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Renewed and emerging concerns over production and emission of ozone-depleting substances

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- Ozone recovery is expected mid-century owing to adherence to the Montreal Protocol. Yet a number of recent trends could challenge its timely recovery and are highlighted here.
- The apparent illicit production of CFC-11 is one such challenge to ozone recovery, but the added damage to the ozone layer depends on how rapidly the CFC-11 emissions are mitigated.
- A number of industrial processes that are allowed by the Montreal Protocol contribute considerable amounts of chlorinated gas emissions to the atmosphere.
- Increases in ozone-depleting chlorine from a number of human-produced short-lived gases has led to some increased ozone-depletion, although their future impacts on ozone depend on future uses.
- Natural processes also affect the balance of ozone in the stratosphere in a number of ways, and could change in the future as climate responds to increases in atmospheric greenhouse gas concentrations.

Abstract. Stratospheric ozone depletion, first observed in the 1980s, has been caused by the increased production and use of substances such as chlorofluorocarbons (CFCs), halons and other chlorine-containing and bromine-containing compounds, collectively termed ozone-depleting substances (ODSs). Following controls on the production of major long-lived ODSs by the Montreal Protocol, the ozone layer is now showing initial signs of recovery, and is anticipated to return to pre-depletion levels in the mid-to-late 21st century, likely 2050-2060. These return dates assume widespread compliance with the Montreal Protocol and thereby continued reductions in ODS emissions. However, recent observations reveal increasing emissions of some controlled (for example CFC-11, as in eastern China) and uncontrolled substances (for example very short-lived substances, VSLS). Indeed, the emissions of a number of uncontrolled VSLSs are adding significant amounts of ozone-depleting chlorine to the atmosphere. In this Review, we discuss recent emissions of both long-lived ODSs and halogenated VSLSs, and how these might lead to a delay in ozone recovery. Continued improvements in observational tools and modelling approaches are needed to assess these emerging challenges to a timely recovery of the ozone layer.

[H1] Introduction

The stratospheric ozone layer absorbs harmful ultraviolet (UV) radiation, preventing most from reaching the surface where it can cause skin cancer in humans and damage to plants[1]. Ozone (O_3) also absorbs outgoing terrestrial infrared radiation in both the stratosphere **[G]** and troposphere **[G]**, which together with stratospheric heating from UV absorption, exerts a key influence in determining the temperature structure of the atmosphere[2]. Hence, changes in the ozone layer can also affect surface climate, an impact that has been identified in the summertime southern hemisphere[3] with, for example, a poleward shift of the midlatitude jet[4]. Depletion of the stratospheric ozone layer[5,6] is therefore a major environmental concern, especially since the discovery of the Antarctic ozone hole in 1985[7]. For example, mean column ozone has been depleted by about 50% in the Antarctic spring and by a maximum of around 4% decade^{-1} in northern midlatitudes[8].

Ozone depletion is caused by an increased abundance of stratospheric chlorine and bromine[8], derived from long-lived anthropogenically produced ozone-depleting substances (ODSs)[9,10], that destroy ozone molecules by converting them to oxygen (O_2; **Fig. 1a**). ODSs were used in air conditioning, as refrigerants, solvents and fire-extinguishing agents. To mitigate the damage already caused by ODSs and to prevent further ozone destruction, the Montreal Protocol on Substances that Deplete the Ozone Layer was signed in 1987 and ratified two years later. With several subsequent adjustments and amendments, accepted by almost all countries worldwide, the production and consumption of all of the primary long-lived ODSs – such as chlorofluorocarbons (CFCs) and bromine-containing halons – has been controlled **[G]** and largely stopped through strict phase-out schedules. The latest of these was the phase-out of CFCs in 2010. In response, stratospheric levels of chlorine and bromine have slowly declined since their peaks in the 1990s[11,12] (**Fig. 1b**), primarily due to decreasing concentrations of the controlled substances methyl chloroform (CH_3CCl_3), CFCs, methyl bromide (CH_3Br), and the halons (see Supplementary Information Table S1 for summary of chemical species, formulae, alternative names and abbreviations).

As a result of the Montreal Protocol, increasing concentrations of stratospheric ozone have been detected in the upper stratosphere[13] and the Antarctic[14–16] (**Fig. 1c**), suggesting that initial stages of recovery are now underway. Multiple processes contribute to the initial recovery observed to date, and separating the influence of the ODS declines to climate-change-related trends is difficult, especially for the Antarctic lower stratosphere[17]. Ozone levels are predicted to return to 1980 concentrations (that is, those prior to any large-scale depletion) around the middle of the 21st century, provided continued compliance with the controls in the Protocol and minimal increases in ozone-depleting halogen levels from uncontrolled sources[18–20]. As such, the Montreal Protocol has been hailed as the most successful international environmental treaty to date.

However, there are many threats to the ongoing success of the treaty and timely recovery of the ozone layer, in particular the increasing emissions of controlled substances that were reportedly phased out and of other chlorinated substances that have never been controlled by the Protocol. Although production of the primary ODSs (CFCs, CCl_4, CH_3CCl_3, halons, CH_3Br) has largely ceased, recent observations reveal increased emissions of CFC-11, believed to be the result of new production and non-compliance with Montreal Protocol controls[21,22]. Moreover, ODS emissions can persist for various legitimate reasons, including, the escape or use of stocks or banks **[G]** of ODSs (typically CFCs, HCFCs and halons) produced before the mandated phase-out of production, and inadvertent by-product formation and emission associated with allowed production of controlled substances (including CFCs, HCFCs, and hydrofluorocarbons, or HFCs[23,24]), for example when used solely for non-emissive **[G]** purposes (such as further chemical manufacture).

Additional chlorine is further reaching the stratosphere from increased production of some uncontrolled **[G]** very short-lived substances (VSLSs), which are largely removed naturally from the atmosphere in <0.5 yrs and have historically been responsible for only a small amount of ozone-depleting bromine and chlorine[25]. Recent observed increases in their concentrations add a new concern to the timely recovery of stratospheric ozone[26,27]. Unlike long-lived ODSs, the short tropospheric lifetimes **[G]** of VSLSs mean that transport processes determine how efficiently emissions reach the stratosphere. Both VSLS transport and chemical loss rates vary in space and time, thus their ozone depletion potentials **[G]** (ODPs) depend on the region and season of emission[28–30].

In this Review, we describe the emission trends of the abundant anthropogenic ODSs, including the recent increases in emissions of CFC-11, likely associated with illicit production, and those of uncontrolled VSLSs. We relate these trends to compliance with the Protocol and discuss possible future variations in ODSs and VSLSs. We then discuss the possible impact on the timescale for ozone recovery.

[H1] Recent observations

Independent global-scale air sampling networks maintained by the National Oceanic and Atmospheric Administration (NOAA) and the Advanced Global Atmospheric Gases Experiment (AGAGE) provide measures of the surface abundances of a range of halogenated gases that affect stratospheric ozone. We begin by summarising recent trends in the global concentrations of important controlled and uncontrolled substances as determined by these networks (**Fig. 2**).

[H2] Long-lived controlled ODSs

The chemicals most responsible for ozone layer destruction are a subset of chlorine- and bromine-containing human-produced gases that persist in the atmosphere for decades to centuries after being emitted. These 'long-lived' gases are eventually transported to the stratosphere where they then release their ozone-depleting chlorine and bromine (**Fig 1a**).

