Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone

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Halogens released from long-lived anthropogenic substances, such as chlorofluorocarbons, are the principal cause of recent depletion of stratospheric ozone, a greenhouse gas[1-3]. Recent observations show that very short-lived substances, with lifetimes generally under six months, are also an important source of stratospheric halogens[4,5]. Short-lived bromine substances are produced naturally by seaweed and phytoplankton, whereas short-lived chlorine substances are primarily anthropogenic. Here we used a chemical transport model to quantify the depletion of ozone in the lower stratosphere from short-lived halogen substances, and a radiative transfer model to quantify the radiative effects of that ozone depletion. According to our simulations, ozone loss from short-lived substances had a radiative effect nearly half that from long-lived halocarbons in 2011 and, since pre-industrial times, has contributed a total of about $-0.02\,\mathrm{W\,m^{-2}}$ to global radiative forcing. We find natural short-lived bromine substances exert a 3.6 times larger ozone radiative effect than long-lived halocarbons, normalized by halogen content, and show atmospheric levels of dichloromethane, a short-lived chlorine substance not controlled by the Montreal Protocol, are rapidly increasing. We conclude that potential further significant increases in the atmospheric abundance of short-lived halogen substances, through changing natural processes[6-8] or continued anthropogenic emissions[9], could be important for future climate.

Stratospheric ozone (O_3) concentrations are maintained by a balance between photochemical production and loss. Increases in the loss rate, for example, through emission of ozone-depleting substances[3] (ODSs), leads to net O_3 depletion, such as the formation of the Antarctic O_3 hole. In addition to long-lived ODSs, such as chlorofluorocarbons (CFCs) and halons, recent observations show that very short-lived substances (VSLSs), with lifetimes $<\sim$6 months, are an important source of stratospheric bromine and chlorine[4,5,10]. Their absolute contribution is uncertain owing to poor constraints on the magnitude and distribution of VSLS emissions[11], a limited understanding of their tropospheric processing[12], and a paucity of VSLS observations (and their product gases) near the tropopause. At present, VSLSs probably account for $\sim$25% of stratospheric bromine and a few per cent of stratospheric chlorine[3]. These relative contributions will increase in the future, as long-lived anthropogenic ODSs are phased out under the terms of the Montreal Protocol—the international treaty designed to safeguard the ozone layer. Bromine VSLSs are mainly of oceanic origin, produced by various species of seaweed[3]—a number of which are farmed[9]—and by phytoplankton. Once transported to the stratosphere they affect the natural balance of O_3, particularly in the lower stratosphere[13-15] (altitudes $\sim$12 to 25 km), where O_3 perturbations strongly impact surface temperature and climate[1,2]. The radiative impacts of VSLS-driven O_3 perturbations are unknown but important to understand as models predict that stratospheric VSLS loading may increase in the future[6,7].

Two models were used to quantify the impact of VSLSs on O_3 and climate (Methods). First, a state-of-the-art three-dimensional atmospheric model[16], TOMCAT, was used to simulate the transport and breakdown of bromine-, chlorine- and iodine-containing VSLSs (and their product gases) in the troposphere and stratosphere. The model contains a comprehensive treatment of atmospheric chemistry and has been widely used to study global O_3 (ref. 14). Experiments were performed, including a control run with no VSLSs, to determine the relative contribution of each halogen and the net impact of VSLSs on O_3 (Supplementary Table 1). Second, an offline radiative transfer model[17,18] was used to diagnose the net change (long-wave + short-wave) in radiation at the tropopause due to VSLS-driven O_3 perturbations in 2011 (that is, the difference between simulations with/without VSLSs). This 'radiative effect' (RE) is used to estimate the significance of VSLS-driven O_3 loss on climate and is compared with the ozone RE due to long-lived ODSs, calculated similarly for 2011. The related measure of 'radiative forcing' (RF) here describes the change in RE between 2011 and pre-industrial times.

