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The Influence of Short-Lived Halogens on Atmospheric Chemistry and Climate

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Preface

Observations have demonstrated the ubiquity of short-lived halogens (SLH), defined as organic and inorganic chlorine, bromine, and iodine compounds with an overall atmospheric lifetime of less than six months, in the global atmosphere. They are primarily emitted naturally from the ocean, cryosphere, volcanoes, salt lakes and the biosphere. However, unregulated anthropogenic sources are increasingly contributing to their atmospheric loading. Some of their natural emissions have increased over time because of anthropogenic pollution, for example, the increased oceanic emissions of iodine compounds due to the deposition of ozone on the sea surface. SLH affect chemical processes, such as ozone and methane chemistry, and thus influence air quality and climate. Nevertheless, some of their sources and

chemistry are not included in air quality and climate models used in international assessment reports. Here we describe in detail the various impacts of SLH on air quality and climate, and make a case for the inclusion of more comprehensive SLH chemistry in future atmospheric, air quality and climate assessments. In doing so, we also identify gaps in our knowledge of SLH emissions, chemistry, and environmental and climate impacts.

Main Text

Short-lived halogens (SLH), which include organic halogenated very short-lived substances (VSLS) and inorganic halogen species (see Table 1 for a detailed list of SLH), result from direct emissions by various natural and anthropogenic sources and the atmospheric degradation of these source gases. Research over the last two decades has demonstrated the importance of SLH on atmospheric chemistry and climate, including stratospheric and tropospheric chemistry, tropospheric oxidising capacity, viz, the rate at which carbon monoxide, methane (CH_4) and volatile organic compounds (VOCs) are oxidized by hydroxyl radicals (OH), ozone (O_3), nitrate radicals (NO_3) and Cl atoms, methane and mercury lifetimes, air quality, aerosol formation and, therefore, the overall Earth's radiation budget.

Bromine and iodine-containing SLH are naturally emitted from oceans, the cryosphere, lithosphere and the biosphere, whereas chlorine-containing SLH have, in addition, important contributions from anthropogenic sources. In the stratosphere, chlorine- and bromine-containing SLH, and, to a lesser extent, iodine-containing compounds, enhance the chemical loss of ozone. In the troposphere, iodine-containing species play the largest role of SLH in modulating ozone, followed by bromine- and chlorine-containing compounds.

Models contributing to assessments of tropospheric and stratospheric ozone and methane by organisations such as the Intergovernmental Panel on Climate Change (IPCC), the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP), which neglect an accurate and detailed description of SLH chemistry, can yield inaccurate evaluations resulting in mismatches between observations and predictions, and missing mechanisms that lead to unintended feedbacks or erroneous decisions. More specifically, these omissions lead to an incomplete understanding of budgets of key atmospheric constituents, and hence, flawed projections, for example, the underestimation of the depletion and the recovery of stratospheric ozone and the lifetime of atmospheric methane.

1. Current understanding and importance of SLH

SLH play an important role in several aspects of atmospheric chemistry. Their effects extend from the boundary layer up to the stratosphere and from the tropics to the polar regions. Below we describe some of the most important ways in which SLH influence atmospheric chemistry and climate.

1.1 Importance for stratospheric chemistry

Research in halogen chemistry in the atmosphere was initially driven by its role in stratospheric ozone loss[1]. In the mid-1970s, it was first proposed that anthropogenic long-lived species, such as chlorofluorocarbons (CFCs), methyl chloroform (CH_3CCl_3), methyl bromide (CH_3Br)[2] and later halons (bromofluorocarbons)[3], could deplete stratospheric ozone. The long-lived anthropogenic species commonly referred to as ozone-depleting substances (ODSs) increased the natural halogen loadings by a factor of ~6 for Cl and ~2 for Br at the peak[4]. A non-negligible fraction of the stratospheric chlorine and bromine loading is of natural origin (e.g. methyl chloride (CH_3Cl) and methyl bromide (CH_3Br))[5,6], which have tropospheric removal lifetimes of less than one year.

During the last few decades, research has confirmed that SLH chemistry influences stratospheric chemistry, the ozone layer and its future evolution[6–15]. Brominated compounds increase ozone depletion in the upper-troposphere-lower-stratosphere (UTLS)[6,13,16], and iodine compounds can also impact stratospheric ozone[8,11,17–19]. SLH are particularly effective at destroying ozone close to the tropopause as they release halogen atoms rapidly when reaching these altitudes, while longer-lived halocarbons are broken down only in the mid- to upper-stratosphere. Including SLH compounds in models improves the agreement with observed ozone concentrations and trends in the lower-mid stratosphere[20] and the depth and size of the Antarctic ozone hole[21–23], although considerable uncertainties remain[24]. In 2020, SLH were estimated to contribute 4%, 26%, and 100% of the total stratospheric chlorine, bromine and iodine loadings, respectively[4] (Figure 1). Modelled HCl trends are more accurate when SLH are considered. The Cl and Br contributions by natural SLH will increase further as anthropogenic long-lived halogen emissions decline. A small proportion of stratospheric SLH are of natural volcanic origin, although estimates of their impact through past[13,25] and future[26] volcanic eruptions on stratospheric ozone depletion are uncertain. Finally, the ozone depletion caused by a hypothetical climate intervention through stratospheric aerosol injection will increase due to the presence of SLH[27].

