measurements of sea-air fluxes of bromocarbons in the North Atlantic, a link with marine biological precursors was confirmed.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,^{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.¹⁶⁷ Hossaini and co-workers¹⁷³ 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 bromine. For iodine, sea salt aerosol particles represent a sink rather than a source¹⁶ and virtually all inorganic iodine that is present in the MBL originates from decomposition of natural iodocarbons such as CH_3I and CH_2I_2 and the inorganic precursors HOI and I_2 .³⁰ The reactions involved in ozone-

mediated iodide release via HOI are shown in reactions 13 and 14



Recent laboratory studies quantifying these reactions coupled with modeling has been successful at predicting field IO observations.^{85,174–176} Model calculations of IO and its organic precursors^{154,177} 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 1981.¹⁷⁸

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.^{30,67,86,179–183} 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.^{59,154} 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^{184–190} but the reaction pathways leading to the differences in speciations which vary with location and time are not yet fully understood.¹⁵⁷

Iodine oxide in the remote MBL has been observed at Tenerife, Tasmania,⁸⁷ Cape Verde,^{59,154} the West-Pacific,¹⁹¹ and East-Pacific.^{192,193} At all these locations, comparisons of model results with field data suggest that organic iodine precursors are insufficient to explain the observed levels of IO,^{154,177,191} 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.^{85,174–176} At Cape Verde, I₂ was measured recently⁶⁶ 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-workers¹⁹⁴ 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-workers¹⁹² 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-workers¹⁹³ at Galapagos and by Prados-Roman and co-workers.¹⁹⁴ A correlation with sea surface temperature might be the result of iodide in surface water showing a reasonable correlation with the sea surface temperature,¹⁹⁵ 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 CH₃I decadal trends at five Pacific sites by Yokouchi and co-workers¹⁹⁶ 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 CH₃I fluxes. Prados-Roman and co-workers¹⁹⁴ 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-workers¹⁹⁷ 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 Donaldson¹⁷⁵ 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-workers¹⁹⁸ 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 group¹⁹⁹ found that fulvic acids enhanced I₂ production, but a number of other similar humic-like substances did not affect these reactions. Shaw and Carpenter²⁰⁰ found that marine-origin DOC suppressed the production of I₂ by roughly a factor of 2 in laboratory samples with reactivity ratios between I⁻ to DOC similar to natural seawater. Pillar and co-workers²⁰¹ 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-workers²⁰² 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^{29,31,42} have addressed this heterogeneous process under tropospheric conditions. Recently, Roberts and co-workers²⁰³ 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 I₂. This work is supported by recent measurements and associated modeling of iodine species in marine environments, which indicate that heterogeneous uptake of O₃ 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 IO has been shown recently to be widespread at low levels across the world's oceans.

3.3. NO_x Pollution-Related Halogen Chemistry

For decades, there has been significant interest in reactive halogen chemistry occurring in polluted regions.^{19,24,54,75,148,157,158,204,205} 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,^{49,204,206} as well as the lifetime of primary pollutants such as hydrocarbons and their oxidation products.^{50,101,207} 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 HNO₃ and H₂SO₄ 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 HO₂ 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 N₂O₅ heterogeneous chemistry to form nitryl halides.^{55,57,77–79,208–212} 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 ClNO₂ by N₂O₅ 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. Dihalogens Cl₂, Br₂, and I₂ all have been observed in polluted coastal air,^{19,54,55,61,148,158} albeit at fairly

different mixing ratios: low pmol/mol for Br₂ and I₂ and up to 200 pmol/mol for Cl₂, as shown in Table 1. Interestingly, BrCl has only sporadically been detected, or not detected at all outside of polar regions.¹⁰⁷ While substantial mixing ratios of Cl₂ have been detected in polluted coastal regions,^{19,54,55,61,148,158,205} or pollution impacted remote regions,^{19,66,148,157,205} the mechanisms by which the Cl₂ is produced remain uncertain. Additionally, instrumental methods for detection of Cl₂ are challenging, opening the possibility of large measurement uncertainties. Possible chemical sources of Cl₂ include light activated reactions, multiphase chemistry of nitryl halides, or reactions of BrCl and HOCl 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 Cl₂,²¹¹ but these point sources can usually be distinguished from regional sources of Cl₂, which seem to have diurnal patterns that depend upon location. There is no consensus on the most important sources of dihalogens 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 (XNO₂, where X = Cl, Br, I), such as ClNO₂ (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 O₃ to NO₃, which can react with NO₂ to form N₂O₅. N₂O₅ can then react with halide-containing particles or on halide surfaces to produce XNO₂. The activation of halogens by N₂O₅ is therefore tied to NO_x sources, ozone concentrations, the homogeneous reactivity of NO₃, and availability of halide-containing aerosol particles; all of which vary with season and location. Photolysis of XNO₂ is slower than dihalogens, but fast enough to contribute significantly to the morning radical budget.^{50,55,213} 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.²¹⁴ XNO₂ formation and photolysis also affect the reactive nitrogen budget and partitioning with indirect impacts on oxidants.