Figure 1 shows the simulated stratospheric column O_3 change due to all VSLSs from natural and anthropogenic processes (relative to the control). Ozone concentrations are reduced globally, with a maximum column decrease of -6% (-3 to -8%) occurring over Antarctica (Fig. 1a)—corresponding to $\sim$15 (8 to 21) Dobson units. The range (Fig. 1b) quoted is due to uncertainty in the stratospheric loading of VSLSs. Cycles including bromine account for approximately half of the total chemical O_3 loss in the springtime Antarctic ozone hole[3] and here contribute 81% of the total VSLS-driven O_3 loss in this region. Chlorine VSLSs account for a further 16% (that is, a column O_3 decrease from chlorine of $\sim$1%) and iodine 3% of the total. Globally, we calculate a RE of -0.08 (-0.04 to -0.11) $\mathrm{W\,m^{-2}}$ due to the presence of natural and anthropogenic VSLSs and their influence on stratospheric O_3 in 2011 (Fig. 1c,d).

Owing to their short atmospheric lifetimes, if VSLSs (or their degradation products) reach the lower stratosphere they readily release halogens in a region where surface temperature and climate are most sensitive to O_3 perturbations. We calculate that VSLSs reduce O_3 by up to $\sim$100 (50–140) parts per billion (ppb) in the lower stratosphere (Fig. 2a) at present, corresponding to percentage decreases in the range 4–12%. Bromine, predominantly from naturally emitted oceanic VSLSs such as bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), is responsible for most ($\sim$85%) of the lower-stratospheric O_3 decrease. The analogous chlorinated gases, chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2), have anthropogenic sources[19,20] with applications as industrial solvents, foam blowing agents, and fumigants, and use in the paper and pulp

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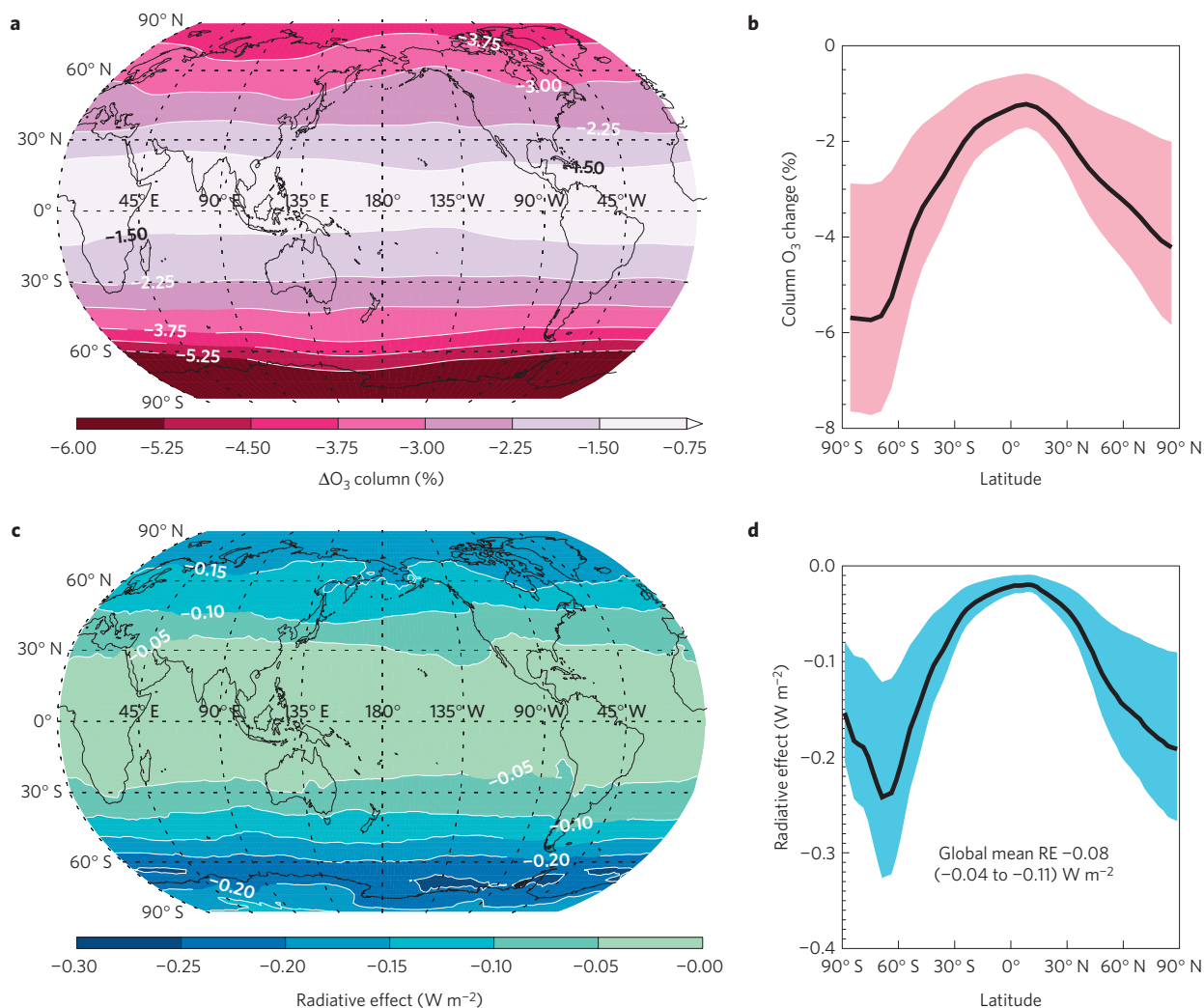
Figure 1 | Column ozone decrease due to VSLSs and RE. a, Annual mean (2011) percentage change in stratospheric column ozone due to best estimated stratospheric loading of bromine, chlorine and iodine from VSLSs. **b**, Latitude dependence of column ozone change. Solid line denotes best estimate; shaded region represents the range due to uncertainty in VSLS loading. **c**, Net (long-wave + short-wave) RE (W m^{-2}) due to VSLS-driven ozone loss calculated at the tropopause. **d**, Latitude dependence of RE. Solid line denotes best estimate; shaded region represents the range due to uncertainty in VSLS loading.