1.2 SLH in the Polar Troposphere

Scientific interest in the role of SLH in tropospheric chemistry was stimulated by reports of boundary layer ozone depletion events (ODEs) initially in the Arctic and later in the Antarctic[28–32]. Emissions of bromine from snow-covered sea-ice and coastal tundra, and blowing snow, initiate autocatalytic heterogeneous reactions that cause 'bromine explosions' which lead to ODEs, atmospheric mercury deposition events, and affect the atmospheric oxidising capacity[3,28–30,33–39]. Large bromine monoxide (BrO) plumes have been discovered in the Arctic and Antarctic[34,40,41], and are an active research area. In addition to the role of bromine, observations showed that iodine compounds also contribute to boundary layer ozone depletion in the Antarctic[42] and, more recently, in the Arctic[43–45], although our knowledge of iodine sources is inadequate[46–49]. Recent observations of polar iodine-initiated new particle formation imply direct and indirect radiative effects of SLH[50,51]. High levels of reactive chlorine species have also been reported in the Arctic, associated with reactions on snow surfaces[52,53]. Further observations of gas-phase bromine chloride (BrCl) point to the connections between these SLHs[54,55], and the observation of cyanogen bromide (BrCN) during ODEs shows that the ‘bromine explosion’ mechanism is more complex than previously thought[56]. It has been suggested that Arctic halogens can also influence ozone loss over the mid-latitudes of the Northern Hemisphere[57].

1.3 Impacts on the Global Troposphere

Although initial laboratory work had suggested an important role of iodine emissions from the sea surface on atmospheric chemistry[58,59], by the early 2000s, the general perception was that SLH mattered only in the polar boundary layer or the intertidal zone (see Section 1.4). However, subsequent observations showed that SLH play a key role in the global marine boundary layer, accounting for up to 45% of the ozone loss in the open ocean regions[35,60–63]. Aircraft observations and modelling studies also showed that the relative contribution of SLH to ozone destruction is largest in the free troposphere[64,65]. Over the last two decades, a growing body of evidence has demonstrated the influence of SLH to be ubiquitous throughout the troposphere[13,66–70], affecting the concentration of key species such as HO_x (OH and hydroperoxyl (HO_2) radicals), NO_x (nitrogen oxide (NO) and nitrogen dioxide (NO_2)) and ozone on regional[71–73] and global scales[64,74–80] (Figure 2). Globally averaged, SLH reduce the modelled tropospheric ozone burden by approximately 17-20% (Figure 1), resulting in tropospheric columns that lie on the low edge of current observationally-derived estimates[64,74,81], although its estimates remain uncertain. SLH chemistry decreases the global net atmospheric oxidising capacity due to changes in the concentrations of the main oxidants (Cl: +778%, O_3: −20%, NO_3: −36% and OH: −13%)[82] (Figure 1). The change in oxidants leads to an increase in the global methane lifetime by 6-9% (Figure 1), resulting in an increase in the modelled methane burden (up to 400 Tg or +8% by 2100 under the Representative Concentrations Pathways 6.0 (RCP6.0) scenario)[83]. The resulting increase in the modelled CH_4 burden due to indirect SLH effects (~300 Tg in the present day) is estimated to be equivalent to the observed atmospheric CH_4 growth during the last three decades (Figure 1). As a result, models which do not include SLH underestimate CH_4 abundances. The SLH-mediated reduction in OH and the increased direct oxidation by Cl also affect the formation of secondary organic aerosols (SOA) from volatile organic compounds, and the formation of sulphate and ammonium nitrate aerosols[84]. The net effect of SLH is a reduction in sulphate (−3%) and ammonium nitrate (net: −10%) aerosols but an enhancement of SOA (net: 2%)[84] (Figure 1). This net effect results directly from the reactions with SLH and indirectly from changes in the amounts of the oxidants O_3 and OH (Figure 1).

1.4 Regional effects and air quality

The emission and activation of SLH impacts the amounts and distributions of key atmospheric species and thus air quality on regional scales. This is a consequence of the changes in lifetimes and fates of primary emissions, such as NO_x and VOCs, and by influencing the mechanisms and production rates of regulated secondary pollutants such as O_3 and $PM_{2.5}$. Outside of polar regions, the role of SLH on regional scales was first proposed following studies showing the formation of photochemically active chlorine[85,86] and bromine[28,29] compounds from various sources, such as sea and road salts[87,88]. Later, detection of iodine species (molecular iodine (I_2) and hypoiodous acid (HOI)) emitted by macroalgae showed that iodine-induced new particle formation increases particle mass and number concentration in inter-tidal zones[89–92]. In the past two decades, research has shown that SLH play a role in modulating air quality and modifying daytime and nighttime chemistry in polluted coastal environments[73,88,93–97]. These widespread effects extend beyond coastal environments, with salt lakes and dried lakebed (playa) dust contributing to inland halogen chemistry[98–100].