[H3] CFC-113 and methyl chloroform

How an ODS is or was used industrially influences the persistence of its emission after production is phased-out. For example, as CFC-113 and methyl chloroform (**Fig. 2a,b**) were used as solvents or cleaning agents, emissions occurred mostly during use and there was no build-up of a large bank of produced-but-not-yet-emitted ODSs[31]. Hence, emissions of ODSs used primarily in these applications declined rapidly after production ceased. Global concentrations of methyl chloroform, for instance, decreased by ~18% yr^{-1} after 1998, from 130 parts per trillion (ppt) in the 1990s to <2 ppt in 2018, indicating near-zero emissions since the year 2000 given its atmospheric lifetime of 5 yrs (REF[32]) (see Supplementary Information for discussion of link between emissions, lifetime and atmospheric abundance). Similar rapid declines in emissions of CFC-113 have also been observed, although its atmospheric abundance has declined much more slowly compared to methyl chloroform given its longer lifetime of ~93 yrs (REF[25]). Because emissions of chemicals used by humans are largest in the northern hemisphere, concurrent declines in the hemispheric concentration difference further support the implied emission reductions[33].

[H3] CFC-12

By contrast, ODSs that were used as working fluids in refrigeration and air conditioning systems, such as CFC-12 (**Fig 2c**), accumulated substantial banks before production was phased out. As a result, emissions of these ODSs have declined more slowly due to persistent ongoing emissions from these reservoirs[25]. In addition, CFCs have long lifetimes that also limit the speed of their decrease in the absence of emission. For example, despite its production being phased out in 2010, global concentrations of CFC-12 have decreased by only 0.6% yr^{-1} in the recent ~5 years, lower than the 1% yr^{-1} decline expected based on its 102-yr lifetime[32] if emissions had ceased. These lower rates of change thereby indicate ongoing CFC-12 emissions, presumably from banks in older refrigerators and air conditioners (see Supplementary Information). Northern-southern hemispheric concentration differences also show slow decreases over time, from 6-8 ppt in the late 1990s, to ~1 ppt in 2018 (REF[25]), consistent with slowly declining emissions.

[H3] CFC-11

ODSs such as CFC-11 (**Fig. 2d**) have been used as blowing agents in foam production, resulting in emissions on slow and fast timescales depending on the type of foam produced; ODSs used to produce insulating closed-cell foams become trapped, slowly leaking to the atmosphere, whereas those in open-cell cushioning foams rapidly escape[31]. Therefore, when CFC-11 production began decreasing in 1990, its atmospheric concentrations started to decline shortly thereafter following escape from open-cell foams. However, emissions from the slow-release foams persisted and the concentration decline did not accelerate in subsequent years beyond -0.8% yr^{-1}, slower than the limiting decline rate of -2% yr^{-1} expected in the absence of emission given its ~50-yr lifetime. The measured concentration declines suggest that CFC-11 emissions remained constant for the 2002-2012 decade, which was unexpected given that new production of CFC-11 was negligible by 2007 and had reportedly ended by 2010 (REF[21]). In the absence of new production, emissions from banks should have decreased slowly over time as the closed-cell foam reservoir became depleted.

Furthermore, global CFC-11 concentration declines between 2016 and 2018 were only half as fast as those observed between 2002 and 2012 (**Fig. 2d**), suggesting that emissions had actually increased in recent years. Whereas projections had anticipated CFC-11 reductions of 14.8 ppt between 2013 and 2018 (REF[34]), the observed decline was only ~6.7 ppt (REF[21])

(**Fig. 2d**). Even in a scenario in which the global concentration decline had not accelerated as projected after 2013, but had remained constant at a rate of 0.8% yr^{-1}, the 2018 global surface concentration of CFC-11 was elevated by ~4 ppt (corresponding to 12 pptCl) relative to 2013[21]. These values are substantial when compared with the annual decline in chlorine from all controlled substances in recent years, which averaged 12.7 pptCl yr^{-1} from 2012 to 2016 (REF[25]). In addition, the hemispheric concentration difference increased from 2 ppt to approximately 3 ppt after 2012. Taken together, these observations point to an increase in CFC-11 emissions in the northern hemisphere, likely from new production rather than foam banks, after the 2010 phase-out, in violation of Montreal Protocol controls[21,22]. Results from globally-distributed remote locations suggested that the emission increase stemmed, in part, from eastern Asia[21]. Subsequent measurements from that region further confirmed that approximately half of the global emission increase originated from two industrialised provinces in eastern China, Shandong and Hebei[22].

Uncertainties in the total amount of newly-produced CFC-11, as well as its application (for example, closed-cell foam versus solvents, the former generating an ODS bank), contribute to an absence of clarity regarding the impact on the ozone layer and its recovery. If the new CFC-11 is used for closed-cell foams, for example, production magnitudes could be up to six times larger (~78 Gg yr^{-1}) than the observed emission increase (13 Gg yr^{-1}, REF[35]). The resulting impact on ozone depletion would therefore be much larger than if the new CFC-11 were being used as a solvent or in other applications, thereby implying smaller production and future emission magnitudes and no augmentation of ODS banks.

In addition to this CFC-11 impacting the ozone layer directly, there could have also been CFC-12 produced given that both CFCs are typically produced during the fluorination **[G]** of carbon tetrachloride[31] (see Supplementary Information for discussion of industrial chlorine processes). This CFC-12, which might be as much as 40% of the CFC-11 produced, could be intentionally vented or later escape to the atmosphere and exacerbate ozone depletion. However, emissions of CFC-12 do not show signs of substantial increases in recent years either globally (**Fig. 2c**) or downwind of China[22]. A number of possibilities can explain this apparent absence of increased CFC-12 emissions in the presence of new CFC-11 production: minimal formation of CFC-12 by-product; use of CFC-12 by-product as feedstock for other chemicals without residual emissions; or storage of CFC-12 by-product in closed (slow-release) applications (refrigeration or air conditioning)[21,22].

Other observations also show unexpected increases in abundances or emissions of a number of minor controlled CFCs (CFC-13, CFC-113a, CFC-114 and CFC-115) since 2010 (REF[24,36]).

These can be partly traced to South-East Asia, and while these increases may not represent violations of the Protocol and their concentrations may be low – suggesting minimal risk to ozone depletion – these increases are contrary to the aims of the Montreal Protocol.

[H2] Methyl bromide

Like CFCs, anthropogenic production of methyl bromide (CH_3Br; **Fig. 2e**), a potent ODS, has also declined due to the phase-out of controlled uses in the mid-1990s (REF[37,38]). From a peak of 9.1 ppt in the late 1990s, global mean concentrations decreased 27% to 6.6 ppt in 2018 (REF[25]). Furthermore, the hemispheric concentration difference decreased from 2.3 ppt in 1996 to 1998 to 0.6 ppt in 2018. However, the 2018 global and southern hemispheric concentrations (6.3 ppt) remain appreciably higher than the natural background southern hemispheric level of 5.5 ± 0.2 ppt derived from Antarctic firn-air and ice bubble air[25,39,40], attributable, in part, to the incomplete phase out of all production for emissive uses by the Montreal Protocol. Specifically, methyl bromide has essential uses that prevent the spread of noxious pests and biota across international boundaries, referred to as quarantine and pre-shipment (QPS) applications. Today, QPS uses a total of ~10 Gg methyl bromide per year, which has remained relatively constant since the year 2000. However, because QPS is not controlled by the Protocol, any future increase in production for this use would not be a violation of the Montreal Protocol. Other human-related sources, such as rapeseed oil production or farming plants in the Brassica family[41] are also thought to contribute to the present-day atmospheric concentration, but increases in these sources are thought to be fairly small[25].

Atmospheric methyl bromide concentrations are sustained today primarily by emissions from natural sources such as biomass burning[42] and from the ocean. During the 2015-2016 El Nino, global concentrations of methyl bromide were enhanced by 0.2 ppt, likely because of increases in these non-industrial sources. It was the first appreciable increase in global concentration of methyl bromide since the cap on industrial production[25] and is an important reminder that future variations in its concentration will be determined by how sensitive these natural sources and sinks are to changing temperatures, precipitation, and other climate-related variables, expected in the future.

[H2] Uncontrolled anthropogenic VSLS

The Montreal Protocol does not currently control halogenated VSLS, which contributed 3% of total tropospheric chlorine in 2016 (REF[25]). As the atmospheric concentrations and ozone-depleting chlorine from two VSLSs have increased substantially in recent years[43–45], the issue of uncontrolled VSLS emissions has gained increasing recognition.