industry. Anthropogenic sources account for ∼25% and 80–100% of total $CHCl_3$ and CH_2Cl_2 emissions, respectively[3]. As these gases are not controlled by the Montreal Protocol and given potential for industrial growth, quantifying their impact on O_3 is important. We find that all chlorine VSLSs reduce O_3 in the lower stratosphere by ∼11 (6–18) ppb (0.6–1.6%). A larger absolute impact is found in the upper stratosphere (∼40 km) with decreases in the range 17–54 ppb, although at this altitude the O_3 change relative to the control is <1%. An upper limit of O_3 reduction due to methyl iodide (CH_3I), the only iodine-containing VSLS with a sufficiently long lifetime to allow significant transport into the stratosphere, is ∼3 ppb (<0.5%), suggesting a minor stratospheric role for iodine[3,21].

Bromine (chlorine, iodine) accounts for ∼87% (9%, 4%) of the global RE due to VSLS-driven stratospheric O_3 loss (Supplementary Table 2). The relatively large RE of −0.07 (−0.035 to −0.096) W m^{-2} due to O_3 loss from bromine VSLSs can be compared to the RE from stratospheric O_3 changes driven by long-lived anthropogenic ODSs (Fig. 2b). For 2011, we calculate the latter RE to be −0.17 W m^{-2} (Methods), which also corresponds to a radiative forcing as anthropogenic ODSs were not present in the pre-industrial atmosphere. Normalized by equivalent stratospheric chlorine (ESC), the RE due to bromine VSLSs is ∼3.6 times larger

than that caused by long-lived anthropogenic ODSs, owing to their influence on O_3 in the climate-sensitive lower stratosphere. Compared with long-lived gases synonymous with ozone depletion, such as CFCs, VSLSs possess significantly larger leverage to influence climate through ozone. Whereas CFCs, for example, are themselves potent greenhouse gases that have caused a large positive RF, this is not the case for VSLSs owing to their low abundances and short lifetimes; VSLSs cause a cooling effect through O_3 loss without a corresponding warming effect due to their presence in the atmosphere. Accounting for VSLSs will improve simulations of stratospheric O_3, reducing uncertainty on related estimates of ozone-driven climate forcing.