Emissions of halogens from volcanoes[101], and anthropogenic emissions of SLH [102–107] affect air quality and atmospheric chemistry on regional scales over continents and oceans[108–114]. Industrial emissions of SLH, such as dihalogens and chloramines, may also influence regional aerosol loadings[115]. Photochemically active chlorine compounds, such as nitryl chloride ($ClNO_2$), form in the troposphere[88] and on saline snow[116] through the heterogeneous recycling of nitrogen pentoxide (N_2O_5) or through acid-displacement reactions[85]. These photolabile sources of Cl drive VOC oxidation, as their reactions with Cl are often much faster than with OH, and this consequently causes OH and ozone production[117]. Biomass-burning plumes from wildfire or agricultural sources are a source of SLH and halogen activation that affect the atmospheric composition[118,119]. Biomass burning is estimated to contribute up to 10% of global chloride and initiate the release of other forms of active halogens from sea salt and other aerosols, changing regional ozone[120].

Multiple regional studies have demonstrated the role of SLH in increasing both SOA and secondary inorganic aerosol[84,94], although the chemical mechanisms are complex and uncertain. SLH interactions with O_3 production and loss cycles are also complex and non-linear, and may both increase or decrease regional ozone[71,72,95,121,122]. Air quality models including SLH increase regional SOA (>100% in some regions) and sulphate/nitrate (>20%) formation, and result in surface ozone perturbations (up to ±60% regionally)[72,73,94].

SLH dominate global mercury oxidation (~75% in the troposphere[123]) with natural SLH emissions resulting in increased mercury deposition in remote environments, and anthropogenic SLH emissions increasing deposition over areas close to their sources, increasing human exposure to mercury[15]. Halogens are much more efficient at oxidising mercury than OH[124]: bromine in the troposphere[123] and chlorine in the stratosphere[38,125]. There is also an indirect influence because other mercury oxidants, OH and O_3, are affected by halogens. Figure 2 shows the geographical distributions of the impacts of SLH on HO_x, NO_x, SO_x, O_3, aerosol loading, CH_4 and the radiative effect across the globe, highlighting the regional heterogeneity. The role of SLH in the removal of other atmospheric metals has not yet been investigated.

1.5 Effect on Earth's Radiative Budget

The main drivers of climate change are increases in the atmospheric abundance of greenhouse gases such as CO_2 (radiative forcing since 1750-2019 of 2.16 W m^{-2}), CH_4 (0.54 W m^{-2}) and long-lived halocarbons (0.41 W m^{-2})[126]. However, due to their chemical impacts on short-lived climate forcers (i.e., O_3, CH_4, and aerosols[64,84,127]), SLH also indirectly impact climate change. A recent study estimates that overall, SLH exert a net radiative cooling effect at present[84] (−0.13 W m^{-2}), which arises from indirect halogen-mediated radiative cooling on O_3 (−0.24 W m^{-2}) that counteracts the SLH-driven radiative warming through CH_4 (+0.09 W m^{-2}), with minor and highly uncertain contributions from aerosols and stratospheric water vapour (Figure 1). This is of a similar magnitude but opposite in sign to the contrail-induced cirrus forcing. The study also showed that the anthropogenic amplification of natural emissions (see Section 1.6) has led to an increase in the cooling effect due to SLH since 1750 by 61%, and is projected to change further (18-31% by 2100) depending on climate warming projections[84]. The change in radiative forcing caused by SLH over the industrial era (−0.05 W m^{-2}) is similar to that produced by the direct radiative increase due to dust emissions (−0.07 W m^{-2})[128].

In the lower stratosphere, SLH-driven ozone depletion induces an indirect radiative effect (estimated at −0.02 W m^{-2}) equivalent to nearly half of the ozone impact of all anthropogenic long-lived halocarbons[127]. In addition, some stratospheric SLH, which are mainly degradation products of these long-lived halocarbons (e.g. chlorine nitrate ($ClONO_2$) and phosgene ($COCl_2$)), also have a small direct radiative impact (+7 ± 0.8 mW m^{-2})[129]. Due to the spatio-temporal variability of SLH sources and photochemical cycling in different environments, significant regional, latitudinal and seasonal changes in the SLH-driven radiative perturbations exist (Figure 2). However, there are large uncertainties that need to be addressed, as discussed in Section 3.

1.6 Evolution Over Time

Measurements of ice cores and tree rings show that the emissions of natural iodine-containing SLH have increased by a factor of two to three since pre-industrial times[130–132], which is attributed to a positive feedback between anthropogenic pollution and oceanic emissions[133–135] (Figure 3). Indeed, emissions of SLH have been variable on paleo-timescales[136,137]. The highest iodine levels occur during interglacial periods, and volcanic signals of halogens are observed in ice cores. This emission variability correlated with abrupt climate changes during the Dansgaard/Oeschger events, illustrating a response to abrupt climate changes[136]. Ice cores also show an increase in bromine and chlorine from pre-industrial times to the 1970s, followed by a decrease driven by anthropogenic fossil fuel combustion[138,139]. The change in bromine emissions impacts the deposition of mercury in the Arctic on paleo timescales[140].