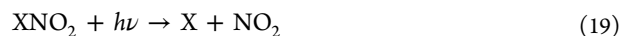


Figure 7 shows a time series of N₂O₅ and ClNO₂ measured at the Scripps Institution of Oceanography Pier by Bertram, Kim, and co-workers.²¹² The expected nocturnal enhancement of ClNO₂ and its correlation with N₂O₅ are both clearly illustrated.

The reactions of N₂O₅ in atmospheric particles has been reviewed recently.^{35,36} The mechanism is thought to proceed through a positively ionized intermediate, NO₂⁺, which undergoes nucleophilic attack by halide ions to form the nitryl halide (XNO₂, X = Cl, Br, I)²¹⁵ in competition with hydrolysis by H₂O. Several laboratory measurements^{215–217} suggest that

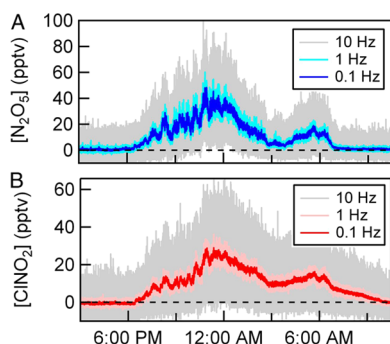


Figure 7. Nighttime observations of NO_x polluted air containing N_2O_5 and produced reactive halogen precursor, nitryl chloride, ClNO_2 , measured at the Scripps Institution of Oceanography Pier. Reprinted with permission from Kim and co-workers (2014).²¹² Copyright 2014 National Academy of Sciences.

chloride attack of the NO_2^+ intermediate is a factor of ~ 500 more efficient than that of water. Thus, nitryl halide production by N_2O_5 competes with N_2O_5 hydrolysis down to $<0.1\%$ halide solute mass fractions.²¹⁷ Figure 8 shows that ClNO_2 product

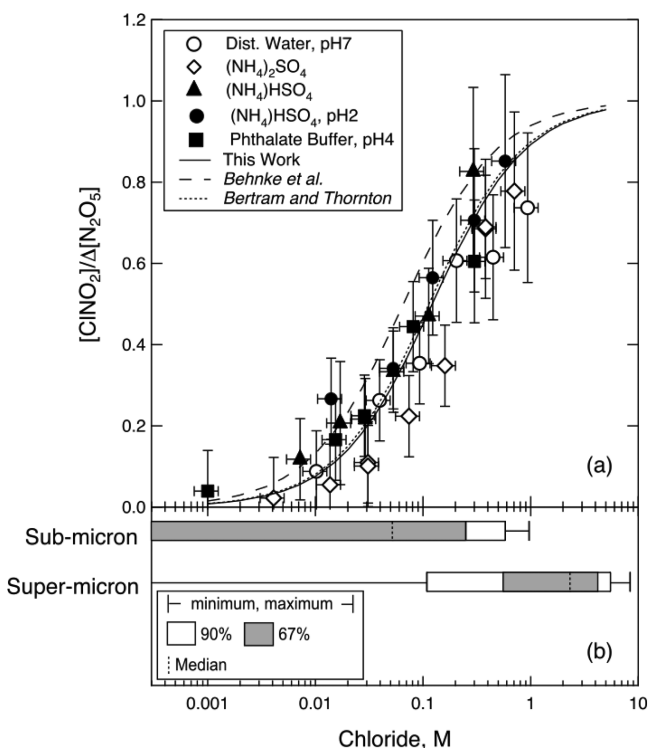


Figure 8. Conversion efficiency for production of ClNO_2 from N_2O_5 from laboratory measurements along with models. Panel b shows ranges of particulate chloride composition from the TexAQS-GoMACCS 2006 field campaign. Reprinted with permission from Roberts and co-workers (2009).²¹⁷ Copyright 2009 American Geophysical Union.