In addition to the stratosphere, recent work has highlighted the significance of tropospheric halogen chemistry and its impact on O_3 (refs 22–24). The true VSLS RE is therefore probably greater if tropospheric O_3 impacts are also considered. We calculated a global mean RE due to tropospheric O_3 loss from VSLSs (Methods and Supplementary Table 3) of −0.12 W m^{-2}, 50% larger than the stratospheric RE, in good agreement with previous estimates[23]. Bromine and iodine combined contribute virtually all of this tropospheric RE, most of which is from O_3 loss in the upper troposphere (Supplementary Fig. 1). Chlorine from VSLSs has a
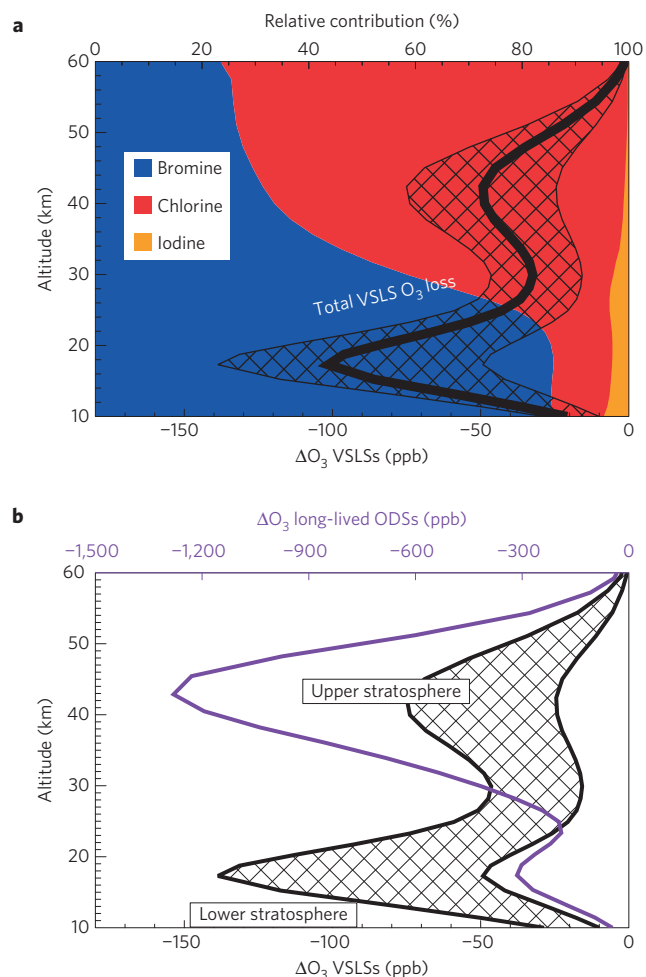
Figure 2 | Altitude-resolved ozone decrease due to VSLSs and long-lived ODSs. a, Annual global mean (2011) change in stratospheric ozone (O_3) volume mixing ratio (ppb) due to VSLSs (bottom x axis). The grated area shows the range due to uncertainty in VSLS loading. The shaded regions represent the contribution of each halogen to the total O_3 loss due to VSLSs, expressed as a percentage (%; top x axis). **b**, The same as in **a** but with the 2011 O_3 change due to long-lived anthropogenic ODSs also shown to highlight the difference in altitude of the O_3 changes.
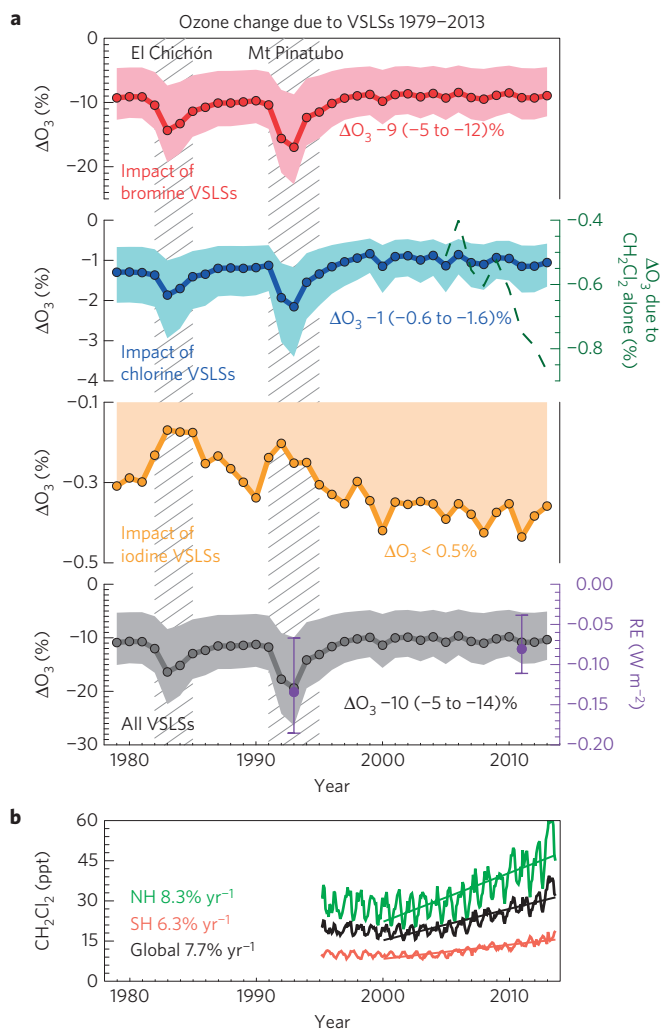