The Arctic is undergoing rapid climate change that will alter the production and cycling of SLH[141]. Reductions in sea ice extent, thickness and age, combined with ice fracturing, snow depth and seasonal changes, are altering the snowpack photochemistry that is a source of SLH[39,45]. An example of the impact of this complex interaction is the ubiquitous presence of iodine in the Arctic[43]. When the Arctic becomes ice-free in summer, it is expected to become seasonally more like mid-latitude remote oceans, with unquantified implications for the emissions and impacts of SLH. Increasing Arctic development, resource extraction and shipping with associated combustion emissions will alter Arctic halogen oxidation pathways. Thus, the evidence suggests that emissions and impacts of SLH will change in future climate scenarios[84].

2. Moving forward

At present, discrepancies between models and observations arise from uncertainties in emissions and sinks, a lack of widespread and long-term observations to constrain emission inventories and assess model performance, as well as mechanisms and kinetics of processes (especially heterogeneous reactions) included in the models. We need more accurate parameterisations to represent natural emissions and recycling of SLH, in addition to improving the quantification of anthropogenic emissions. These gaps in knowledge hinder our ability to accurately determine environmental and climate feedbacks. Key focus areas that are discussed below are presented in Table 2.

2.1 Observational networks and emissions

Observations of SLH are scarcer than long-lived anthropogenic halogenated gases (such as the network of CFCs, hydrochlorofluorocarbons (HCFCs, and hydrofluorocarbons (HFCs) and halon measurements)[4]. Understanding the broad impacts of SLH on atmospheric chemistry requires multi-instrument observational studies that can capture the wide range of organic and inorganic SLH and their important reservoirs and drivers. An increase in the density (in space and time) of observations is crucial because of the relatively high reactivity and correspondingly short lifetime of SLH, which leads to variability in their spatial and temporal distribution. There has been success in measuring some SLH, including Cl_2, Br_2, BrO, IO, ClO, OClO, OIO and $ClNO_2$[35]. However, the detection and measurement of some important intermediate and reservoir halogen species (e.g., ClNO, $BrNO_2$, $IONO_2$, I_xO_y, HOI) are still virtually absent, which limits a detailed understanding of the processing and impacts of SLH in the atmosphere. Analytical techniques and/or calibration standards for these and other SLH species at atmospheric levels are needed. For example, observations of halogen nitrates could help to understand the presence of unexplained high BrO mixing ratios in polluted environments[142]. We also lack direct observations of Cl atom abundance over the oceans, which are needed to constrain the influence of Cl on the atmospheric lifetime of methane and other hydrocarbons.

While SLH predominantly originate from the ocean, anthropogenic emission sources exist and are often poorly constrained. Monitoring is needed for newer SLH, such as hydrofluoroolefins (HFOs), that are increasingly being used by industry as alternatives to the longer-lived HFCs[143]. Emissions of chlorinated SLH, like dichloromethane (CH_2Cl_2) have grown dramatically through industrial usage[102–104], and emerging compounds like 1,2-dichloroethane (CH_2ClCH_2Cl) have now been observed in the upper troposphere[144]. These compounds potentially offset some of the benefits of ozone layer recovery achieved through the Montreal Protocol[145]. Other chlorine-containing SLH, such as chloramines, have also been observed in the atmosphere[146,147]. The global sources of these chlorinated SLH, their growth rates, and their impacts are not well defined. Lastly, the impacts of iodine propulsion systems in microsatellites, which have the potential to deplete stratospheric ozone[148], need to be evaluated.

Observations of inorganic SLH have been made mainly in Europe, the USA, and East Asia, along with a few cruise-based and aircraft measurements. Organic SLH have been observed in more locations, but are still sparse. The southern hemisphere, in particular, is under-sampled. Vertical profile observations of most SLH are still scarce and limit our interpretation of satellite data and understanding of the impacts throughout the atmosphere. Water, land use, and changing climate are expected to alter chlorine chemistry through the expansion of playas and increasing dust, such that land management policies are expected to alter SLH and need to be investigated. Observations are needed in diverse environments because coastal, open oceans, cryosphere, biosphere, volcanoes, salt lakes, and anthropogenic sources, all contribute to the atmospheric SLH burden. Such observations will lead to more accurate emission inventories and provide stricter validation for global and regional models. The observations will have to be multi-platform (ship, land, aircraft, satellite, etc.) in nature and need provide long-term records across existing measurement networks and new locations.

