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

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

33
34 **Abstract.** Stratospheric ozone depletion, first observed in the 1980s, has been caused by the
35 increased production and use of substances such as chlorofluorocarbons (CFCs), halons and
36 other chlorine-containing and bromine-containing compounds, collectively termed ozone-

37 depleting substances (ODSs). Following controls on the production of major long-lived ODSs
38 by the Montreal Protocol, the ozone layer is now showing initial signs of recovery, and is
39 anticipated to return to pre-depletion levels in the mid-to-late 21st century, likely 2050-2060.
40 These return dates assume widespread compliance with the Montreal Protocol and thereby
41 continued reductions in ODS emissions. However, recent observations reveal increasing
42 emissions of some controlled (for example CFC-11, as in eastern China) and uncontrolled
43 substances (for example very short-lived substances, VSLs). Indeed, the emissions of a
44 number of uncontrolled VSLs are adding significant amounts of ozone-depleting chlorine to
45 the atmosphere. In this Review, we discuss recent emissions of both long-lived ODSs and
46 halogenated VSLs, and how these might lead to a delay in ozone recovery. Continued
47 improvements in observational tools and modelling approaches are needed to assess these
48 emerging challenges to a timely recovery of the ozone layer.

49

50 **[H1] Introduction**

51

52 The stratospheric ozone layer absorbs harmful ultraviolet (UV) radiation, preventing most from
53 reaching the surface where it can cause skin cancer in humans and damage to plants¹. Ozone
54 (O₃) also absorbs outgoing terrestrial infrared radiation in both the **stratosphere [G]** and
55 **troposphere [G]**, which together with stratospheric heating from UV absorption, exerts a key
56 influence in determining the temperature structure of the atmosphere². Hence, changes in the
57 ozone layer can also affect surface climate, an impact that has been identified in the
58 summertime southern hemisphere³ with, for example, a poleward shift of the midlatitude jet⁴.
59 Depletion of the stratospheric ozone layer^{5,6} is therefore a major environmental concern,
60 especially since the discovery of the Antarctic ozone hole in 1985⁷. For example, mean column
61 ozone has been depleted by about 50% in the Antarctic spring and by a maximum of around
62 4% decade⁻¹ in northern midlatitudes⁸.

63

64 Ozone depletion is caused by an increased abundance of stratospheric chlorine and bromine⁸,
65 derived from long-lived anthropogenically produced ozone-depleting substances (ODSs)^{9,10},
66 that destroy ozone molecules by converting them to oxygen (O₂; **Fig. 1a**). ODSs were used in
67 air conditioning, as refrigerants, solvents and fire-extinguishing agents. To mitigate the
68 damage already caused by ODSs and to prevent further ozone destruction, the Montreal
69 Protocol on Substances that Deplete the Ozone Layer was signed in 1987 and ratified two
70 years later. With several subsequent adjustments and amendments, accepted by almost all
71 countries worldwide, the production and consumption of all of the primary long-lived ODSs –
72 such as chlorofluorocarbons (CFCs) and bromine-containing halons – has been **controlled [G]**
73 and largely stopped through strict phase-out schedules. The latest of these was the phase-

74 out of CFCs in 2010. In response, stratospheric levels of chlorine and bromine have slowly
75 declined since their peaks in the 1990s^{11,12} (**Fig. 1b**), primarily due to decreasing
76 concentrations of the controlled substances methyl chloroform (CH₃CCl₃), CFCs, methyl
77 bromide (CH₃Br), and the halons (see Supplementary Information Table S1 for summary of
78 chemical species, formulae, alternative names and abbreviations).

79

80 As a result of the Montreal Protocol, increasing concentrations of stratospheric ozone have
81 been detected in the upper stratosphere¹³ and the Antarctic^{14–16} (**Fig. 1c**), suggesting that
82 initial stages of recovery are now underway. Multiple processes contribute to the initial
83 recovery observed to date, and separating the influence of the ODS declines to climate-
84 change-related trends is difficult, especially for the Antarctic lower stratosphere¹⁷. Ozone
85 levels are predicted to return to 1980 concentrations (that is, those prior to any large-scale
86 depletion) around the middle of the 21st century, provided continued compliance with the
87 controls in the Protocol and minimal increases in ozone-depleting halogen levels from
88 uncontrolled sources^{18–20}. As such, the Montreal Protocol has been hailed as the most
89 successful international environmental treaty to date.

90

91 However, there are many threats to the ongoing success of the treaty and timely recovery of
92 the ozone layer, in particular the increasing emissions of controlled substances that were
93 reportedly phased out and of other chlorinated substances that have never been controlled by
94 the Protocol. Although production of the primary ODSs (CFCs, CCl₄, CH₃CCl₃, halons, CH₃Br)
95 has largely ceased, recent observations reveal increased emissions of CFC-11, believed to
96 be the result of new production and non-compliance with Montreal Protocol controls^{21,22}.
97 Moreover, ODS emissions can persist for various legitimate reasons, including, the escape or
98 use of stocks or **banks [G]** of ODSs (typically CFCs, HCFCs and halons) produced before the
99 mandated phase-out of production, and inadvertent by-product formation and emission
100 associated with allowed production of controlled substances (including CFCs, HCFCs, and
101 hydrofluorocarbons, or HFCs^{23,24}), for example when used solely for **non-emissive [G]**
102 purposes (such as further chemical manufacture).