Figure 3 | Trend in VSLS-driven ozone loss and CH_2Cl_2 growth. a, Annual global mean ozone change (%) due to VSLSs in the lower stratosphere (1979–2013). Solid lines denote best estimate; shading indicates range due to uncertainty in VSLS loading. 2003–2013 mean O_3 change is annotated. RE (W m^{-2}) of VSLS-driven ozone loss and range due to uncertainty in VSLS loading is shown with error bars (purple). Dashed line (green) denotes ozone change due to CH_2Cl_2 alone. Hashing represents periods affected by volcanic eruptions. **b**, Observed monthly mean surface CH_2Cl_2 mixing ratio (ppt) and trend. Annotated are 2000–2012 hemispheric growth rates (% yr^{-1}). NH: Northern Hemisphere.

negligible impact owing to the relatively long lifetime of the main VSLSs themselves and because their degradation product gases (both organic intermediates and HCl) are subject to relatively efficient tropospheric wet removal in rainwater. Considering both the troposphere and stratosphere, we estimate a whole atmosphere RE of −0.20 (−0.16 to −0.23) W m^{-2} due to VSLS-driven O_3 loss.

We found no trend in the influence of VSLSs on global O_3 between 1979 and 2013. However, in addition to bromine—whose impact on O_3 is enhanced following volcanic eruptions[13–15]— we find stratospheric O_3 loss due to chlorine VSLSs was also enhanced (up to ~2×) following the eruptions of El Chichón (1982) and Mount Pinatubo (1991), relative to volcanically quiescent years (Fig. 3a). The model slightly overestimates the relative O_3 decrease following the Pinatubo eruption (Supplementary Fig. 2) but generally reproduces observed O_3 variations well. The sensitivity of VSLS-driven O_3 perturbations (and RE) to the aerosol loading are, therefore, relevant for understanding the full impacts of geoengineering approaches to combat climate change by stratospheric injection of particles[25].

At present, there is no evidence of a historical trend in the stratospheric loading of natural bromine VSLSs, beyond

shorter-term fluctuations due to the El Niño/Southern Oscillation[12]. However, the pre-industrial influence of bromine VSLSs on global O_3, before anthropogenic input of chlorine into the stratosphere, was ~30% smaller than present day (Supplementary Fig. 3); anthropogenic activity has enhanced natural stratospheric O_3 loss cycles. We calculate that this O_3 trend caused a contribution to the climate RF of −0.014 (−0.007 to −0.018) W m^{-2} (out of the −0.17 W m^{-2} RF from long-lived anthropogenic ODSs quoted above), which will probably be reversed as stratospheric chlorine declines during the twenty-first century, in response to the Montreal Protocol. A future increase in VSLS emissions, potentially due to a climate-driven increase in their ocean-to-air flux[8] or a rise in seaweed cultivation[9]—a rapidly growing industry—would offset some of this reversal.