[H3] Dichloromethane

The most prominent example of a VSLS whose atmospheric concentration has increased recently is dichloromethane (DCM, CH_2Cl_2) (REF[44]), which has a mean tropospheric lifetime of ~0.5 yrs. DCM is used primarily as a solvent in many different applications and is also used in the production of HFC-32 (see Supplementary Information, REF[46]). Its global atmospheric abundance has more than doubled since the early 2000s, from an average of ~19 ppt during 1998 to 2004 to 42 ppt in 2018 (**Fig. 2f**). This increase has occurred despite the presence of regulations in some regions, including the US and European Union, to reduce the use and emissions of DCM given its suspected carcinogenic properties[47]. Models suggest that about 80% of the chlorine represented by the global surface mean mixing ratio of DCM enters the stratosphere[27], implying that DCM contributed nearly 70 pptCl to the stratosphere in 2018. As the global DCM concentration in 1980 is not well documented, it is difficult to quantify DCM's impact on changes in ozone levels since then. Regardless, the observed 24 ppt DCM increase at the surface since 2000 has led to a chlorine addition to the stratosphere that is only slightly smaller than total Cl currently contributed by HCFC-141b, and it is nearly twice as large as the current contribution of HCFC-142b, chemicals whose production for dispersive use is currently being phased out globally by the Montreal Protocol.

[H3] Chloroform

Chloroform (CFM, $CHCl_3$) is another VSLS for which the global concentration has increased (by 30% or 2.5 ppt) since the late 2000s, reaching a global mean surface concentration of ~10 ppt in 2018 (REF[48]) (**Fig. 2g**). Modelling studies suggest the inferred increase in global $CHCl_3$ emissions between 2010 and 2015 may be almost entirely explained by growth in emissions from China[45], where it is produced during the industrial manufacture of chloromethanes[49] (see Supplementary Information), and is an essential component to the production of polytetrafluoroethylene (PTFE), a robust fluoroplastic. Like DCM, chloroform has a mean tropospheric lifetime of around 0.5 yrs, with an estimated 2017 stratospheric chlorine contribution of ~17-22 pptCl based on high-altitude aircraft observations and model estimates[25,27], though the increase since 2010 has only been around 4 pptCl. Unlike DCM, natural emissions of chloroform from the terrestrial biosphere are substantial and include emissions from peatlands, tundra, salt marshes and forest soils, among others (REF[50]). The ocean has further been suggested as a source for both of these VSLSs[51,52], but the contribution of this source to total emissions is not well constrained. In the case of chloroform, natural emissions were estimated to account in the early 2000s for up to 75% of total global emissions (REF[53]), though a more recent assessment has not been performed.

[H3] Other Chlorinated VSLS

Other chlorinated VSLSs include perchloroethylene (PCE, C_2Cl_4), trichloroethylene (TCE, C_2HCl_3), and 1,2-dichloroethane (1,2-DCE, CH_2ClCH_2Cl), all of which have predominantly anthropogenic sources. Like other chlorinated VSLS, PCE has found use as both a solvent, for instance in dry-cleaning applications, and as an intermediate in chemical synthesis. Measurements from the NOAA and AGAGE global monitoring networks show a long-term decrease in surface PCE concentration, from 3 ppt in 1995, to ~1 ppt in 2018 (REF[25,54]). Like PCE, TCE was initially used as an industrial solvent, notably in metal degreasing. TCE solvent usage has also rapidly declined in Europe and North America since being confirmed as a kidney carcinogen[55], although confirmation of that decrease in atmospheric data is still lacking. Now, TCE is largely used as an intermediate in producing the mobile air-conditioning refrigerant fluid (HFC-134a) (**Fig. 2j**), which is subject to phase-down in the future provided global ratification of the Montreal Protocol's Kigali Amendment. Today the production and consumption of TCE for both solvent and HFC-134a purposes is known to be large in China[56]. No long-term surface network data for 1,2-DCE are currently available so it is largely unknown whether atmospheric concentrations have changed over time. Nevertheless, a limited set of aircraft measurements show that northern hemisphere boundary layer 1,2-DCE concentrations appear to be ~10-20 ppt (REF[25]), with this compound contributing 5-15 pptCl to stratospheric chlorine[27].

[H3] VSLS atmospheric chlorine contribution

The principal VSLS (CH_2Cl_2, $CHCl_3$, C_2Cl_4, C_2HCl_3, CH_2ClCH_2Cl) are estimated to have provided a total of 69 (55-83, ±1 standard deviation) pptCl to the stratosphere in 2000, increasing to 111 (89-133) pptCl in 2017, based on measured surface concentration changes incorporated into a global model study[27]. This contribution represents ~3.5% of total stratospheric chlorine. A similar best estimate of 115 (75–160) pptCl for the year 2016 was reported in the 2018 WMO/UNEP Ozone Assessment[25]. Both estimates include the chlorine delivered to the stratosphere from the VSLS themselves (source gas injection), accounting for around 80% of the total, and from the fraction of their degradation products containing chlorine that also reach the stratosphere (product gas injection or PGI). In addition to surface measurements, direct observational evidence for an increase in chlorine source gas injection is also provided by measurements of VSLS (primarily DCM) in the upper troposphere and lower stratosphere over the last two decades[57]. In contrast, surface or aircraft observations alone provide limited means to constrain the magnitude of chlorine PGI, thus the estimated contribution is model-based and includes large uncertainty. This uncertainty arises because the atmospheric concentrations of VSLS degradation products, including hydrogen chloride (HCl) and phosgene ($COCl_2$), are also products in the oxidation of non-VSLS chlorocarbons.

For example, phosgene is a degradation product of long-lived CCl_4 and CH_3CCl_3, in addition to several VSLS. Phosgene concentration trends over the 8-30 km altitude range derived from satellite data, were negative between 2004 and 2016, in keeping with the expectation that phosgene concentrations should decline in response to ongoing decreases in the atmospheric concentration of its long-lived precursors. However, positive phosgene concentration trends have been observed in the upper troposphere, and the sign of this trend is reproduced by global models only when the measured increases in VSLS are considered. Taken together, these observations provide some evidence for an increase in stratospheric chlorine from VSLS degradation products since the mid-2000s[58].

Analysis of ground-based and satellite HCl measurements are used to evaluate changes in stratospheric inorganic chlorine over time[59,60]; the major source of HCl is degradation of the long-lived chlorinated ODSs. In the upper stratosphere (≥10 hPa, ~30 km), measurements from the ACE-FTS instrument show that HCl (60°S to 60°N) declined at a rate of around -0.5% per decade between 2004-2017[25,61]. Over the same period, increases in stratospheric chlorine from VSLS may have slowed the rate of HCl decline. **Fig. 3** compares HCl trends from a 3-D chemical transport model with and without chlorinated VSLS. It is evident that large interannual dynamical variability confounds HCl trend analysis, particularly in the lower stratosphere, where trends are most uncertain. In the upper stratosphere, where trends are less influenced by dynamical variability, it is estimated that increases in VSLS reduced the rate of HCl decline by ~15% between 2004 and 2017. This modest offset may partly explain some of the systematic difference between observed HCl trends and models which do not consider VSLS[62]. Furthermore, it implies that anthropogenic VSLS are offsetting some of the benefits of the Montreal Protocol.

[H2] Natural VSLS

While ozone depletion since the 1980s has been primarily driven by increases in anthropogenic ODSs, short-lived gases emitted from natural sources, especially bromine, also contribute to stratospheric halogen loading and thereby influence stratospheric ozone[25,63].