103

104 Additional chlorine is further reaching the stratosphere from increased production of some
105 **uncontrolled [G]** very short-lived substances (VSLs), which are largely removed naturally
106 from the atmosphere in <0.5 yrs and have historically been responsible for only a small amount
107 of ozone-depleting bromine and chlorine²⁵. Recent observed increases in their concentrations
108 add a new concern to the timely recovery of stratospheric ozone^{26,27}. Unlike long-lived ODSs,
109 the short tropospheric **lifetimes [G]** of VSLs mean that transport processes determine how
110 efficiently emissions reach the stratosphere. Both VSL transport and chemical loss rates vary

111 in space and time, thus their **ozone depletion potentials [G]** (ODPs) depend on the region and
112 season of emission^{28–30}.

113

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

119

120

121 **[H1] Recent observations**

122

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

129

130 **[H2] Long-lived controlled ODSs**

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

135

136 **[H3] CFC-113 and methyl chloroform**

137 How an ODS is or was used industrially influences the persistence of its emission after
138 production is phased-out. For example, as CFC-113 and methyl chloroform (**Fig. 2a,b**) were
139 used as solvents or cleaning agents, emissions occurred mostly during use and there was no
140 build-up of a large bank of produced-but-not-yet-emitted ODSs³¹. Hence, emissions of ODSs
141 used primarily in these applications declined rapidly after production ceased. Global
142 concentrations of methyl chloroform, for instance, decreased by ~18% yr⁻¹ after 1998, from
143 130 parts per trillion (ppt) in the 1990s to <2 ppt in 2018, indicating near-zero emissions since
144 the year 2000 given its atmospheric lifetime of 5 yrs (REF³²) (see Supplementary Information
145 for discussion of link between emissions, lifetime and atmospheric abundance). Similar rapid
146 declines in emissions of CFC-113 have also been observed, although its atmospheric
147 abundance has declined much more slowly compared to methyl chloroform given its longer

148 lifetime of ~93 yrs (REF²⁵). Because emissions of chemicals used by humans are largest in
149 the northern hemisphere, concurrent declines in the hemispheric concentration difference
150 further support the implied emission reductions³³.

151

152 [H3] CFC-12

153 By contrast, ODSs that were used as working fluids in refrigeration and air conditioning
154 systems, such as CFC-12 (Fig 2c), accumulated substantial banks before production was
155 phased out. As a result, emissions of these ODSs have declined more slowly due to persistent
156 ongoing emissions from these reservoirs²⁵. In addition, CFCs have long lifetimes that also limit
157 the speed of their decrease in the absence of emission. For example, despite its production
158 being phased out in 2010, global concentrations of CFC-12 have decreased by only 0.6% yr⁻¹
159 in the recent ~5 years, lower than the 1% yr⁻¹ decline expected based on its 102-yr lifetime³²
160 if emissions had ceased. These lower rates of change thereby indicate ongoing CFC-12
161 emissions, presumably from banks in older refrigerators and air conditioners (see
162 Supplementary Information). Northern-southern hemispheric concentration differences also
163 show slow decreases over time, from 6-8 ppt in the late 1990s, to ~1 ppt in 2018 (REF²⁵),
164 consistent with slowly declining emissions.

165

166 [H3] CFC-11

167 ODSs such as CFC-11 (Fig. 2d) have been used as blowing agents in foam production,
168 resulting in emissions on slow and fast timescales depending on the type of foam produced;
169 ODSs used to produce insulating closed-cell foams become trapped, slowly leaking to the
170 atmosphere, whereas those in open-cell cushioning foams rapidly escape³¹. Therefore, when
171 CFC-11 production began decreasing in 1990, its atmospheric concentrations started to
172 decline shortly thereafter following escape from open-cell foams. However, emissions from
173 the slow-release foams persisted and the concentration decline did not accelerate in
174 subsequent years beyond -0.8% yr⁻¹, slower than the limiting decline rate of -2% yr⁻¹ expected
175 in the absence of emission given its ~50-yr lifetime. The measured concentration declines
176 suggest that CFC-11 emissions remained constant for the 2002-2012 decade, which was
177 unexpected given that new production of CFC-11 was negligible by 2007 and had reportedly
178 ended by 2010 (REF²¹). In the absence of new production, emissions from banks should have
179 decreased slowly over time as the closed-cell foam reservoir became depleted.

180

181 Furthermore, global CFC-11 concentration declines between 2016 and 2018 were only half
182 as fast as those observed between 2002 and 2012 (Fig. 2d), suggesting that emissions had
183 actually increased in recent years. Whereas projections had anticipated CFC-11 reductions of
184 14.8 ppt between 2013 and 2018 (REF³⁴), the observed decline was only ~6.7 ppt (REF²¹)

185 (Fig. 2d). Even in a scenario in which the global concentration decline had not accelerated as
186 projected after 2013, but had remained constant at a rate of 0.8% yr⁻¹, the 2018 global surface
187 concentration of CFC-11 was elevated by ~4 ppt (corresponding to 12 pptCl) relative to 2013²¹.
188 These values are substantial when compared with the annual decline in chlorine from all
189 controlled substances in recent years, which averaged 12.7 pptCl yr⁻¹ from 2012 to 2016
190 (REF²⁵). In addition, the hemispheric concentration difference increased from 2 ppt to
191 approximately 3 ppt after 2012. Taken together, these observations point to an increase in
192 CFC-11 emissions in the northern hemisphere, likely from new production rather than foam
193 banks, after the 2010 phase-out, in violation of Montreal Protocol controls^{21,22}. Results from
194 globally-distributed remote locations suggested that the emission increase stemmed, in part,
195 from eastern Asia²¹. Subsequent measurements from that region further confirmed that
196 approximately half of the global emission increase originated from two industrialised provinces
197 in eastern China, Shandong and Hebei²².