yield per N_2O_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_2O_5 reaction probability on most aqueous aerosol particles (the exception being nitrate containing particles²¹⁵) 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_2O_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 ClNO_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_2O_5 reactive uptake to halide-doped ices and bromide salts, where Br_2 not BrNO_2 was always the dominant product.²¹⁸ Similar findings of enhanced multiphase reactivity of BrNO_2 were obtained in studies of uptake to aqueous solutions.²¹⁹ Thus, ClNO_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_2O_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-workers²²⁰ showed that at highly acidic pH ($\text{pH} < 2$), N_2O_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 ClNO_2 several hundreds of kilometers inland from sea spray sources such as near Denver in the U.S., Calgary in Canada, Uintah Basin of the U.S., and Frankfurt in Germany,^{51,55,57,78,79,209,221} and the significant concentrations produced in polluted coastal regions. Osthoff and co-workers⁷⁷ and Thornton and co-workers⁷⁸ 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,²¹¹ there are secondary impacts of ClNO_2 production on the abundance and sources of OH, which would further enhance the methane loss rate in regions with significant ClNO_2 . Thus, the budget and spatial distribution of ClNO_2 production are important to constrain in order to develop accurate estimates of methane removal.

A key scientific question with respect to ClNO_2 distributions is not so much related to the mechanism of ClNO_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 ClNO_2 is predicted well inland of the polluted coastal regions²²² (see Figure 9 below). The model predicted that with just these sources mean nighttime maximum ClNO_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 $\sim 15\%$ of reactive nitrogen, generally consistent with observational based estimates.⁷⁸ Peak ClNO_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.²²³ Vertical profiles of ClNO_2 measured outside of Denver, CO, provide evidence for a source of chloride and ClNO_2 production within coal-fired power plant plumes.²¹¹ The magnitude of such a source compared to sea spray transport and biomass burning remains uncertain due, in part, to a lack of measurements of chloride and ClNO_2 within isolated power plant plumes.