There is a need for efforts to improve and exploit the global observation of SLH using satellites in both the troposphere (BrO and IO) and the stratosphere (ClO, OClO, BrO, and IO). There are decades-long timeseries available from satellites both in the troposphere (BrO and IO) and stratosphere (ClO), which need to be continued and improved in spatial and temporal sampling. In the near term, nadir-sounding instruments such as Sentinel-4 and Sentinel-5 should be leveraged to achieve higher spatial resolution for BrO, OClO, and IO measurements. Sentinel-4, GEMS and TEMPO can provide diurnal measurements, which will improve our current capability to validate models. Additionally, limb measurements capable of detecting ClO and BrO are urgently needed, using UV and microwave passive remote sensing. These nadir and limb measurements must be improved in spatial resolution and sustained into the future. Similarly, spaceborne FTIR limb measurements are essential for monitoring stratospheric halogen reservoirs.

Finally, it is critical to develop records of past atmospheric levels of SLH to establish accurate pre-industrial baselines and understand the relationship between climate and atmospheric SLH levels. Only a few data from ice cores are available[130,131,136,137]. Further analysis of ice and sediment cores from different environments is needed to establish SLH levels during different past climate periods, to understand how post-depositional processing influences the various proxies, and to validate chemistry/climate models. These efforts will ultimately improve our ability to understand and predict future climate and air quality changes. New observations will also help create a sufficiently large dataset to train new tools, such as machine learning, for making more accurate emission inventories and estimate their trends across timescales.

2.2 Fundamental SLH chemistry

Fundamental laboratory and theoretical studies underpin the SLH research. Major uncertainties remain in our quantitative understanding of multiphase processes, affecting our ability to model active halogen sources in the atmosphere accurately and the rates of active halogen recycling. Even for one of the best-studied reactions, in which N_2O_5 oxidises particulate chloride, levels of the observed $ClNO_2$ product do not adequately match model predictions[149]. While laboratory studies of chemically simplified substrates can provide a molecular-level understanding of the chemistry, they rarely capture the full complexity of the real atmosphere in terms of the wide variety of chemical species present, the subtle interplay that exists between interfacial and bulk processes, and the impacts of substrate phase, viscosity, acidity, and ionic strength[150,151]. Important emerging topics include halogen activation on wildfire particles in the lower stratosphere[119], halogen activation on particles produced from ablating space debris in the upper stratosphere and mesosphere[148], and chemistry on cirrus ice that can impact ozone and the amount of SLH that is transported to the stratosphere[11]. Additional areas of interest are halogen recycling on sea spray and mineral dust aerosol[69,152], the impact of the sea-surface microlayer in modifying halogen emissions[153], snow/ice chemistry relevant to the polar boundary layer[154], and the magma-to-gas transition that leads to volcanic halogen emissions[101,155].

In general, an important gap in our understanding of gas-phase processes is the effect of temperature on reaction kinetics and mechanisms, especially under the significantly colder conditions of the free troposphere and polar boundary layer. Given the importance of halogen chemistry in polluted regions, further studies of the chemical mechanisms, kinetics, and yields of VOC oxidation by Cl and Br atoms are needed, including for SOA formation. Another specific area of importance includes the complex chemistry that leads to new particle formation from iodine[156–159], where further studies of the associated gas-phase chemistry are warranted. In addition, the kinetics and degradation mechanisms of emerging refrigerants such as HFOs should be better addressed: some of them produce highly persistent "forever" chemicals such as trifluoroacetic acid in high yield[160] and potentially generate long-lived oxidation products that could increase the indirect global warming potentials of these HFC replacements.

Fundamental studies are most useful when tied to atmospheric observations and modelling. In particular, new atmospheric observations of SLH, such as $ClNO_2$[88,93], chloramines such as NCl_3,[146,147] chlorine oxyacids,[161] Br[38], BrCN[56], $BrONO_2$,[162] HOI[163] and HIO_3[51] motivate fundamental studies to help understand their atmospheric behaviour. While laboratory studies inspired measurements of some of these species, one species observed in the lab but not yet measured is ClNO, for which sensitive detection techniques are needed. Fundamental studies addressing the release of iodine from the ocean have also indicated the need to study both abiotic and biotic mechanisms, with the abiotic mechanism strongly controlled by iodide availability in the region of the surface microlayer. This illustrates an important chemical coupling between oceanic mixing and biological processes that needs to be better explored in the ocean-atmosphere interface.[133,164] Lastly, lab studies of stable halogenated products can identify tracers that can be measured in the field as markers of SLH[165].

With advances in computational methods, fundamental quantum chemistry and molecular dynamics calculations are emerging as powerful in not only explaining observations but also in making predictions. Pursuing a molecular-level understanding of the gas phase and multiphase processes is helpful in eventually providing predictive capabilities.

2.3 Inclusion of SLH in models

SLH affect almost every aspect of tropospheric and stratospheric chemistry, including ozone budgets, oxidising capacity, radiation budget, aerosol loading and air quality. The representation of SLH in models used for atmospheric chemistry, air quality and climate assessments has been limited and inconsistent[126]. For example, inclusion of SLH can directly lead to improved estimates of the tropospheric ozone burden in climate-chemistry models, e.g., Coupled Model Intercomparison Project (CMIP) projections[166]. A first step forward has been taken in the recent stratospheric ozone assessments[4]. Inadequate representation of SLH chemistry in chemistry-climate models can omit important atmospheric cycles and feedbacks, and misattribute the drivers of trends in ozone and other radiatively important gases. For example, the global atmospheric methane sink is overestimated unless SLH chemistry is considered[167].