198
199 Uncertainties in the total amount of newly-produced CFC-11, as well as its application (for
200 example, closed-cell foam versus solvents, the former generating an ODS bank), contribute
201 to an absence of clarity regarding the impact on the ozone layer and its recovery. If the new
202 CFC-11 is used for closed-cell foams, for example, production magnitudes could be up to six
203 times larger (~78 Gg yr⁻¹) than the observed emission increase (13 Gg yr⁻¹, REF³⁵). The
204 resulting impact on ozone depletion would therefore be much larger than if the new CFC-11
205 were being used as a solvent or in other applications, thereby implying smaller production and
206 future emission magnitudes and no augmentation of ODS banks.

207
208 In addition to this CFC-11 impacting the ozone layer directly, there could have also been CFC-
209 12 produced given that both CFCs are typically produced during the fluorination [G] of carbon
210 tetrachloride³¹ (see Supplementary Information for discussion of industrial chlorine
211 processes). This CFC-12, which might be as much as 40% of the CFC-11 produced, could be
212 intentionally vented or later escape to the atmosphere and exacerbate ozone depletion.
213 However, emissions of CFC-12 do not show signs of substantial increases in recent years
214 either globally (Fig. 2c) or downwind of China²². A number of possibilities can explain this
215 apparent absence of increased CFC-12 emissions in the presence of new CFC-11 production:
216 minimal formation of CFC-12 by-product; use of CFC-12 by-product as feedstock for other
217 chemicals without residual emissions; or storage of CFC-12 by-product in closed (slow-
218 release) applications (refrigeration or air conditioning)^{21,22}.

219
220 Other observations also show unexpected increases in abundances or emissions of a number
221 of minor controlled CFCs (CFC-13, CFC-113a, CFC-114 and CFC-115) since 2010 (REF^{24,36}).

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

225

226 **[H2] Methyl bromide**

227 Like CFCs, anthropogenic production of methyl bromide (CH_3Br ; **Fig. 2e**), a potent ODS, has
228 also declined due to the phase-out of controlled uses in the mid-1990s (REF^{37,38}). From a peak
229 of 9.1 ppt in the late 1990s, global mean concentrations decreased 27% to 6.6 ppt in 2018
230 (REF²⁵). Furthermore, the hemispheric concentration difference decreased from 2.3 ppt in
231 1996 to 1998 to 0.6 ppt in 2018. However, the 2018 global and southern hemispheric
232 concentrations (6.3 ppt) remain appreciably higher than the natural background southern
233 hemispheric level of 5.5 ± 0.2 ppt derived from Antarctic firn-air and ice bubble air^{25,39,40},
234 attributable, in part, to the incomplete phase out of all production for emissive uses by the
235 Montreal Protocol. Specifically, methyl bromide has essential uses that prevent the spread of
236 noxious pests and biota across international boundaries, referred to as quarantine and pre-
237 shipment (QPS) applications. Today, QPS uses a total of ~10 Gg methyl bromide per year,
238 which has remained relatively constant since the year 2000. However, because QPS is not
239 controlled by the Protocol, any future increase in production for this use would not be a
240 violation of the Montreal Protocol. Other human-related sources, such as rapeseed oil
241 production or farming plants in the Brassica family⁴¹ are also thought to contribute to the
242 present-day atmospheric concentration, but increases in these sources are thought to be fairly
243 small²⁵.

244

245 Atmospheric methyl bromide concentrations are sustained today primarily by emissions from
246 natural sources such as biomass burning⁴² and from the ocean. During the 2015-2016 El Niño,
247 global concentrations of methyl bromide were enhanced by 0.2 ppt, likely because of
248 increases in these non-industrial sources. It was the first appreciable increase in global
249 concentration of methyl bromide since the cap on industrial production²⁵ and is an important
250 reminder that future variations in its concentration will be determined by how sensitive these
251 natural sources and sinks are to changing temperatures, precipitation, and other climate-
252 related variables, expected in the future.

253

254 **[H2] Uncontrolled anthropogenic VSLs**

255 The Montreal Protocol does not currently control halogenated VSLs, which contributed 3% of
256 total tropospheric chlorine in 2016 (REF²⁵). As the atmospheric concentrations and ozone-
257 depleting chlorine from two VSLs have increased substantially in recent years^{43–45}, the issue
258 of uncontrolled VSL emissions has gained increasing recognition.