The most abundant brominated VSLSs are bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), which are largely produced in tropical, subtropical, and shelf regions of the ocean[64,65] (**Fig. 4**). However, they do also have some small anthropogenic sources (see section on Bromocarbon Production). Natural production of $CHBr_3$ involves marine organisms such as macroalgae and phytoplankton[66], while CH_2Br_2 is co-formed and its concentration correlates with $CHBr_3$ in water and air[67]. Within the first several months after these VSLSs are emitted to the atmosphere, they can be photochemically oxidised or react with hydroxyl radicals, and contribute to the pool of reactive atmospheric bromine[68]. Reactive bromine participates in the depletion of ozone by catalytic cycles and can thus impact tropospheric and stratospheric ozone chemistry.

The ODP-weighted bromine emissions of bromoform (120–820 Gg Br yr^{-1}) currently amount to approximately 20% (REF[69]) of those from total halons and methyl bromide. These estimates carry large uncertainty due to the spatiotemporal variability of VSLS emissions[70,71], which are driven by changes in primary productivity, biogeochemical cycling, sea surface temperature, and meteorology. Upper atmospheric abundances are similarly heterogeneous, due to the combined effects of highly variable emissions and highly variable atmospheric transport timescales with fastest uplifts in deep convective events[72,73]. A recent update[74] of the measurement-based bromoform and dibromomethane emission estimates (update of [75]) shows enhanced emissions in the tropical Indian Ocean and subtropical northern Atlantic in addition to the known elevated emissions along the coastlines and in upwelling regions (**Fig 4**). For the west Indian Ocean, updated bromoform emissions are almost twice as large a previous estimates and can reach the stratosphere via two transport pathways; locally through convection and in the south-eastern part of the Asian monsoon anticyclone[71] highlighting this area as a potentially important source region.

In total, brominated VSLSs—including bromoform and dibromomethane, as well as other minor natural species chlorodibromomethane ($CHBr_2Cl$), bromochloromethane (CH_2BrCl) and bromodichloromethane ($CHBrCl_2$)—are estimated to contribute 5 (uncertainty range 3-7) pptBr (~26%) to stratospheric inorganic bromine (Br_y) in 2016 (REF[25,76]). This range is based on a combination of high-altitude aircraft measurements of source gases around the tropical tropopause and model calculations of bromine product gas injection[25,76]. There is no evidence for a long-term change in this contribution, as variations (an increase followed by current decrease) in total stratospheric bromine have been driven by trends in methyl bromide and halons[25], with brominated VSLSs providing a constant contribution. While natural brominated VSLS currently have a relatively minor impact on stratospheric ozone compared to anthropogenic halogens, their oceanic production, air-sea fluxes, as well as atmospheric lifetimes and transport pathways are sensitive to climate parameters that may change in the future[72,73].

In summary, emissions of long-lived ODSs have decreased dramatically over the past few decades due to their phase-out by the Montreal Protocol, leading to unequivocal detection of ozone layer recovery. However, the recently discovered increase in global emissions of CFC-11 is a concern. Moreover, some anthropogenic chlorinated VSLS emissions, which together contribute around 3% to stratospheric chlorine and are not subject to the Protocol, are increasing due to industrial production for solvent and feedstock uses. Additionally, the ozone influence of natural sources of bromine contained in short-lived gases, which contributes around 26% to the current stratospheric bromine loading, is becoming better constrained through increased sampling and improved modelling.

[H1] Current production of ODSs

Despite the successful control of the production of most major ODSs for emissive uses by the Montreal Protocol, chemicals that can deplete ozone are still produced today. Production of ODSs for feedstock use is allowed and uncontrolled shorter-lived species are produced for a variety of purposes (see Supplementary Information).

[H2] Chlorocarbon production

Chlorinated C_1 and C_2 hydrocarbons are produced extensively, both as chemical intermediates and as solvents for the pharmaceutical and electronics industries as well as in metal and apparel cleaning. Long-lived substances such as carbon tetrachloride (CTC, CCl_4) and methyl chloroform (MCF, CH_3CCl_3) are globally no longer used as solvents, because they are ODSs and have been phased-out under the Montreal Protocol. On-going emissions of uncontrolled, shorter-lived chlorocarbons to the atmosphere are due to fugitive emissions from solvent uses, emissions from production plants (which are inevitable) and feedstock production losses during production of other substances (such as HCFCs and HFCs) (**Fig. 5**).

The group of chlorinated C_1 hydrocarbons (chloromethanes) is composed of methyl chloride, (CH_3Cl), DCM (CH_2Cl_2), chloroform ($CHCl_3$) and CTC (CCl_4). Methyl chloride is used as a chemical intermediate in the silicone industry and in the production of CH_2Cl_2, $CHCl_3$ and CCl_4 in a variety of smaller uses, such as methyl cellulose production. The production of methyl chloride, virtually all by the addition of HCl to methanol, is usually conducted on the site where it will be processed. Emissions of methyl chloride are negligible compared to its large natural emissions[25]. The chlorination of methyl chloride inevitably produces the higher chloromethanes DCM, chloroform and CTC (**Fig. 5**). Of the estimated 1162 Gg of DCM produced in 2016, 85% (988 Gg) is calculated to have been emitted by solvent applications (assuming that 100% of the amount used as solvent is emitted within the year), and 15% (174 Gg) was used as feedstock in the production of HFC-32. By contrast, more than 95% of the estimated 1472 Gg of chloroform produced in 2016 was consumed as feedstock in the production of HCFC-22, and only 54 Gg emissions arose from solvent uses, most typically from pharmaceutical manufacture. These emissions are considerably smaller than natural emissions. Until 2010, global emissions were stable at around 300 Gg yr^{-1} or less. However, in the recent years an increase of around 50 Gg yr^{-1} has occurred[25], which could mostly be related to emissions from eastern China[45]. It is unclear if these emissions are due to solvent use or, less likely, emissions from feedstock use.

The estimated 203 Gg of CTC produced in 2016 was, in addition to the co-production from chloromethane plants, also made on-demand in perchloroethylene (PCE)-CTC reactors. Produced amounts were used as feedstock for the production of HFC-245fa, HFC-365mfc, HFO-1233xd, HFO-1234yf, and HFO-1234ze as well as of synthetic pyrethroids such as cypermethrin. An additional important use of CTC is its conversion into PCE. If CTC cannot be consumed by industrial feedstock use, it must be destroyed by permitted processes. It is estimated that most of the CTC produced in 2016 was consumed as feedstock and the balance incinerated, with bottom-up emissions from all sources calculated at 15 Gg (REF[77]).

The group of chlorinated C_2 hydrocarbons includes perchloroethylene (PCE, C_2Cl_4), trichloroethylene (TCE, C_2HCl_3), and MCF (CH_3CCl_3). Global production of PCE was estimated to be 405 Gg in 2016 (NSA data), of which 200 Gg was used in emissive solvent applications and the balance of 205 Gg being used as chemical intermediate, mainly to CFC-113 and CFC-113a and their further derivatives, such as HFC-134a, HFC-125 and chlorotrifluoroethylene (CTFE) monomer. TCE production was estimated at 465 Gg in 2016 (based on Nolan Sherry & Associates, or NSA, data), with 340 Gg being used as chemical intermediate mainly to HFC-134a, and the balance of 125 Gg being used in emissive solvent applications. MCF is produced in Europe and USA, solely for feedstock use for the production of HCFC-141b, HCFC-142b, and HFC-143a, with an estimated quantity of 95 Gg in 2016 (NSA data), and the related MCF emissions due to these applications are thought to be less than 1%.