The most recent generation of Earth system models (ESMs) aims to incorporate higher spatial resolutions to resolve smaller-scale weather systems, enabling more detailed estimates of climate change. However, a comprehensive representation of the interactions between physical and chemical climate processes must complement these advances[168]. Considering the broad impacts of SLH, and the fact that they act as indirect short-lived climate forcers[84,126], it is important to incorporate SLH chemistry into ESMs to improve their predictive skills of climate change.

While the inclusion of SLH effects in ESMs is the long-term goal, only one chemistry-climate model (CESM/CAM-Chem) has been used to quantify the comprehensive role of SLH in the climate system[84]. A few chemistry transport models also implemented a limited representation[71,74,76,169,170], but most of these models consider only short-lived bromine and/or chlorine, but not iodine. Indeed, most of these developments are based on the original implementation in CAM-Chem[64]. Even CAM-Chem lacks a complete description of the complexity of halogen aerosol chemistry due to the limited process-level understanding. Currently, there is a large difference between the impacts of different SLH schemes in models[127]. This can lead to inaccuracies in estimates of ozone loss or the methane lifetime[171] (Figure 1). Even for the stratosphere, most models do not have a detailed representation of SLH, which hampers accurate assessments of the recovery of the ozone layer. Models need to consider the transport of SLH and their degradation products to the stratosphere. Most models focused on the polar and snow-covered regions still do not include detailed emissions of SLH and are missing recently discovered chemistry and recycling mechanisms. Consequently, many models neglect the important role of reactive halogens in the troposphere. Acknowledging that a full inclusion of SLH sources and chemistry in most models, including ESMs, will be computationally expensive, one option is to parameterise natural and anthropogenic SLH to ensure their impact is not overlooked. This is especially important as model projections imply that the relative importance of SLH chemistry in determining the ozone and methane budgets will increase[24,83,172].

We propose that models, particularly those participating in global model inter-comparisons and included in the IPCC/WMO reports and ozone assessments, consider SLH, at least with a parameterized approach, in both the baseline pristine system as well as the anthropogenically perturbed system, to provide a more realistic representation of the atmosphere in the pre-industrial period, the present day, and in the future. Including SLH chemistry and emission sources in regional/local models is essential for formulating air quality regulations. As with observations, regional modelling of SLH effects currently focuses on the more developed regions (Europe, USA, and East Asia); however, global modelling studies (mostly constrained with observations collected in developed regions) have also shown a potential role of SLH in less developed areas, e.g., South Asia[72], Africa, Central and South America, etc. Indeed, considering SLH affect regional and local air quality, more model studies on finer scales are required.

2.4 Climate Intervention Strategies

Finally, besides understanding the natural and anthropogenically amplified effects of SLH on atmospheric composition, the possibility of using SLH for climate intervention has been raised. Indeed, one study has already pointed to the special role of chlorine emissions, because Cl atoms react rapidly with methane, thereby reducing its atmospheric lifetime[152] (Figure 4). Based on a single model, it was shown that adding 630 Tg, 1250 Tg, and 1880 Tg of molecular chlorine per year (compared to the current loading of 0.7 Mg) decreases the surface temperature by 0.2 °C, 0.4 °C, and 0.6 °C by 2050, respectively. SLH-induced changes in methane dominate this cooling, although secondary or side impacts on ozone and aerosols significantly contribute to the net balance. SLH-related climate intervention method could involve using desert dust to enhance iron-induced chlorine emissions[69]. However, the net emission flux of chlorine must remain much higher than natural levels to reduce the methane burden and avoid obtaining a positive radiative effect from an increase in methane lifetime (Figure 4 inset). Therefore, the range of benefits and risks needs to be much better studied in the laboratory and the field, as well as by an ensemble of multiple models to identify non-linear responses, overall efficiencies, feedbacks and potential adverse side effects.

An example of secondary impacts of SLH is that their consideration in projections of stratospheric aerosol (sulphur) injection results in increased estimates of the erythemal ultraviolet radiation reaching the Earth's surface[27]. Another example is the effect of marine cloud brightening, which is proposed to offset global warming by emitting sea salt aerosols. A study has shown that by emitting more sea salt (212-559 Tg year^{-1}), tropospheric chlorine and bromine would increase (20–40%), leading to decreased ozone (-3 to -6%) and OH (-3 to -5%), with a consequent increase in methane lifetime (3–6%)[173]. A quantitative assessment of the secondary impacts of these SLH-related climate intervention strategies and how they could evolve in the future remains to be addressed. One open question is the role of SLH as the Earth moves to the use of hydrogen to replace fossil fuels, which will certainly affect the tropospheric oxidative capacity through SLH-HO_x coupling. More studies are needed to identify the impacts, including unexpected indirect feedbacks, on different ecosystems through these chemistry-climate interventions.