259

260 [H3] Dichloromethane

261 The most prominent example of a VSLs whose atmospheric concentration has increased
262 recently is dichloromethane (DCM, CH_2Cl_2) (REF⁴⁴), which has a mean tropospheric lifetime
263 of ~0.5 yrs. DCM is used primarily as a solvent in many different applications and is also used
264 in the production of HFC-32 (see Supplementary Information, REF⁴⁶). Its global atmospheric
265 abundance has more than doubled since the early 2000s, from an average of ~19 ppt during
266 1998 to 2004 to 42 ppt in 2018 (Fig. 2f). This increase has occurred despite the presence of
267 regulations in some regions, including the US and European Union, to reduce the use and
268 emissions of DCM given its suspected carcinogenic properties⁴⁷. Models suggest that about
269 80% of the chlorine represented by the global surface mean mixing ratio of DCM enters the
270 stratosphere²⁷, implying that DCM contributed nearly 70 pptCl to the stratosphere in 2018. As
271 the global DCM concentration in 1980 is not well documented, it is difficult to quantify DCM's
272 impact on changes in ozone levels since then. Regardless, the observed 24 ppt DCM increase
273 at the surface since 2000 has led to a chlorine addition to the stratosphere that is only slightly
274 smaller than total Cl currently contributed by HCFC-141b, and it is nearly twice as large as the
275 current contribution of HCFC-142b, chemicals whose production for dispersive use is currently
276 being phased out globally by the Montreal Protocol.

277

278 [H3] Chloroform

279 Chloroform (CFM, CHCl_3) is another VSLs for which the global concentration has increased
280 (by 30% or 2.5 ppt) since the late 2000s, reaching a global mean surface concentration of ~10
281 ppt in 2018 (REF⁴⁸) (Fig. 2g). Modelling studies suggest the inferred increase in global CHCl_3
282 emissions between 2010 and 2015 may be almost entirely explained by growth in emissions
283 from China⁴⁵, where it is produced during the industrial manufacture of chloromethanes⁴⁹ (see
284 Supplementary Information), and is an essential component to the production of
285 polytetrafluoroethylene (PTFE), a robust fluoroplastic. Like DCM, chloroform has a mean
286 tropospheric lifetime of around 0.5 yrs, with an estimated 2017 stratospheric chlorine
287 contribution of ~17-22 pptCl based on high-altitude aircraft observations and model
288 estimates^{25,27}, though the increase since 2010 has only been around 4 pptCl. Unlike DCM,
289 natural emissions of chloroform from the terrestrial biosphere are substantial and include
290 emissions from peatlands, tundra, salt marshes and forest soils, among others (REF⁵⁰). The
291 ocean has further been suggested as a source for both of these VSLs^{51,52}, but the
292 contribution of this source to total emissions is not well constrained. In the case of chloroform,
293 natural emissions were estimated to account in the early 2000s for up to 75% of total global
294 emissions (REF⁵³), though a more recent assessment has not been performed.

295

296 [H3] Other Chlorinated VSLS

297 Other chlorinated VSLSs include perchloroethylene (PCE, C_2Cl_4), trichloroethylene (TCE,
298 C_2HCl_3), and 1,2-dichloroethane (1,2-DCE, CH_2ClCH_2Cl), all of which have predominantly
299 anthropogenic sources. Like other chlorinated VSLS, PCE has found use as both a solvent,
300 for instance in dry-cleaning applications, and as an intermediate in chemical synthesis.
301 Measurements from the NOAA and AGAGE global monitoring networks show a long-term
302 decrease in surface PCE concentration, from 3 ppt in 1995, to ~1 ppt in 2018 (REF^{25,54}). Like
303 PCE, TCE was initially used as an industrial solvent, notably in metal degreasing. TCE solvent
304 usage has also rapidly declined in Europe and North America since being confirmed as a
305 kidney carcinogen⁵⁵, although confirmation of that decrease in atmospheric data is still lacking.
306 Now, TCE is largely used as an intermediate in producing the mobile air-conditioning
307 refrigerant fluid (HFC-134a) (Fig. 2j), which is subject to phase-down in the future provided
308 global ratification of the Montreal Protocol's Kigali Amendment. Today the production and
309 consumption of TCE for both solvent and HFC-134a purposes is known to be large in China⁵⁶.
310 No long-term surface network data for 1,2-DCE are currently available so it is largely unknown
311 whether atmospheric concentrations have changed over time. Nevertheless, a limited set of
312 aircraft measurements show that northern hemisphere boundary layer 1,2-DCE
313 concentrations appear to be ~10-20 ppt (REF²⁵), with this compound contributing 5-15 pptCl
314 to stratospheric chlorine²⁷.