In summary, the current (2020) outlook for use of these C_1 and C_2 chlorocarbons is as follows. The use of DCM as a solvent (resulting in emissions) is thought to be stable to increasing, and its feedstock use in the production of HFC-32 is also increasing. The small solvent use of CFM is stable to decreasing. Its use as an intermediate in the production of HCFC-22 (used in air conditioners) should see a short-term fall due to restrictions in the Montreal Protocol. In the long-term, usage of CFM will likely increase as the use of HCFC-22 as chemical intermediate is expected grow. CTC is only used as an intermediate, which is increasing due to growing HFO production. MCF production is also growing: use in HFC-143a production is believed to have stopped, but its use in HCFC-142b production is increasing, as HCFC-142b is further processed to vinylidene fluoride-based polymers for electronics. There are different routes to produce HCFC-142b without using MCF, such as vinylidene chloride. Solvent use of PCE is thought to be stable to declining, with its feedstock use to HFC-125 and HFC-134a also declining. Finally, both TCE solvent and feedstock uses appear to be declining.

[H2] Bromocarbon production

In addition to their natural origin, brominated VSLSs such as bromoform, which are not controlled by the Montreal Protocol, have various industrial sources such as cooling units, desalination plants, ballast and waste water treatment, and seawater toilets. In order to limit biofouling and minimise the survival of organisms, marine water is normally disinfected when used by industry. Chemical disinfection techniques such as chlorination and ozonisation produce a variety of disinfection by-products with bromoform being the main by-product[78]. The magnitude of bromoform produced during disinfection can vary strongly depending on processing method[79], application, and chemical water characteristics. When the treated water is released, it will spread in the marine environment and is emitted into the atmosphere[80]. Atmospheric measurements cannot readily distinguish between naturally and industrially produced bromoform, making it difficult to measure large-scale bromine emissions from ballast water and assess their impact on the ozone layer.

In treated ship ballast water, an average bromoform concentration of 226 ± 142 µg L^{-1} can be expected, which is up to a million times higher than abundances found in the natural environment[80]. If all ballast water in the Rotterdam port, for instance, was treated via chlorination and ozonisation, modelling suggests that bromoform concentrations in the inner harbour waters would be up to 0.4 µg L^{-1}, which is about 100-1000 times higher than typical near-shore concentrations. However, model-based estimates show that the total bromine emissions from ballast water is likely too small to be important globally[80].

Bromoform concentrations in treated cooling waters such as power plants with 60 ± 40 µg $CHBr_3$ L^{-1} are considerably smaller than in treated ballast water[81]. Despite the smaller concentrations, anthropogenic bromine from industrial cooling water can be expected to be more important, as the total amount of water used is around 200 times larger. For instance, in coastal areas where these cooling waters are dumped, bromoform concentrations range between 0.5 and 50 µg L^{-1} (REFS[81,82]). For South-East Asia alone, anthropogenic emissions are on average 24 Gg Br yr^{-1} (REF[83]), which is 30% more than the measurement-based estimate of total emission derived for the same region (18 Gg Br yr^{-1}; from REF[74], **Fig. 4**).

The final anthropogenic source of brominated VSLS production discussed here is commercial seaweed farming. In Southeast Asia, where substantial amounts of seaweed are cultivated, current estimates suggest only minor contributions of aquaculture to total VSLS emissions, for example 2% of bromoform from farmed seaweed compared to natural seaweed in Malaysia[84]. However, projected increases in coastal aquaculture as well as their potential farming in the open ocean in future climate mitigation could substantially increase the brominated VSLS contribution[84]. Thus, potential VSLS emissions from seaweed cultivation should be further investigated for climate change mitigation and food production scenarios that rely on aquaculture.

[H1] Outlook for the future

The Montreal Protocol has resulted in decreased ODS emissions and initial recovery of the ozone layer. Given full compliance, and all else being constant, the ozone layer should return to 1980 levels around the mid- 21st century[20]. However, due to the new and renewed concerns associated with ODS production and emission discussed in this Review, the ozone layer might recover at a slower rate than originally anticipated. In this final section, we consider future expected trends in ODS and VSLS emissions and their implications for the timescale of ozone layer recovery.

[H2] Future ODS and VSLS emissions

Future emissions of ODSs will depend on further regulation, compliance, industrial, and environmental factors, making them difficult to predict confidently. However, modelling approaches can provide some insight into what might be expected in the near future, and how these might impact ozone recovery[85–87]. For example, if one of the most concerning ODS trends, the increase in CFC-11 emissions, continues unabated then by 2060 another 180 pptCl would be added to the atmosphere above the amounts expected (~3000 pptCl; **Fig. 1**), if all controls in the Montreal Protocol had been followed[85] **(Fig. 6)**. This extreme scenario, while unlikely, would delay the return of the Antarctic ozone hole to 1980 levels by approximately ten years, to ~2060[85]. Similarly, continued chlorinated VSLS emissions (which are allowed under the protocol) could slow the healing of the ozone layer. For instance, eliminating some of the anthropogenic VSLS contributions to stratospheric chlorine would advance the ozone return date by about 1 year for each 17 pptCl reduction compared to business as usual emissions[85].

In addition to non-compliant CFC-11 and uncontrolled VSLS emissions, demand for carbon tetrachloride is expected to increase by well over 50% by 2025, in comparison to the 203 Gg produced in 2016 (REF[77,88]) as more HFOs (which replace many HCFCs and HFCs) are produced using CTC as a feedstock. The increased demand will likely lead to higher emissions from this production[89]. Chloroform emissions, as well, could increase with any increased use as feedstock for HCFC-22. Increased emissions of these chlorocarbons would delay the ozone return date in relation to how much enhanced chlorine is delivered to the stratosphere, as discussed above.

Finally, future natural ODS emissions and atmospheric transport might be influenced by climate change, though long-term changes are yet to be observed. For example, increases in biomass burning could add to the methyl bromide concentration in the atmosphere. Additionally, ocean acidification, changing sea-ice extent, changing ocean primary production and varying meteorological conditions at the ocean surface could influence production of methyl bromide or brominated VSLS in the ocean and their emissions into the atmosphere[90,91]. Investment in large-scale macroalgae farming could result in increased VSLS emissions, especially if located in the tropics[84]. Climate-driven changes of the tropospheric oxidising capacity would affect lifetimes of CH_3Br and VSLS[73], while dynamical changes would affect the troposphere–stratosphere transport of VSLSs and thus their contribution to the stratospheric halogen budget[92]. The net ozone impact of these possible future changes depends on the sensitivity of these processes to changes in climate, and are largely uncharacterised. The emergence of Earth system models that include accurate representations of comprehensive ocean biogeochemistry and stratospheric chemistry could provide further constraints in coming years, although observationally-derived improvements in our understanding of these systems and their feedbacks are also needed.

[H2] Ensuring timely ozone recovery

It is clear that the phase-out of ODS production has overall been an international success. Also important in ensuring that the ozone layer ultimately recovers, however, was the early detection of newly increased CFC-11 emissions, which was a triumph for atmospheric monitoring because it involved detecting a small slowdown in the atmospheric concentration decline. Furthermore, the existing network enabled an indication of which region was contributing to the unexpected emissions[22,93], which is information critical for enabling the mitigation of the illicit production. However, there are key research needs that would facilitate a timely recovery of the ozone layer. One such need is improved observational networks and modelling capabilities to monitor and assess progress, as current capabilities, although they have improved greatly in recent years, are still limited in ways that hamper effective and rapid mitigation. This improvement will allow more accurate attribution of atmospheric observations to specific emission locations. Moreover, the anticipated controls on greenhouse gases, in addition to the current ODS controls, will put more demands on compliance monitoring as the most abundant greenhouse gases have a wider variety of sources, source distributions, and sinks than the ODSs. Such progress can be achieved through ongoing and major enhancements in our scientific capabilities to observe and understand changes in our atmospheric environment, such as better spatially resolved observations and high resolution modelling. Finally, there are specific, immediate needs to determine the location of the increased CFC-11 emissions originating outside of eastern China[22].