3. Conclusion

SLH are a key component of the natural chemistry and climate system. They affect several aspects of atmospheric chemistry and composition, including air quality, tropospheric oxidising capacity, stratospheric ozone chemistry, aerosol formation and the Earth's radiation budget. These effects vary over time with changing climate and anthropogenic emissions. Currently, these effects are not fully accounted for in air quality or chemistry-climate model assessments. Addressing these gaps in our knowledge requires improvement in global measurement networks, satellite observation systems and in our understanding of relevant chemical and photochemical SLH reactions, as well as physical and biogeochemical processes. Finally, we need to parameterise natural and anthropogenic SLH in air quality, climate and earth system models to reduce current uncertainties on the evolution of Earth's atmospheric chemistry and radiative budget in the past, present, and future climates.

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Tables:

Table 1: A comprehensive list of SLH species observed in the atmosphere. SLH are defined as organic and inorganic chlorine, bromine, and iodine compounds with an overall lifetime of less than six months. Note that inorganic species are considered as SLH if they are either produced from the decomposition of organic halogenated VSLS or are primary emitted. Most of the HCl and $ClONO_2$ in the lower stratosphere is derived from CH_3Cl and long-lived ozone-depleting substances, and a substantial fraction of the inorganic bromine also comes from longer-lived CH_3Br and halons.

Main Halogen Element	**Type of SLH**	**Compounds**
Chlorine	Organic	Chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), tetrachloroethylene (C_2Cl_4), 1,2-dichloroethane (CH_2ClCH_2Cl), trichloroethylene (C_2HCl_3), bromochloromethane (CH_2BrCl), iodochloromethane (CH_2ICl), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$)
	Inorganic	atomic chlorine (Cl), molecular chlorine (Cl_2), chlorine oxide (ClO), chlorine dioxide (OClO), chlorine peroxide (Cl_2O_2), hydrochloric acid (HCl), hypochlorous acid (HOCl), chloric acid ($HClO_3$), perchloric acid ($HClO_4$), chlorine nitrate ($ClONO_2$), nitryl chloride ($ClNO_2$), bromine chloride (BrCl), iodine chloride (ICl), chloramines (NH_2Cl, $NHCl_2$, NCl_3)
Bromine	Organic	Bromoform ($CHBr_3$), dibromomethane (CH_2Br_2), bromochloromethane (CH_2BrCl), iodobromomethane (CH_2IBr), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$)
	Inorganic	atomic bromine (Br), molecular bromine (Br_2), bromine monoxide (BrO), hydrobromic acid (HBr), hypobromous acid (HOBr), bromine nitrate ($BrONO_2$), nitryl bromide ($BrNO_2$), bromine chloride (BrCl), iodine bromide (IBr), cyanogen bromide (BrCN)
Iodine	Organic	Methyl iodide (CH_3I), diiodomethane (CH_2I_2), iodochloromethane (CH_2ICl), iodobromomethane (CH_2IBr)
	Inorganic	atomic iodine (I), molecular iodine (I_2), iodine oxide (IO), iodine dioxide (OIO), hydroiodic acid (HI), hypoiodous acid (HOI), iodine nitrate ($IONO_2$), nitryl iodide (INO_2), nitrosyl iodide (INO), iodine bromide (IBr), iodine chloride (ICl), higher iodine oxides (I_xO_y, where x, y ≥ 2), iodic acid (HIO_3)

Table 2: Key focus areas for atmospheric SLH chemistry moving forward. These efforts will help improve our capability to determine accurately the multi-pronged environmental and climate feedbacks of SLH.

Observational networks and emissions	**Fundamental SLH chemistry**	**Inclusion of SLH in models and assessments**
1) Standardised measurement of SLH, starting with CH_2Cl_2, $CHCl_3$, $CHBr_3$, $ClNO_2$, CH_3I, CH_2Br_2, Cl_2, Br_2, I_2, BrCl, ICl, IO, BrO, ClO, OClO, HCl, HBr, HI and particulate halides across existing measurement networks and in field intensives to validate and motivate fundamental chemistry studies and models 2) Development and deployment of measurement methods for observing intermediate and reservoir halogen species, e.g., ClNO, $ClONO_2$, $BrONO_2$, $BrNO_2$, $IONO_2$, HOI, I_xO_y, etc. 3) Observations of emerging SLH such as HIO_3, $HClO_3$, $HClO_4$, hydrofluoroolefins, chloramines and satellite propulsion system emissions 4) Improved spatial and temporal resolution of key SLH (e.g., ClO, BrO, IO, etc.) by expanding nadir and limb sounding satellite observations	1) Studies of multiphase processes should increasingly address the chemical complexity inherent to “real world” reaction systems, prioritising heterogeneous chemistry in the stratosphere due to wildfire particles, space debris, and cirrus ice 2) Studies of gas phase chemistry are particularly needed at low temperatures characteristic of the free troposphere and polar boundary layer, with additional work needed to address new particle formation chemistry driven by iodine and the degradation pathways of HFO refrigerants 3) The complex couplings between physical and biological processes that control the marine source of iodine and other biogenic SLH need to be better established 4) Studies of VOC oxidation by Cl and Br, including chemical mechanisms, kinetics, yields, and SOA formation	1) Increased inclusion of SLH chemistry in air quality models (urban and remote environment) 2) Integration of new processes, including new SLH chemistry, heterogeneous chemistry and SLH-driven aerosol formation in models 3) Develop parameterisations for natural and anthropogenic SLH emissions in models with increased spatio-temporal resolution 4) Improved data assimilation with extended observational datasets 5) Multi-model assessment of the impact of SLH 6) Make progress towards a fully coupled ESM, including SLH