315

316 [H3] VSLS atmospheric chlorine contribution

317 The principal VSLS (CH_2Cl_2 , $CHCl_3$, C_2Cl_4 , C_2HCl_3 , CH_2ClCH_2Cl) are estimated to have
318 provided a total of 69 (55-83, ± 1 standard deviation) pptCl to the stratosphere in 2000,
319 increasing to 111 (89-133) pptCl in 2017, based on measured surface concentration changes
320 incorporated into a global model study²⁷. This contribution represents ~3.5% of total
321 stratospheric chlorine. A similar best estimate of 115 (75–160) pptCl for the year 2016 was
322 reported in the 2018 WMO/UNEP Ozone Assessment²⁵. Both estimates include the chlorine
323 delivered to the stratosphere from the VSLS themselves (source gas injection), accounting for
324 around 80% of the total, and from the fraction of their degradation products containing chlorine
325 that also reach the stratosphere (product gas injection or PGI). In addition to surface
326 measurements, direct observational evidence for an increase in chlorine source gas injection
327 is also provided by measurements of VSLS (primarily DCM) in the upper troposphere and
328 lower stratosphere over the last two decades⁵⁷. In contrast, surface or aircraft observations
329 alone provide limited means to constrain the magnitude of chlorine PGI, thus the estimated
330 contribution is model-based and includes large uncertainty. This uncertainty arises because
331 the atmospheric concentrations of VSLS degradation products, including hydrogen chloride
332 (HCl) and phosgene ($COCl_2$), are also products in the oxidation of non-VSLS chlorocarbons.

333 For example, phosgene is a degradation product of long-lived CCl_4 and CH_3CCl_3 , in addition
334 to several VSLs. Phosgene concentration trends over the 8-30 km altitude range derived from
335 satellite data, were negative between 2004 and 2016, in keeping with the expectation that
336 phosgene concentrations should decline in response to ongoing decreases in the atmospheric
337 concentration of its long-lived precursors. However, positive phosgene concentration trends
338 have been observed in the upper troposphere, and the sign of this trend is reproduced by
339 global models only when the measured increases in VSLs are considered. Taken together,
340 these observations provide some evidence for an increase in stratospheric chlorine from VSLs
341 degradation products since the mid-2000s⁵⁸.

342
343 Analysis of ground-based and satellite HCl measurements are used to evaluate changes in
344 stratospheric inorganic chlorine over time^{59,60}; the major source of HCl is degradation of the
345 long-lived chlorinated ODSs. In the upper stratosphere (≥ 10 hPa, ~ 30 km), measurements
346 from the ACE-FTS instrument show that HCl (60°S to 60°N) declined at a rate of around -0.5%
347 per decade between 2004-2017^{25,61}. Over the same period, increases in stratospheric chlorine
348 from VSLs may have slowed the rate of HCl decline. **Fig. 3** compares HCl trends from a 3-D
349 chemical transport model with and without chlorinated VSLs. It is evident that large interannual
350 dynamical variability confounds HCl trend analysis, particularly in the lower stratosphere,
351 where trends are most uncertain. In the upper stratosphere, where trends are less influenced
352 by dynamical variability, it is estimated that increases in VSLs reduced the rate of HCl decline
353 by $\sim 15\%$ between 2004 and 2017. This modest offset may partly explain some of the
354 systematic difference between observed HCl trends and models which do not consider
355 VSLs⁶². Furthermore, it implies that anthropogenic VSLs are offsetting some of the benefits
356 of the Montreal Protocol.

357

358 **[H2] Natural VSLs**

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

362

363 The most abundant brominated VSLs are bromoform (CHBr_3) and dibromomethane
364 (CH_2Br_2), which are largely produced in tropical, subtropical, and shelf regions of the ocean^{64,65}
365 (**Fig. 4**). However, they do also have some small anthropogenic sources (see section on
366 Bromocarbon Production). Natural production of CHBr_3 involves marine organisms such as
367 macroalgae and phytoplankton⁶⁶, while CH_2Br_2 is co-formed and its concentration correlates
368 with CHBr_3 in water and air⁶⁷. Within the first several months after these VSLs are emitted to
369 the atmosphere, they can be photochemically oxidised or react with hydroxyl radicals, and

370 contribute to the pool of reactive atmospheric bromine⁶⁸. Reactive bromine participates in the
371 depletion of ozone by catalytic cycles and can thus impact tropospheric and stratospheric
372 ozone chemistry.

373

374 The ODP-weighted bromine emissions of bromoform (120–820 Gg Br yr⁻¹) currently amount
375 to approximately 20% (REF⁶⁹) of those from total halons and methyl bromide. These estimates
376 carry large uncertainty due to the spatiotemporal variability of VSLs emissions^{70,71}, which are
377 driven by changes in primary productivity, biogeochemical cycling, sea surface temperature,
378 and meteorology. Upper atmospheric abundances are similarly heterogeneous, due to the
379 combined effects of highly variable emissions and highly variable atmospheric transport
380 timescales with fastest uplifts in deep convective events^{72,73}. A recent update⁷⁴ of the
381 measurement-based bromoform and dibromomethane emission estimates (update of ⁷⁵)
382 shows enhanced emissions in the tropical Indian Ocean and subtropical northern Atlantic in
383 addition to the known elevated emissions along the coastlines and in upwelling regions (**Fig**
384 **4**). For the west Indian Ocean, updated bromoform emissions are almost twice as large a
385 previous estimates and can reach the stratosphere via two transport pathways; locally through
386 convection and in the south-eastern part of the Asian monsoon anticyclone⁷¹ highlighting this
387 area as a potentially important source region.