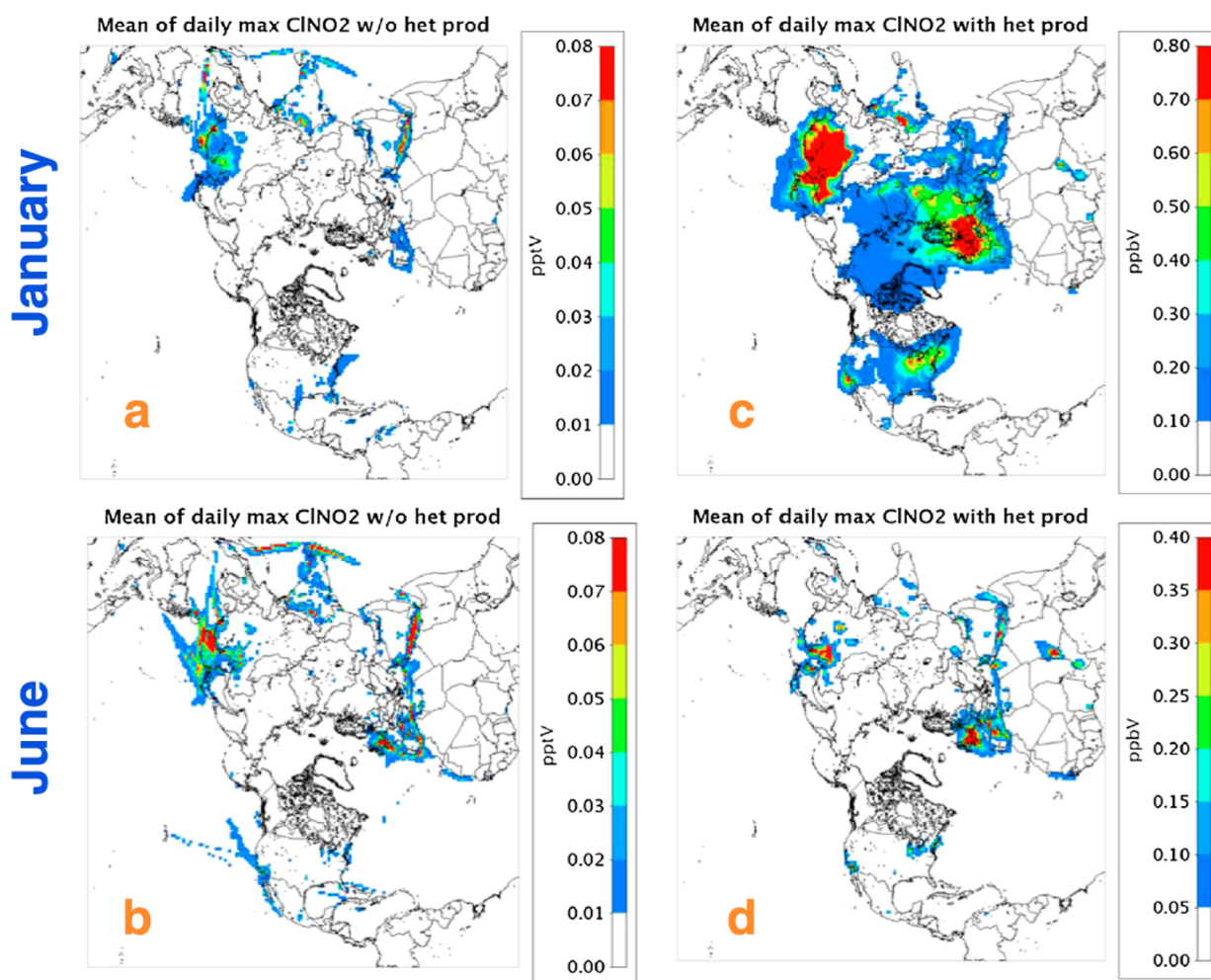


Figure 9. Mean of nightly 1 h maximum ClNO_2 in January without the heterogeneous ClNO_2 production (pptv = pmol/mol), (b) mean of nightly 1 h maximum ClNO_2 in June without the heterogeneous ClNO_2 production (pptv = pmol/mol), (c) mean of nightly 1 h maximum ClNO_2 in January with the heterogeneous ClNO_2 production (ppbv = nmol/mol), and (d) mean of nightly 1 h maximum ClNO_2 in June with the heterogeneous ClNO_2 production (ppbv = nmol/mol). Reprinted with permission from Sarwar and co-workers (2014).²²² Copyright 2014 American Geophysical Union.

The literature demonstrating high levels of ClNO_2 far from the coast has grown in recent years. Mielke and co-workers²⁰⁹ observed nighttime ClNO_2 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-workers⁷⁹ found ClNO_2 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-workers²²¹ in 2012 observed median levels of ClNO_2 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,⁵¹ observed somewhat lower ClNO_2 levels, with peaks \sim 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 ClNO_2 and Cl_2 were detected in recent studies. Riedel and co-workers⁵⁵ observed nighttime ClNO_2 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-workers²¹⁰ considered the sea breeze/land breeze circulation pattern in the Los Angeles

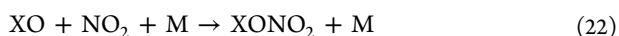
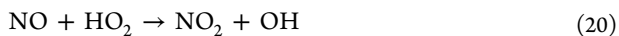
basin and modeled the role of in situ production versus transport of nitryl chloride. They found that on most nights the majority of ClNO_2 is produced in the basin over land and transported offshore by the land breeze. More variable levels of activation of Cl_2 with peak levels up to 200 pmol/mol were observed. Mielke and co-workers⁵⁷ observed ClNO_2 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 ClNO_2 abundance constituted more than 20% of non- NO_x reactive nitrogen oxides. As shown in Figure 7, ClNO_2 was observed in the marine boundary layer near San Diego, California.²¹² This study used a fast-response detector and the eddy-covariance technique to measure the deposition flux of both N_2O_5 and ClNO_2 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 ClNO_2 by Young and co-workers²¹³ 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 ClNO₂. Crisp and co-workers²²⁴ made measurements off the Californian coast and found a very good correlation of HCl with non-NO_x reactive nitrogen, NO_z = NO_y - NO_x. 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 (ClNO) 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 ClNO mixing ratios in polluted marine areas could reach parts per billion mixing ratios or higher, that is, similar to ClNO₂ concentrations detected in such regions. However, these theoretical and laboratory studies have yet to be confirmed by field measurements of ClNO in ambient air. A possible explanation is that hydrolysis of ClNO at moderate and high relative humidity (RH > 20%) is likely sufficiently rapid to prevent the buildup of appreciable atmospheric concentrations of ClNO.²²⁶ Further attempts to quantify ClNO 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 CH₄.²³ 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 partition to the gas-phase, and photolyze to form halogen atoms thereby completing the cycle.