Figure Captions:

Figure 1. Direct and indirect influence of SLH on atmospheric composition, radiation and climate: Most of the natural short-lived halogen emissions arise from the oceans, sea-salt recycling and snow/ice-covered polar regions, with significant contributions from continental anthropogenic and natural activities. The green and grey upwards arrows represent direct natural and anthropogenic SLH emissions, respectively, while the U-shaped arrows denote the natural atmospheric cycling of halogenated chemical reservoirs and their connection with other atmospheric components and pollutants (greenish tail). Due to anthropogenic influence, these lead to anthropogenically amplified natural emissions (AANE, orange head). Once in the atmosphere, organic and inorganic SLH species are photochemically decomposed, releasing highly reactive Cl, Br and I atoms that rapidly interconvert between reactive and reservoir species. SLH influence the climate system through direct and indirect perturbations of radiatively-active short-lived climate forcers such as O_3, CH_4 and aerosols, increasing the halogen-driven mercury oxidation and altering the atmospheric hydrogen (OH/HO_2) and nitrogen (NO/NO_2) oxides partitioning (widening of light-blue photochemical arrows indicate direct enhancement by SLH). The relative importance of the dominant halogen family altering each atmospheric process is shown next to the arrow (e.g., Cl > Br > I). In addition, SLH indirectly alter the net photochemical production of OH and other atmospheric oxidants through non-linear chemistry (dark-blue photochemical arrow), where the thinning of the arrows represents a reduction in the efficiency of the indirect OH-driven chemical coupling. Individual panels on the periphery quantify the influence of SLH on different atmospheric components in comparison with other chemical families and/or processes, highlighting the confidence level of current estimations. The contribution of the direct and indirect perturbations induced by SLH on each atmospheric component is represented, respectively, with solid light-blue and dashed dark blue connecting arrows, where the length of the arrowhead indicates the predominance of indirect (left panels) and direct (right panels) processes. The climate influence of SLH on radiatively-active species is shown by dashed orange straight connectors reaching the middle-top radiation budget panel.

Figure 2: Geographical distribution of changes in various atmospheric constituents and the net change in global radiative effect due to SLH. The individual panels show the percentage change in surface HO_x, NO_x, O_3, SO_x, aerosol, and methane concentrations and the radiative effect around the globe due to the inclusion of SLH chemistry in global models. The blue colours indicate a reduction in concentrations while the red colours indicate an increase for HO_x, NO_x, SO_x, aerosols and O_3. HO_x, NO_x and SO_x show a decrease over the oceans, while an increase is observed over the continental regions. Aerosol concentrations are also reduced, especially over the Southern Ocean and Antarctica. The radiative effect changes show an overall net cooling due to SLH, which is driven by the indirect changes in O_3, CH_4, aerosols and water vapour. The changes show the large geographical heterogeneity of SLH impacts over different environments, which are caused by non-linear chemistry and due to direct and indirect chemical effects through which SLH affect each atmospheric constituent. Results based on[84].

Figure 3: The increase in iodine concentrations in the recent past (top panel) observed in ice cores and tree rings from the Alps, Greenland and Tibet coincide with the increase in tropospheric ozone and a reduction in sea ice thickness (bottom panel), showing that the emissions of some SLH are increasing with anthropogenic pollution and climate change. Iodine emissions increase with ozone due to the role of ozone deposition in enhancing oceanic emissions of inorganic iodine compounds. This information from paleo records shows the anthropogenically amplified change in natural emissions of iodine compounds, suggesting that these emissions will change further in the future with increasing tropospheric ozone concentrations and retreating Arctic sea ice. Adapted from [130–132].

Figure 4: The modelled surface temperature change from 2020 to 2050 following the addition of different amounts of chlorine to the atmosphere as a hypothetical climate intervention strategy to reduce global methane levels within the RCP6.0 and RCP8.5 scenarios. The temperature change results from the alterations in radiative forcing arising from the direct and indirect impacts of chlorine on methane, ozone, sulphate aerosol and stratospheric water vapour. The inset figure shows the relationship between additional chlorine emissions, global CH_4 burden (purple line; left axis), and the CH_4 e-folding chemical lifetime (orange line; reversed-right axis). Note that chlorine reduces the methane lifetime, as Cl atoms quickly oxidise methane in the atmosphere. Adapted from[152]. Please note that estimates are currently available only for RCP 6.0 (stabilisation scenario) and RCP 8.5 (worst-case scenario) and have been included accordingly.