388

389 In total, brominated VSLs—including bromoform and dibromomethane, as well as other
390 minor natural species chlorodibromomethane (CHBr₂Cl), bromochloromethane (CH₂BrCl) and
391 bromodichloromethane (CHBrCl₂)—are estimated to contribute 5 (uncertainty range 3-7) pptBr
392 (~26%) to stratospheric inorganic bromine (Br_y) in 2016 (REF^{25,76}). This range is based on a
393 combination of high-altitude aircraft measurements of source gases around the tropical
394 tropopause and model calculations of bromine product gas injection^{25,76}. There is no evidence
395 for a long-term change in this contribution, as variations (an increase followed by current
396 decrease) in total stratospheric bromine have been driven by trends in methyl bromide and
397 halons²⁵, with brominated VSLs providing a constant contribution. While natural brominated
398 VSLs currently have a relatively minor impact on stratospheric ozone compared to
399 anthropogenic halogens, their oceanic production, air-sea fluxes, as well as atmospheric
400 lifetimes and transport pathways are sensitive to climate parameters that may change in the
401 future^{72,73}.

402

403 In summary, emissions of long-lived ODSs have decreased dramatically over the past few
404 decades due to their phase-out by the Montreal Protocol, leading to unequivocal detection of
405 ozone layer recovery. However, the recently discovered increase in global emissions of CFC-
406 11 is a concern. Moreover, some anthropogenic chlorinated VSLs emissions, which together

407 contribute around 3% to stratospheric chlorine and are not subject to the Protocol, are
408 increasing due to industrial production for solvent and feedstock uses. Additionally, the ozone
409 influence of natural sources of bromine contained in short-lived gases, which contributes
410 around 26% to the current stratospheric bromine loading, is becoming better constrained
411 through increased sampling and improved modelling.

412

413

414 **[H1] Current production of ODSs**

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

419

420 **[H2] Chlorocarbon production**

421 Chlorinated C₁ and C₂ hydrocarbons are produced extensively, both as chemical
422 intermediates and as solvents for the pharmaceutical and electronics industries as well as in
423 metal and apparel cleaning. Long-lived substances such as carbon tetrachloride (CTC, CCl₄)
424 and methyl chloroform (MCF, CH₃CCl₃) are globally no longer used as solvents, because they
425 are ODSs and have been phased-out under the Montreal Protocol. On-going emissions of
426 uncontrolled, shorter-lived chlorocarbons to the atmosphere are due to fugitive emissions from
427 solvent uses, emissions from production plants (which are inevitable) and feedstock
428 production losses during production of other substances (such as HCFCs and HFCs) (**Fig. 5**).

429

430 The group of chlorinated C₁ hydrocarbons (chloromethanes) is composed of methyl chloride,
431 (CH₃Cl), DCM (CH₂Cl₂), chloroform (CHCl₃) and CTC (CCl₄). Methyl chloride is used as a
432 chemical intermediate in the silicone industry and in the production of CH₂Cl₂, CHCl₃ and CCl₄
433 in a variety of smaller uses, such as methyl cellulose production. The production of methyl
434 chloride, virtually all by the addition of HCl to methanol, is usually conducted on the site where
435 it will be processed. Emissions of methyl chloride are negligible compared to its large natural
436 emissions²⁵. The chlorination of methyl chloride inevitably produces the higher
437 chloromethanes DCM, chloroform and CTC (**Fig. 5**). Of the estimated 1162 Gg of DCM
438 produced in 2016, 85% (988 Gg) is calculated to have been emitted by solvent applications
439 (assuming that 100% of the amount used as solvent is emitted within the year), and 15% (174
440 Gg) was used as feedstock in the production of HFC-32. By contrast, more than 95% of the
441 estimated 1472 Gg of chloroform produced in 2016 was consumed as feedstock in the
442 production of HCFC-22, and only 54 Gg emissions arose from solvent uses, most typically
443 from pharmaceutical manufacture. These emissions are considerably smaller than natural

444 emissions. Until 2010, global emissions were stable at around 300 Gg yr⁻¹ or less. However,
445 in the recent years an increase of around 50 Gg yr⁻¹ has occurred²⁵, which could mostly be
446 related to emissions from eastern China⁴⁵. It is unclear if these emissions are due to solvent
447 use or, less likely, emissions from feedstock use.

448
449 The estimated 203 Gg of CTC produced in 2016 was, in addition to the co-production from
450 chloromethane plants, also made on-demand in perchloroethylene (PCE)-CTC reactors.
451 Produced amounts were used as feedstock for the production of HFC-245fa, HFC-365mfc,
452 HFO-1233xd, HFO-1234yf, and HFO-1234ze as well as of synthetic pyrethroids such as
453 cypermethrin. An additional important use of CTC is its conversion into PCE. If CTC cannot
454 be consumed by industrial feedstock use, it must be destroyed by permitted processes. It is
455 estimated that most of the CTC produced in 2016 was consumed as feedstock and the
456 balance incinerated, with bottom-up emissions from all sources calculated at 15 Gg (REF⁷⁷).