In polluted regions, the fate of halogen atoms and their oxides, and thus the propagation efficiency of halogen recycling, is strongly affected by the elevated NO_x and VOC present.²²⁷ Because of abundant aldehydes and hydrocarbons, the reactions of Br and Cl radicals to form HBr and HCl, respectively, are competitive with or exceed the rates of their reactions with ozone to produce halogen oxide radicals.^{51,130,221} The exception is atomic iodine, which does not have appreciable reactivity toward hydrocarbons or their oxidation products. Some formation of the halogen oxides (XO) is of course possible, in part because ozone can also be elevated in polluted regions during the daytime relative to remote regions. But, nitric oxide (NO) radicals lower HO₂ radicals and directly react with XO to form X and NO₂, both of which suppress formation of the hypohalous acids.



Riedel and co-workers²²⁸ found that more than two-thirds of ClO reacts with NO (reaction 21) to reform NO₂ under the polluted conditions of the Los Angeles basin. Therefore, under polluted conditions, the X/XO ratio is controlled by NO, whereas in remote regions the NO/NO₂ ratio can be affected by halogens.

In polluted regions, the most likely route to extended halogen recycling would be via formation of the halogen

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 NO₂,²²⁸ 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 N₂O₅ consumes significant amounts of ozone at night, and to the extent that heterogeneous hydrolysis of N₂O₅ occurs, both ozone and NO_x are lost at night, decreasing ozone levels. However, when formation of ClNO₂ happens via reaction of aerosol-particle-accommodated N₂O₅ with Cl⁻, a reservoir is formed that photolyzes (reaction 19) in the morning, releasing NO₂ and the potent oxidizer, chlorine radical atoms. Riedel and co-workers⁵⁵ found that the peak producer of chlorine atomic radicals was the morningtime photolysis of ClNO₂, 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 ClNO₂ 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 ClNO₂ extends out to late afternoon. Another complexity noted in this study²²⁸ is the effect of ClNO₂ in extending the lifetime of NO_x by preventing nocturnal loss via N₂O₅ hydrolysis yet secondary OH produced after morning photolysis of ClNO₂ reduces the lifetime of daytime NO_x lifetime via OH + NO₂ (+ M). Osthoff and co-workers⁷⁷ also presented an MCM model of the effect of ClNO₂ photolysis on ozone production in Houston, TX, showing that inclusion of measured ClNO₂ 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 Angeles²³⁰ and Houston²³¹ that showed considerable sensitivity of ozone to Cl atom sources, but that did not explicitly consider ClNO₂ 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 NO_x.^{101,207} Young and co-workers⁵⁰ showed that in higher NO_x environments characteristic of urban areas, where ClNO₂ 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 ClNO₂ photolysis is the sole primary radical source. At the continental site in the Uintah Basin, Edwards and

co-workers^{51,221} 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. Nitryl 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_x 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 ClNO₂, 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 nitryl halides have yet to be observed in ambient air and may undergo additional heterogeneous chemistry to produce dihalogens. The database for ambient ClNO₂ 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 ClNO₂ photolysis. Chemical transport models that incorporate recent parametrizations of ClNO₂ from N₂O₅ uptake to chloride substrates are consistent with the widespread occurrence of ClNO₂. Nitrosyl halide (XNO) production has also been suggested from laboratory and modeling studies of heterogeneous NO_x 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.