Surface concentrations of CH_2Cl_2, an anthropogenic VSLS, have increased rapidly in recent years (Fig. 3b). Between 2000 and 2012, surface CH_2Cl_2 increased at a global mean growth rate

of 7.7% yr^{-1}. Mean growth rates in the Northern and Southern hemispheres were ∼8.3% yr^{-1} and 6.3% yr^{-1}, respectively, the larger Northern Hemisphere growth reflecting the presence of industrial sources. Between 2012 and 2013, CH_2Cl_2 growth accelerated with a Northern Hemisphere growth rate of 20% yr^{-1}; double the 2010–2013 average (Supplementary Table 4). Although modest at present, the impact of anthropogenic CH_2Cl_2 on O_3 (Fig. 3) would increase significantly if the observed trend continues. This is likely if increases in atmospheric CH_2Cl_2 are associated with the increased industrialization of developing countries and, for example, use of CH_2Cl_2 as a feedstock for hydrofluorocarbon (HFC) production, such as HFC-32 (ref. 26)—a refrigerant used in blends as a substitute for HCFC-22. Production of HFC-32 and other HFCs has increased rapidly in recent years and could increase substantially in the future[27]. Although HFCs do not directly deplete O_3, a broader consideration of their production pathways suggests a potential for direct influences on O_3-layer chemistry and hence climate. We suggest, despite the modest concentration changes so far, that anthropogenic chlorine VSLSs have already contributed −0.005 (−0.003 to −0.008) W m^{-2} to atmospheric RF (Methods). Combined with the larger RF due to bromine VSLSs (discussed above), the total RF from VSLSs is −0.02 (−0.01 to −0.03) W m^{-2} and comparable in magnitude to, for example, the (positive) RF due to aircraft contrails[1].

We have shown that, through interactions with O_3, VSLSs have a disproportionately large climate impact compared with long-lived ODSs, owing to their breakdown at climate-sensitive altitudes. VSLSs have already contributed to climate forcing since the pre-industrial era, although this is so far unlikely to have caused a noticeable change to surface temperature, for example. However, crucially, given the large leverage VSLSs possess to influence climate, future increases in their emissions would drive a negative climate forcing and thereby offset a small fraction of the projected warming influence due to greenhouse gases. We note additionally that the observed atmospheric abundance of anthropogenic CH_2Cl_2, here about ×50 larger than some recently detected CFCs and HCFCs (ref. 28), is, at present, adding many times more chlorine to the atmosphere and, unlike those chemicals, is not controlled by the Montreal Protocol.

Methods

Simulated impact of VSLSs on stratospheric ozone. The three-dimensional chemistry transport model, TOMCAT (ref. 16), was used to simulate the breakdown of VSLSs in the stratosphere. TOMCAT contains a detailed gas-phase/heterogeneous chemistry scheme considering all main stratospheric families: O_x, HO_x, NO_y, Cl_y and Br_y, and here we implemented an iodine scheme[21]. The major VSLSs considered were $CHBr_3$, CH_2Br_2, $CHCl_3$, CH_2Cl_2 and CH_3I. Their degradation occurs by both photolysis and hydroxyl radical oxidation, with photochemical and kinetic data taken from the NASA (National Aeronautics and Space Administration) Jet Propulsion Laboratory evaluation. The surface VSLS mixing ratios were time-independent quantities, scaled to give a range of stratospheric loadings of bromine, chlorine and iodine from VSLSs based on current best estimates and lower/upper limits[3] (Supplementary Table 1).

In all simulations the abundance of long-lived source gases (for example, CFCs, halons, N_2O and CH_4) were constrained with time-dependent surface mixing ratio boundary conditions based on observations. Similarly, a time-dependent sulphate aerosol load was imposed based on Stratospheric Aerosol and Gas Experiment (SAGE) data. Ten model integrations covering the 1979–2013 period were performed. A control experiment, in which VSLSs were not considered, was followed by a series of experiments to determine the impact and relative contribution of bromine, chlorine and iodine VSLSs on O_3. A sensitivity experiment was performed with a time-dependent stratospheric loading of CH_2Cl_2, based on its observed surface trend and modelled tropospheric oxidation, between 2005 and 2013.