457
458 The group of chlorinated C₂ hydrocarbons includes perchloroethylene (PCE, C₂Cl₄),
459 trichloroethylene (TCE, C₂HCl₃), and MCF (CH₃CCl₃). Global production of PCE was
460 estimated to be 405 Gg in 2016 (NSA data), of which 200 Gg was used in emissive solvent
461 applications and the balance of 205 Gg being used as chemical intermediate, mainly to CFC-
462 113 and CFC-113a and their further derivatives, such as HFC-134a, HFC-125 and
463 chlorotrifluoroethylene (CTFE) monomer. TCE production was estimated at 465 Gg in 2016
464 (based on Nolan Sherry & Associates, or NSA, data), with 340 Gg being used as chemical
465 intermediate mainly to HFC-134a, and the balance of 125 Gg being used in emissive solvent
466 applications. MCF is produced in Europe and USA, solely for feedstock use for the production
467 of HCFC-141b, HCFC-142b, and HFC-143a, with an estimated quantity of 95 Gg in 2016 (NSA
468 data), and the related MCF emissions due to these applications are thought to be less than
469 1%.

470
471 In summary, the current (2020) outlook for use of these C₁ and C₂ chlorocarbons is as follows.
472 The use of DCM as a solvent (resulting in emissions) is thought to be stable to increasing, and
473 its feedstock use in the production of HFC-32 is also increasing. The small solvent use of CFM
474 is stable to decreasing. Its use as an intermediate in the production of HCFC-22 (used in air
475 conditioners) should see a short-term fall due to restrictions in the Montreal Protocol. In the
476 long-term, usage of CFM will likely increase as the use of HCFC-22 as chemical intermediate
477 is expected grow. CTC is only used as an intermediate, which is increasing due to growing
478 HFO production. MCF production is also growing: use in HFC-143a production is believed to
479 have stopped, but its use in HCFC-142b production is increasing, as HCFC-142b is further
480 processed to vinylidene fluoride-based polymers for electronics. There are different routes to

481 produce HCFC-142b without using MCF, such as vinylidene chloride. Solvent use of PCE is
482 thought to be stable to declining, with its feedstock use to HFC-125 and HFC-134a also
483 declining. Finally, both TCE solvent and feedstock uses appear to be declining.

484

485 **[H2] Bromocarbon production**

486 In addition to their natural origin, brominated VSLs such as bromoform, which are not
487 controlled by the Montreal Protocol, have various industrial sources such as cooling units,
488 desalination plants, ballast and waste water treatment, and seawater toilets. In order to limit
489 biofouling and minimise the survival of organisms, marine water is normally disinfected when
490 used by industry. Chemical disinfection techniques such as chlorination and ozonisation
491 produce a variety of disinfection by-products with bromoform being the main by-product⁷⁸. The
492 magnitude of bromoform produced during disinfection can vary strongly depending on
493 processing method⁷⁹, application, and chemical water characteristics. When the treated water
494 is released, it will spread in the marine environment and is emitted into the atmosphere⁸⁰.
495 Atmospheric measurements cannot readily distinguish between naturally and industrially
496 produced bromoform, making it difficult to measure large-scale bromine emissions from ballast
497 water and assess their impact on the ozone layer.

498

499 In treated ship ballast water, an average bromoform concentration of $226 \pm 142 \mu\text{g L}^{-1}$ can be
500 expected, which is up to a million times higher than abundances found in the natural
501 environment⁸⁰. If all ballast water in the Rotterdam port, for instance, was treated via
502 chlorination and ozonisation, modelling suggests that bromoform concentrations in the inner
503 harbour waters would be up to $0.4 \mu\text{g L}^{-1}$, which is about 100-1000 times higher than typical
504 near-shore concentrations. However, model-based estimates show that the total bromine
505 emissions from ballast water is likely too small to be important globally⁸⁰.

506

507 Bromoform concentrations in treated cooling waters such as power plants with $60 \pm 40 \mu\text{g}$
508 $\text{CHBr}_3 \text{ L}^{-1}$ are considerably smaller than in treated ballast water⁸¹. Despite the smaller
509 concentrations, anthropogenic bromine from industrial cooling water can be expected to be
510 more important, as the total amount of water used is around 200 times larger. For instance, in
511 coastal areas where these cooling waters are dumped, bromoform concentrations range
512 between 0.5 and $50 \mu\text{g L}^{-1}$ (REFS^{81,82}). For South-East Asia alone, anthropogenic emissions
513 are on average 24 Gg Br yr^{-1} (REF⁸³), which is 30% more than the measurement-based
514 estimate of total emission derived for the same region (18 Gg Br yr^{-1} ; from REF⁷⁴, Fig. 4).

515

516 The final anthropogenic source of brominated VSLs production discussed here is commercial
517 seaweed farming. In Southeast Asia, where substantial amounts of seaweed are cultivated,

518 current estimates suggest only minor contributions of aquaculture to total VSLS emissions, for
519 example 2% of bromoform from farmed seaweed compared to natural seaweed in Malaysia⁸⁴.
520 However, projected increases in coastal aquaculture as well as their potential farming in the
521 open ocean in future climate mitigation could substantially increase the brominated VSLS
522 contribution⁸⁴. Thus, potential VSLS emissions from seaweed cultivation should be further
523 investigated for climate change mitigation and food production scenarios that rely on
524 aquaculture.

525

526

527 **[H1] Outlook for the future**

528

529 The Montreal Protocol has resulted in decreased ODS emissions and initial recovery of the
530 ozone layer. Given full compliance, and all else being constant, the ozone layer should return
531 to 1980 levels around the mid- 21st century²⁰. However, due to the new and renewed concerns
532 associated with ODS production and emission discussed in this Review, the ozone layer might
533 recover at a slower rate than originally anticipated. In this final section, we consider future
534 expected trends in ODS and VSLS emissions and their implications for the timescale of ozone
535 layer recovery.