Nitryl chloride, ClNO₂, 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 NO_x source that will also influence ozone production, though the exact influence will depend on the specific sensitivity of ozone to NO_x 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_y) and iodine (I_y) 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, ClNO₂, 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 NO_x-Related Halogen Chemistry. As discussed in section 3.3.3, NO_x-induced halogen activation via ClNO₂ affects ozone, particularly near coasts. On a regional scale, Sarwar and Bhawe²³² 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^{233,234} incorporated ClNO₂ 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,²³³ they demonstrated that N₂O₅ uptake and ClNO₂ photolysis was by far the largest source of atomic Cl in the region,²³⁴ in contrast to previous results implicating industrial and residential sources.²³¹ They identified key uncertainties in the yield of ClNO₂ from N₂O₅ uptake and in the vertical distribution of ClNO₂ at sunrise.²³⁴ More recently, Sarwar and co-workers²³⁵ updated the chlorine activation mechanism, including the treatment of heterogeneous hydrolysis of N₂O₅ to include ClNO₂ as product and improved emissions inventories.²³⁶ 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 nitryl chloride production on the United States air quality. The results from this work show that the production of ClNO₂ 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 recently²²² to assess the atmospheric role of ClNO₂ chemistry in the whole Northern Hemisphere. Figure 9 shows ClNO₂ 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 ClNO_2 . The largest increase in O_3 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 $\mu\text{g m}^{-3}$ during the winter season over China, India, Western Europe and Western USA, with peak reductions of 2.0–3.0 $\mu\text{g m}^{-3}$ in regions of China.²²² This study also indicates that ClNO_2 could be generated on the surface of biomass burning particles, as much of the ClNO_2 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 CH_3Br 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_y 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_y budget in the stratosphere were those by Dvortsov and co-workers²³⁷ and Nielsen and Douglass.²³⁸ 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 CHBr_3 to Br_y , using uniformly distributed sources of bromoform over the oceans. Dvortsov and co-workers²³⁷ used the Model of Atmospheric Transport and Chemistry (MATCH), the off-line version of NCAR Community Climate Model version 3 (CCM3), while Nielsen and Douglass²³⁸ used the Parameterized Chemistry and Transport Model (PCTM). Warwick and co-workers²³⁹ used the p-TOMCAT model with bromoform emissions concentrated in the tropics and coastal regions to reproduce the latitudinal distribution of a suite of CHBr_3 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 CH_2Br_2 , CH_2BrCl , CHBr_2Cl , and CHBrCl_2 .

Kerkweg and co-workers,²⁴⁰ included the Warwick and co-workers VSL emissions inventory²³⁹ in the ECHAM5/MESy model to simulate bromine chemistry in the troposphere and stratosphere. They modeled that the main tropospheric loss process for CH_3Br , CH_2Br_2 and CH_2ClBr is reaction with OH, while for CHBr_3 , CHCl_2Br and CHClBr_2 the main loss pathway is photolysis. In the stratosphere the dominant decomposition process is photolysis. Aschmann and co-workers²⁴¹ modeled the transport of VSL species into the UTLS using the Sinnhuber and co-workers²⁴² 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 VSLs 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 Hossaini and co-workers,¹⁷³ the TOMCAT 3D CTM was combined with the existing ocean emission inventories (see also section 3.2.2) of CHBr_3 and CH_2Br_2 ^{239,243–245} 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-workers²³⁹ 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,¹⁶⁴ with emission fluxes concentrated in uniform strips over tropical and extratropical oceans. The top-down inventory of Liang and co-workers²⁴⁵ is based on a baseline scenario from Warwick and co-workers²³⁹ adjusted in both magnitude and location to match a variety of observations in the mid troposphere. Ordóñez and co-workers²⁴³ 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-workers²⁴⁴ inventory is a bottom-up estimation in which global emission maps are calculated from marine and atmospheric surface halocarbon concentration maps.

Hossaini and co-workers²⁴⁶ used the TOMCAT/SIMCAT model with a chemical scheme for the degradation of bromoform and dibromomethane. They report 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 recently²⁴⁷ using the same model including the contribution of other species, such as CHBr_3 , CH_2Br_2 , CH_2Br_2 , CHBr_2Cl , CHBrCl_2 , CH_2BrCl , and $\text{C}_2\text{H}_5\text{Br}$, 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 Sinnhuber²⁴⁸ using the B3DCTM global model also reported that VSLs injection to the stratosphere contributes 4.5–6 pmol/mol to the Br_y 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-workers²⁴⁹ 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 Ordóñez and co-workers²⁴³ and Saiz-Lopez and co-workers.²⁵⁰ 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 CHBr_3 , CH_2Br_2 , CH_2BrCl , CHBrCl_2 , and CHBr_2Cl , and the iodocarbons CH_2ICl , CH_2IBr , and CH_2I_2 .