Renewed production of a major (class I) ODS, CFC-11, in violation of the Protocol represents a serious challenge to the Montreal Protocol, and adds urgency to addressing the current scientific needs of the international policy community tasked with ensuring recovery of the stratospheric ozone layer. The Protocol’s advisory Assessment Panels (Scientific, Technology and Economic, and Environmental Effects) have stepped up to assess the initial discoveries and provide insights into the potential cause(s) for the issue and the underlying economic factors that contributed. In addition, all Parties have publicly expressed interest in the issue being rapidly resolved, and are reconsidering aspects of the Protocol’s framework and mechanisms to minimise the risk of further non-compliance. This response is yet another example of the importance of communication between the international science and policy communities for ensuring ozone recovery and, despite the challenges that remain ahead for the ozone layer, continued vigilance by both communities will ensure recovery of the ozone layer without substantial delay.

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Related links

Advanced Global Atmospheric Gases Experiment (AGAGE) monitoring network: https://agage.mit.edu/

National Aeronautics and Space Administration Ozone Watch: https://ozonewatch.gsfc.nasa.gov/

National Oceanic and Atmospheric Administration Earth System Research Laboratory monitoring network: https://www.esrl.noaa.gov/gmd/

United Nations Environment Programme. https://www.unenvironment.org/

United Nations Environment Programme Ozone Country Data. https://ozone.unep.org/countries/data-table

World Meteorological Organization and United Nations Environment Programme Ozone Assessments. https://www.esrl.noaa.gov/csd/assessments/ozone/

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Author contributions

All authors contributed to all aspects of the article.

Competing Interests

The authors declare no competing interests.

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Supplementary information

Supplementary information is available for this paper at https://doi.org/10.1038/s415XX-XXX-XXXX-X

Figures

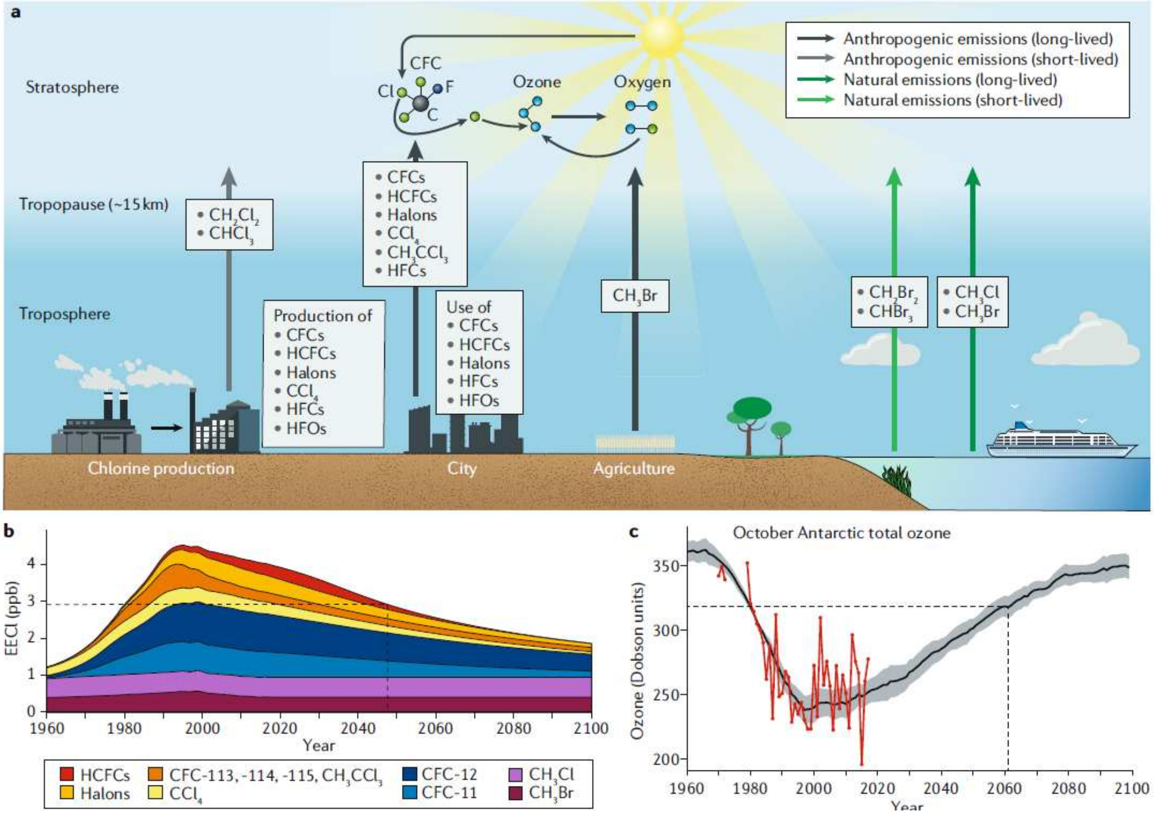

Figure 1. Halogenated source gases and their impact on stratospheric ozone. **a|** Anthropogenic (black and grey arrows) and natural (green arrows) sources of long-lived and short-lived ozone depleting substances. The majority of long-lived Ozone Depleting Substances (ODSs) reach the stratosphere, where they are photochemically decomposed, liberating halogens that destroy ozone (O_3). Short-lived substances largely decompose in the troposphere and only a fraction of the emissions reaches the stratosphere. **b|** Past observations and projections of equivalent effective chlorine (EECl; total chlorine + 65×total bromine at surface, ppb) from different long-lived ODSs between 1960 and 2100. After the signing of the Montreal Protocol and subsequent phase-out of many long-lived ODSs, EECl began to decline and is expected to return to 1980 levels by around 2050, as indicated by the horizontal and vertical dashed lines. **c|** Measured (red line) and predicted (black line, with uncertainty shown as grey shading) for Antarctic October column ozone (Dobson Units; DU) between 1960 and 2100. The Antarctic ozone layer is expected to return to 1980 levels around 2060, around a decade later than EECl (horizontal and vertical dashed lines).