We also performed experiments with a pre-industrial stratospheric halogen loading containing ∼6 ppt of CH_3Br and ∼500 ppt of CH_3Cl, on the basis of ice-core records[29]. From these experiments, we calculated: the difference in the influence of bromine VSLSs on O_3 between the pre-industrial period and 2011 (this was also used to diagnose a RF from bromine VSLSs); and the O_3 change attributable to anthropogenic long-lived ODSs alone (Fig. 2b). Simulations to

quantify the impact of VSLSs on tropospheric O_3 were also performed. Details of these experiments are given in the Supplementary Information.

Climate impact of VSLSs. The RE of VSLS-driven O_3 loss was calculated using an offline radiative transfer model[17]. This model considers six bands in the short-wave, nine bands in the long-wave and uses a delta-Eddington 2-stream scattering solver at all wavelengths. We used monthly mean climatologies of temperature, water vapour and trace gases based on ECMWF (European Centre for Medium-Range Weather Forecasts) reanalysis data, together with surface albedo and cloud fields taken from the International Satellite Cloud Climatology Project archive[18].

We normalized the RE due to bromine VSLSs in the stratosphere (Supplementary Table 2) per unit of equivalent stratospheric chlorine (ESC = Cl + 60×Br). This was performed to compare the RE of VSLS-driven O_3 changes with that of long-lived ODSs, independent of the halogen loading that caused them, and in a way that considers the effectiveness of bromine relative to chlorine for O_3 loss. The stratospheric loading of bromine VSLSs in our model (3, 6 or 8 ppt) corresponds to ESC loadings of 180, 360 and 480 ppt, respectively. The normalized RE from bromine VSLSs is −1.9 × 10^{-4} W m^{-2} (ppt ESC)$^{-1}$. Similarly, we normalized the RE due to stratospheric O_3 loss arising from anthropogenic long-lived ODSs. This O_3 change is shown in Fig. 2b and was caused by an ESC difference of 3,207 ppt from long-lived ODSs (that is, the 2011 minus pre-industrial ESC load). The calculated RE is −0.17 W m^{-2} and the normalized RE is −5.3 × 10^{-5} W m^{-2} (ppt ESC)$^{-1}$; a factor of ∼3.6 smaller than the normalized RE from bromine VSLSs.

The RF contribution due to bromine VSLSs arises because their presence affects the efficiency of O_3 loss from the pre-industrial period to 2011 caused by changes in anthropogenic chlorine from long-lived ODSs. The relative O_3 change due to bromine VSLSs in each period (compared with simulations without bromine VSLSs) was quantified (Supplementary Fig. 3). The calculated difference in the corresponding RE between the two periods corresponds to a pre-industrial to 2011 RF.

The RF due to anthropogenic chlorine VSLSs is due to a time trend in their abundance since the pre-industrial period. This was estimated from the calculated RE limits given in Supplementary Table 2, reduced by 30% to account for the natural component of chlorine VSLSs in the stratosphere[3]; the calculated RF is due to the pre-industrial to 2011 trend in anthropogenic chlorine VSLS concentrations alone.

Long-term observations of CH_2Cl_2. Observations from multiple sites in the ongoing NOAA/ESRL Global Monitoring Program[30] are presented (Supplementary Table 4). Results from paired flask samples collected at remote sites were used to derive surface CH_2Cl_2 mixing ratios over the 1995–2012 period averaged over each hemisphere with a weighting based on sampling latitude[30]. These data are publicly available: http://www.esrl.noaa.gov/gmd/dv/ftpdata.html.

Code availability. The TOMCAT model is supported by NERC and NCAS and is available to UK academic institutions working with these organizations. The output from model simulations used here and post processing code are available on request.

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Author contributions

R.H., M.P.C., W.F. and S.D. designed and performed all experiments using the TOMCAT model. A.R. performed experiments with the radiative transfer model. S.A.M. provided ground-based observations. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to R.H.

Competing financial interests

The authors declare no competing financial interests.

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