This configuration and emissions inventory in CAM-Chem was later employed²⁵¹ together with an improved heterogeneous reactions scheme for HBr, HOBr and BrONO₂ 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.^{247,248} 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_y to the stratosphere. This injection is expected to increase in the future as suggested in the studies of Dessens and co-workers²⁵² and Hossaini and co-workers.²⁵³ Dessens and co-workers²⁵² 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-workers²⁵³ 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_y 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 on 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-workers⁶³ 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-workers⁶⁵ 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_y) in the stratosphere, only two reports^{254,255} have been used to estimate upper limits combining balloon-borne solar occultation DOAS measurements and photochemical modeling. The most recent report²⁵⁵ estimates I_y = 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 ClNO₂ chemistry 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_y 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-workers²⁵⁶ 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 simplified parametrization for heterogeneous recycling of bromine. Yang and co-workers²⁵⁷ 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-workers²⁵⁸ 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,

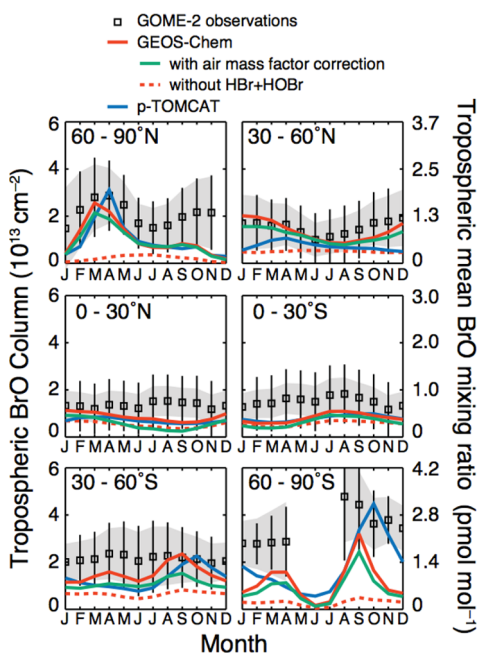


Figure 10. Seasonal variation of mean annual tropospheric BrO simulated by GEOS-Chem along with GOME-2 observations and p-TOMCAT model simulations. The effect of removing the heterogeneous reaction of HBr + HOBr is demonstrated in the GEOS-Chem simulations. Reprinted with permission from Parrella and co-workers (2014).²⁵⁸ Copyright Parrella and co-workers 2014. CC Attribution 3.0 License.

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 ~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-workers²⁵⁰ used the halogen chemistry scheme and VSL inventory implemented in CAM-Chem,²⁴³ 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-workers²⁵⁶ 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.²⁵⁰

The recent work by Saiz-Lopez and co-workers²⁵⁹ included for the first time in a global model (CAM-Chem) the parametrization of MacDonald and co-workers^{85,176} to account for the open ocean ozone oxidation of iodide to I₂ 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-workers²⁵¹ 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-workers¹⁹⁴ 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 O₃, HO_x, NO_x were studied by Long and co-workers¹⁶² 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.²⁵⁸ Holmes and co-workers²⁶⁰ used the p-TOMCAT configuration of a prior study²⁵⁷ to estimate the lifetime of tropospheric elemental mercury (Hg⁰) 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 Hg⁰, mainly in places like the free troposphere. The feasibility of atomic bromine as an alternative Hg⁰ global oxidant was demonstrated using the global 3D model GEOS-Chem.²⁶¹ The topic of mercury deposition to the polar regions is discussed in section 4.2.

Using the GEOS-Chem model, Parrella and co-workers²⁵⁸ 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 Hg⁰, this change in Br levels causes a Hg⁰ lifetime of 4 months in preindustrial simulations as compared to 7 months in present day.

Saiz-Lopez and co-workers²⁵⁰ 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