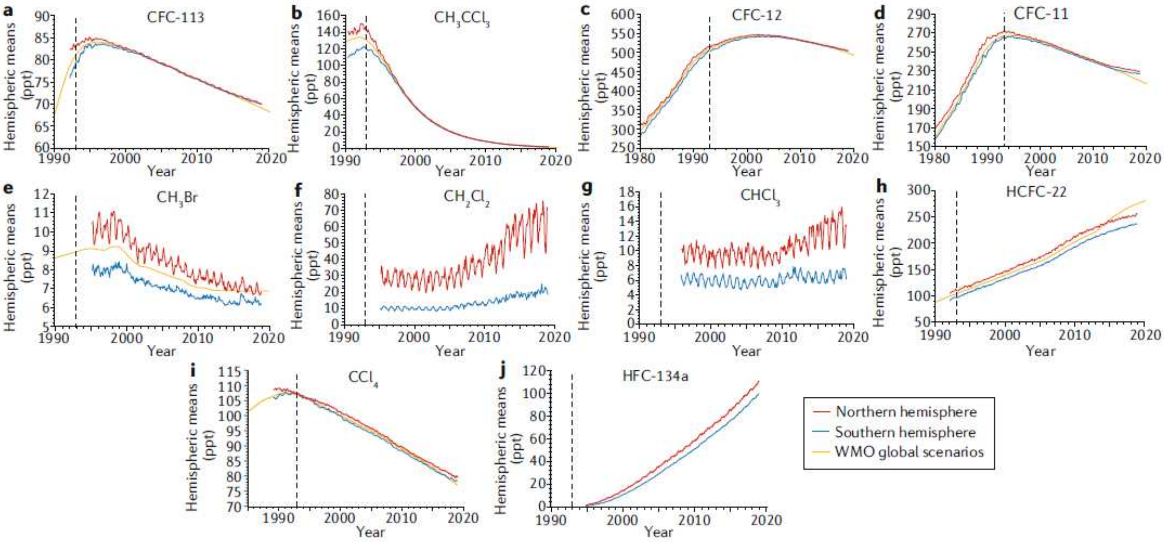

Figure 2. Atmospheric concentrations of selected halogenated gases over time. Hemispheric mean concentrations (or mole fractions, as parts per trillion, or ppt; northern hemisphere in red, southern hemisphere in blue) of long-lived ozone-depleting substances (ODSs; a-e, h, i), two very short-lived substances (VSLS; f, g), and a substitute HFC (j). **a-j|** CFC-113, methyl chloroform (CH_3CCl_3), CFC-12, CFC-11, methyl bromide (CH_3Br), dichloromethane (DCM, CH_2Cl_2), chloroform ($CHCl_3$), HCFC-22, carbon tetrachloride (CCl_4), and HFC-134a concentrations through time. All surface means are derived from NOAA measurements at 4 to 12 remote sites using in-situ and flask collection techniques[11,27,44]. These results, along with those from an independent global network[12], form the basis for WMO scenario records of global concentration changes for Montreal Protocol-controlled substances for years prior to 2014 (yellow lines on long-lived ODS panels; REF[34]). These scenario results are projected into the future based on historical data for production, emissions, and bank reservoirs, and existing production controls. Although an updated scenario analysis is available[94], the older scenario is used here to understand observed vs expected concentration changes since 2014. The year that tropospheric chlorine from long-lived ozone-depleting gases peaked[11] (dashed black line) is provided for reference given that the time-scale differs in the panels. Most ODSs are decreasing over time due to phase out. However, the very short-lived species, DCM and chloroform, both increased during this time period, as did HCFC-22.

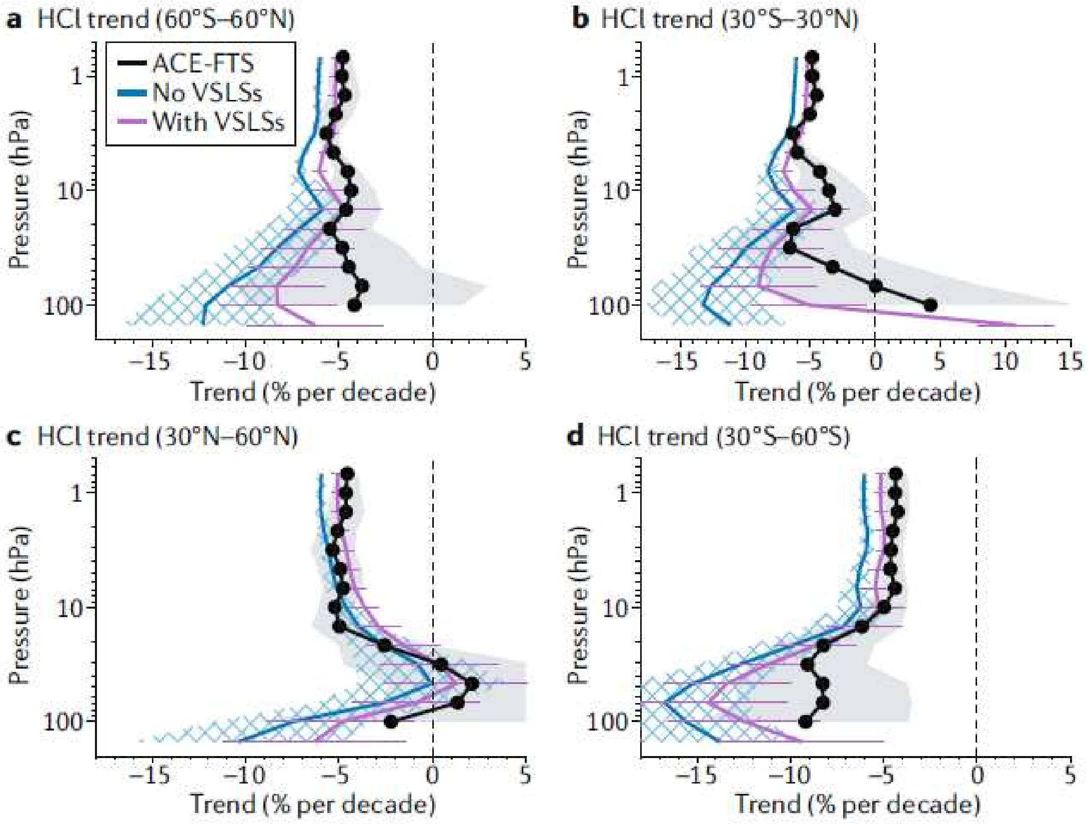

Figure 3. Impact of chlorinated VSLSs on stratospheric HCl trends. a-d| Mean HCl trends (2004-2017) calculated for latitude bands 60°S-60°N, 30°S-30°N, 30°N-60°N, and 30 °S-60°S. Modelled HCl trends (% decade^{-1}) with and without very short-lived substances (VSLSs) are from the TOMCAT 3-D chemical transport model[95]. For the long-lived chlorine source gases the model used global mean surface mixing ratios based on observations[96]. Observed HCl trends are derived from the ACE-FTS satellite instrument[61]. 2σ trend errors denoted by horizontal bars, shading and grating. The panels show that the inclusion of VSLS increases the HCl trend, especially in the lower stratosphere, bringing the model into better agreement with the observations. The observed HCl trend is also affected by atmospheric dynamical variability, leading to a positive trend in northern mid-latitudes and tropics, compared to the expected negative trend elsewhere[97].

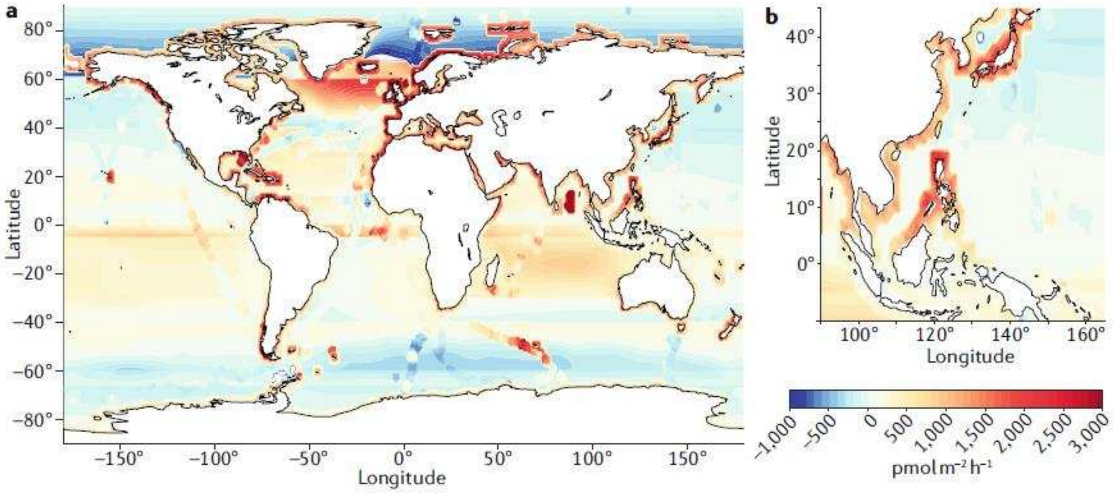

Figure 4. Total and anthropogenic bromoform emissions from the oceans. **a,b|** Global bromoform ($CHBr_3$) emissions are shown for global and East and South-East Asia regions[74] based on a recent update of measurement-based emission estimates[75]. Both panels use the same colour scale. In addition to the known elevated emissions along the coastlines and in upwelling regions, enhanced emissions in the tropical Indian Ocean and subtropical northern Atlantic have been identified. For the west Indian Ocean, updated bromoform emissions almost double and can reach the stratosphere via two transport pathways; locally through convection and in the south-eastern part of the Asian monsoon anticyclone[71] highlighting this area as a potentially important source region.