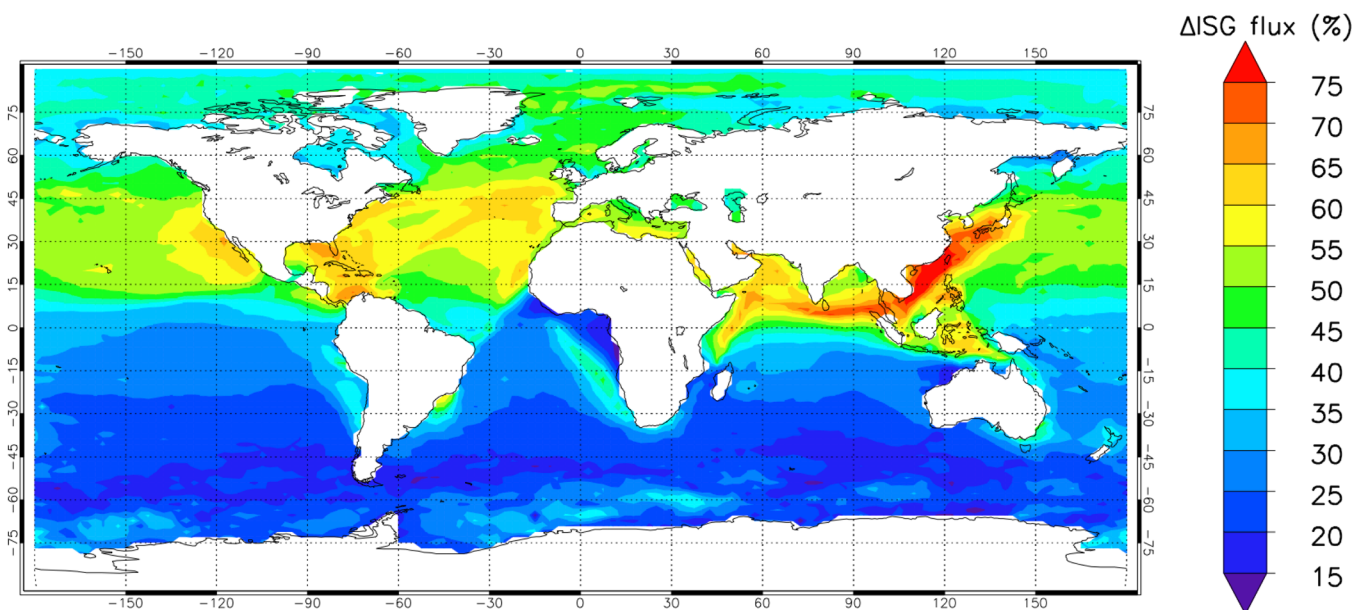


Figure 11. Modeled anthropogenic influence on oceanic iodine source as a percentage change from preindustrial times to current conditions. Reprinted with permission from Prados-Roman and co-workers.²⁶² Copyright Prados-Roman and co-workers 2015. CC Attribution 3.0 License.

column, which accounts for a change of -0.10 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 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-workers²⁵⁹ 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 (HOI 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 O_3 levels and oceanic inorganic iodine emissions. The anthropogenic enhancement of 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” 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 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-workers²⁰⁷ found that 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-workers²⁶⁵ 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-workers²⁶⁶ 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-workers¹⁴⁵ 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-

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,¹⁸³ 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_2O_5 and its heterogeneous reaction with particulate chloride forms $ClNO_2$, which photolyses in the early morning, producing an early start to daytime radical production^{50,55,57,77,79,209,211,213,222,228,235} as well as liberation of NO_2 . That early start to daytime radical chemistry can lead to increased ozone production in the day.²²⁸ On the other hand, nocturnal reactions of nitrogen oxides can also decrease ozone and NO_x through heterogeneous hydrolysis of N_2O_5 , competing with daytime ozone production. The study of the effects of NO_x on halogen radical activation has only recently begun,²²⁷ 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 $ClNO_2$) often leads to production of hydrocarbon radicals that then typically form secondary HO_x radicals⁵⁰ or photolabile carbonyl species that act to amplify radical production.⁵¹ 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 radical 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 $ClNO_2$ 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 $ClNO_2$ and precursors needs further investigation. (9) Field measurements have clearly shown production of $ClNO_2$, 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 NO_x gases in production of photolabile precursor species. Many of these precursors photolyze at longer wavelengths than typical HO_x precursors, allowing halogen chemistry to occur in twilight or in polar regions. The reactions that liberate halogen precursors often consume other radicals such as HO_2 , and thus sources of radicals is a key question for both halogen and all photochemistry. Both halogens and HO_x oxidize hydrocarbon species, producing secondary organic radicals and subsequently HO_x radicals. This two-way coupling between halogen and HO_x 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 I_2 .⁸⁵ In NO_x -polluted regions, we have expanded our observational evidence of the role of nocturnal N_2O_5 chemistry in halogen activation^{55,57,79} 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 NO_x -pollution produced ClNO_2 ²²² 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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William Simpson graduated from Swarthmore College with a B.A. in Chemistry and a Mathematics minor in 1988. He received his Ph.D. in Physical Chemistry from Stanford University in 1995. After two postdoctoral appointments, he joined the faculty at University of Alaska Fairbanks in 1997, where he currently is a Professor of Chemistry. His research group investigates atmospheric halogen and nitrogen chemistry using spectroscopic methods with a focus on the Arctic region and how the changing climate affects halogen activation.



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 currently is 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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