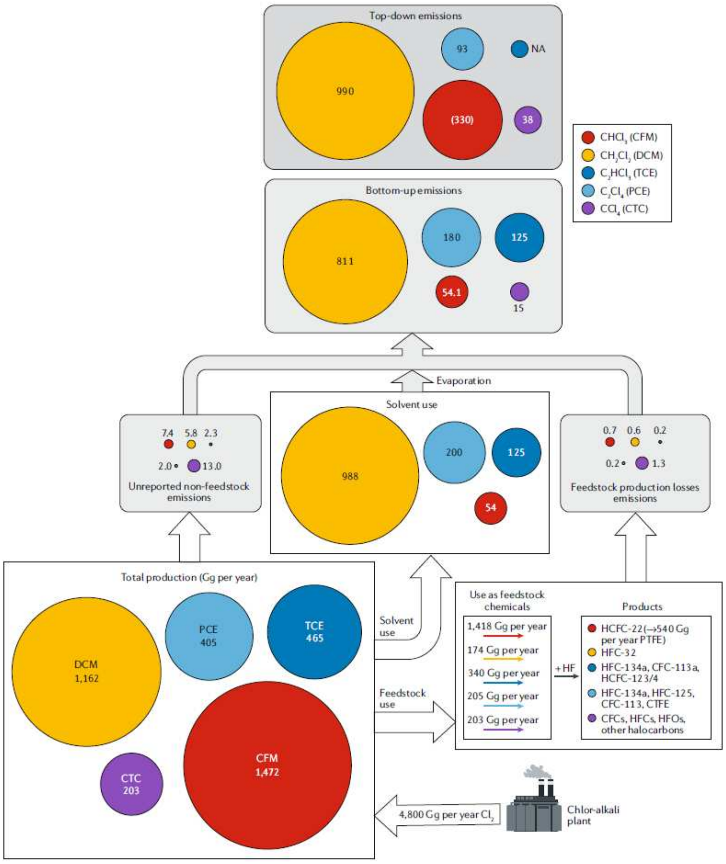

Figure 5. Production of chlorine-containing compounds. Chlorine (Cl_2) from chlor-alkali plants is combined with methanol (CH_3OH) to produce various chlorocarbons. Emissions of these chemicals can occur during their production (unreported non-feedstock emissions); their use as solvents; and their use as feedstock chemicals for chlorofluorocarbons (CFCs; no longer permitted), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), hydrofluoroolefins (HFOs) and other halogenated chemicals. Production or emissions processes are shown as arrows, with estimated amounts (Gg yr^{-1}) for 2016 shown when available. White-filled arrows indicate use; grey-filled arrows indicate emissions. Circles are colour coded by chlorocarbon type and show either total production numbers or emissions. Grey background shading denotes emissions. Global bottom-up emissions estimates for 2016 are derived from production magnitudes, and top-down emission values for 2016 are derived from global atmospheric measurements. Note that total bottom-up emissions do not equal the sum of all contributions because many countries enforce incineration of spent solvents, especially in pharmaceutical uses, leading to lower reported emissions. This figure excludes an additional 10 Gg yr^{-1} carbon tetrachloride (CCl_4) suspected to arise from legacy emissions and from other industrial chlorination processes such as ethylene dichloride and allyl chloride production.

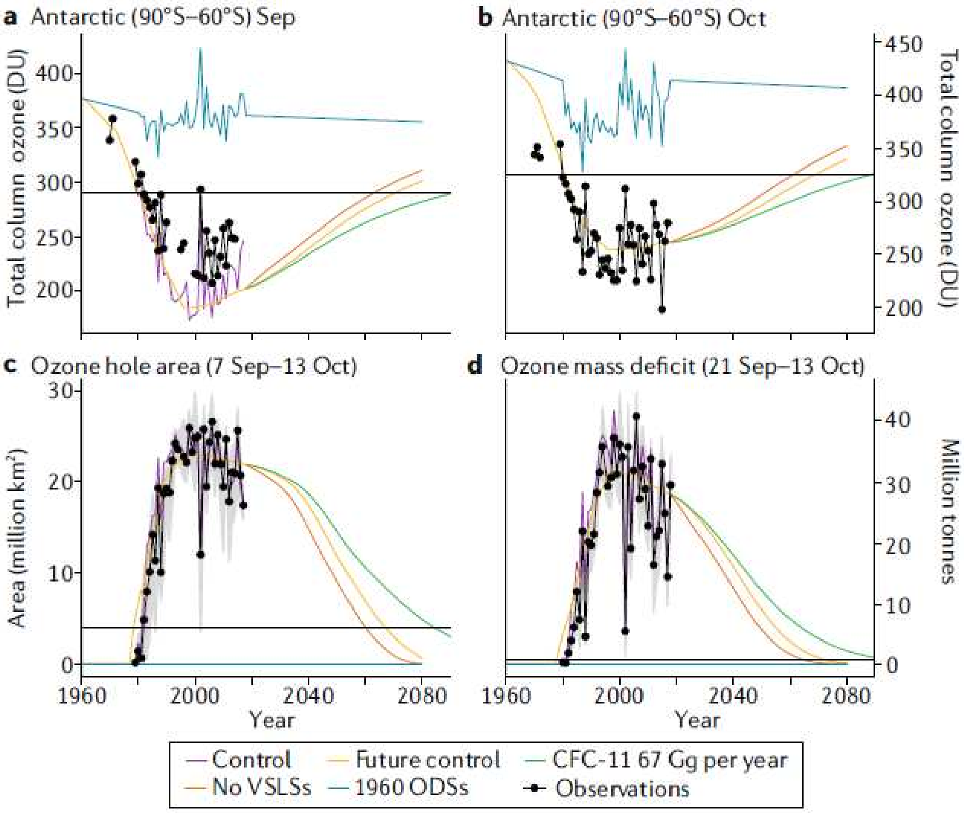

Figure 6. Antarctic ozone and metrics quantifying ozone loss as a function of additional CFC-11 and VSLS emissions. a,b| Mean column ozone (in Dobson Units, DU) averaged from 90°S – 60°S for September and October from five TOMCAT 3-D model[95,98,99] simulations: Control (varying meteorology), future control (2000 meteorology), with constant 67 Gg yr^{-1} emissions of CFC-11, with no chlorinated very short-lived substances (VSLS) and with 1960 levels of ozone-depleting substances (ODS), as well as NASA Solar Backscatter Ultraviolet instrument observations from 1960 to 2090. **c,d|** Estimates of the size of the Antarctic ozone hole under control, future control, 67 Gg yr^{-1} CFC-11 emissions, no VSLS, and 1960 levels of ODS simulations, and observations (based on NASA Ozone Watch information) using (**c**) the area contained within the 220 DU contour (×10^{6} km^{2}) (averaged September 7 – October 13), and (**d**) ozone mass deficit (×10^{6} tonnes) (averaged September 21 – October 13). The panels show that additional emission of CFC-11 at the level assumed will delay recovery of the Antarctic ozone hole, meaning a delay in the date of return to 1980 values of around 10 years. Similarly, elimination of chlorinated VSLS emissions will speed up the ozone return by around 6 years.

Glossary

Bank	Reservoir of produced ODSs stored in equipment or materials and not yet released to atmosphere.
Controlled	ODS included in the Montreal Protocol for limits on consumption and production
Fluorination	Reaction of a feedstock with a fluorine-containing compound to produce a required substance.
Lifetime	Measure of the removal rate (e-folding time) of emitted species by atmospheric processes.
Non-emissive	Application that does not lead to the immediate and direct emission of ODS.
Ozone-depleting substance (ODS)	A man-made gas that causes ozone depletion once it reaches the stratosphere.
Ozone depletion potential (ODP)	Relative amount of ozone loss caused by emission of 1 kg of a substance compared to emission of 1 kg of CFC-11.
Stratosphere	Layer of atmosphere (approximately 15–50 km).
Troposphere	Layer of atmosphere (surface to approximately 15 km).
Uncontrolled	ODS not included in Montreal Protocol for limits on production and consumption.
Very short-lived substance (VSLS)	Substance with an atmospheric lifetime of <0.5 year.