536

537 **[H2] Future ODS and VSLS emissions**

538 Future emissions of ODSs will depend on further regulation, compliance, industrial, and
539 environmental factors, making them difficult to predict confidently. However, modelling
540 approaches can provide some insight into what might be expected in the near future, and how
541 these might impact ozone recovery⁸⁵⁻⁸⁷. For example, if one of the most concerning ODS
542 trends, the increase in CFC-11 emissions, continues unabated then by 2060 another 180 pptCl
543 would be added to the atmosphere above the amounts expected (~3000 pptCl; [Fig. 1](#)), if all
544 controls in the Montreal Protocol had been followed⁸⁵ ([Fig. 6](#)). This extreme scenario, while
545 unlikely, would delay the return of the Antarctic ozone hole to 1980 levels by approximately
546 ten years, to ~2060⁸⁵. Similarly, continued chlorinated VSLS emissions (which are allowed
547 under the protocol) could slow the healing of the ozone layer. For instance, eliminating some
548 of the anthropogenic VSLS contributions to stratospheric chlorine would advance the ozone
549 return date by about 1 year for each 17 pptCl reduction compared to business as usual
550 emissions⁸⁵.

551

552 In addition to non-compliant CFC-11 and uncontrolled VSLS emissions, demand for carbon
553 tetrachloride is expected to increase by well over 50% by 2025, in comparison to the 203 Gg
554 produced in 2016 (REF^{77,88}) as more HFOs (which replace many HCFCs and HFCs) are

555 produced using CTC as a feedstock. The increased demand will likely lead to higher emissions
556 from this production⁸⁹. Chloroform emissions, as well, could increase with any increased use
557 as feedstock for HCFC-22. Increased emissions of these chlorocarbons would delay the ozone
558 return date in relation to how much enhanced chlorine is delivered to the stratosphere, as
559 discussed above.

560

561 Finally, future natural ODS emissions and atmospheric transport might be influenced by
562 climate change, though long-term changes are yet to be observed. For example, increases in
563 biomass burning could add to the methyl bromide concentration in the atmosphere.
564 Additionally, ocean acidification, changing sea-ice extent, changing ocean primary production
565 and varying meteorological conditions at the ocean surface could influence production of
566 methyl bromide or brominated VSLS in the ocean and their emissions into the atmosphere^{90,91}.
567 Investment in large-scale macroalgae farming could result in increased VSLS emissions,
568 especially if located in the tropics⁸⁴. Climate-driven changes of the tropospheric oxidising
569 capacity would affect lifetimes of CH₃Br and VSLS⁷³, while dynamical changes would affect
570 the troposphere–stratosphere transport of VSLSs and thus their contribution to the
571 stratospheric halogen budget⁹². The net ozone impact of these possible future changes
572 depends on the sensitivity of these processes to changes in climate, and are largely
573 uncharacterised. The emergence of Earth system models that include accurate
574 representations of comprehensive ocean biogeochemistry and stratospheric chemistry could
575 provide further constraints in coming years, although observationally-derived improvements
576 in our understanding of these systems and their feedbacks are also needed.

577

578 ***[H2] Ensuring timely ozone recovery***

579 It is clear that the phase-out of ODS production has overall been an international success.
580 Also important in ensuring that the ozone layer ultimately recovers, however, was the early
581 detection of newly increased CFC-11 emissions, which was a triumph for atmospheric
582 monitoring because it involved detecting a small slowdown in the atmospheric concentration
583 decline. Furthermore, the existing network enabled an indication of which region was
584 contributing to the unexpected emissions^{22,93}, which is information critical for enabling the
585 mitigation of the illicit production. However, there are key research needs that would facilitate
586 a timely recovery of the ozone layer. One such need is improved observational networks and
587 modelling capabilities to monitor and assess progress, as current capabilities, although they
588 have improved greatly in recent years, are still limited in ways that hamper effective and rapid
589 mitigation. This improvement will allow more accurate attribution of atmospheric observations
590 to specific emission locations. Moreover, the anticipated controls on greenhouse gases, in
591 addition to the current ODS controls, will put more demands on compliance monitoring as the

592 most abundant greenhouse gases have a wider variety of sources, source distributions, and
593 sinks than the ODSs. Such progress can be achieved through ongoing and major
594 enhancements in our scientific capabilities to observe and understand changes in our
595 atmospheric environment, such as better spatially resolved observations and high resolution
596 modelling. Finally, there are specific, immediate needs to determine the location of the
597 increased CFC-11 emissions originating outside of eastern China²².

598

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

612

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860 **Related links**

861 Advanced Global Atmospheric Gases Experiment (AGAGE) monitoring network:

862 <https://agage.mit.edu/>

863 National Aeronautics and Space Administration Ozone Watch:

864 <https://ozonewatch.gsfc.nasa.gov/>

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

867 United Nations Environment Programme. <https://www.unenvironment.org/>

868 United Nations Environment Programme Ozone Country Data.

869 <https://ozone.unep.org/countries/data-table>

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

872

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878 All authors contributed to all aspects of the article.

879

880 **Competing Interests**

881 The authors declare no competing interests.

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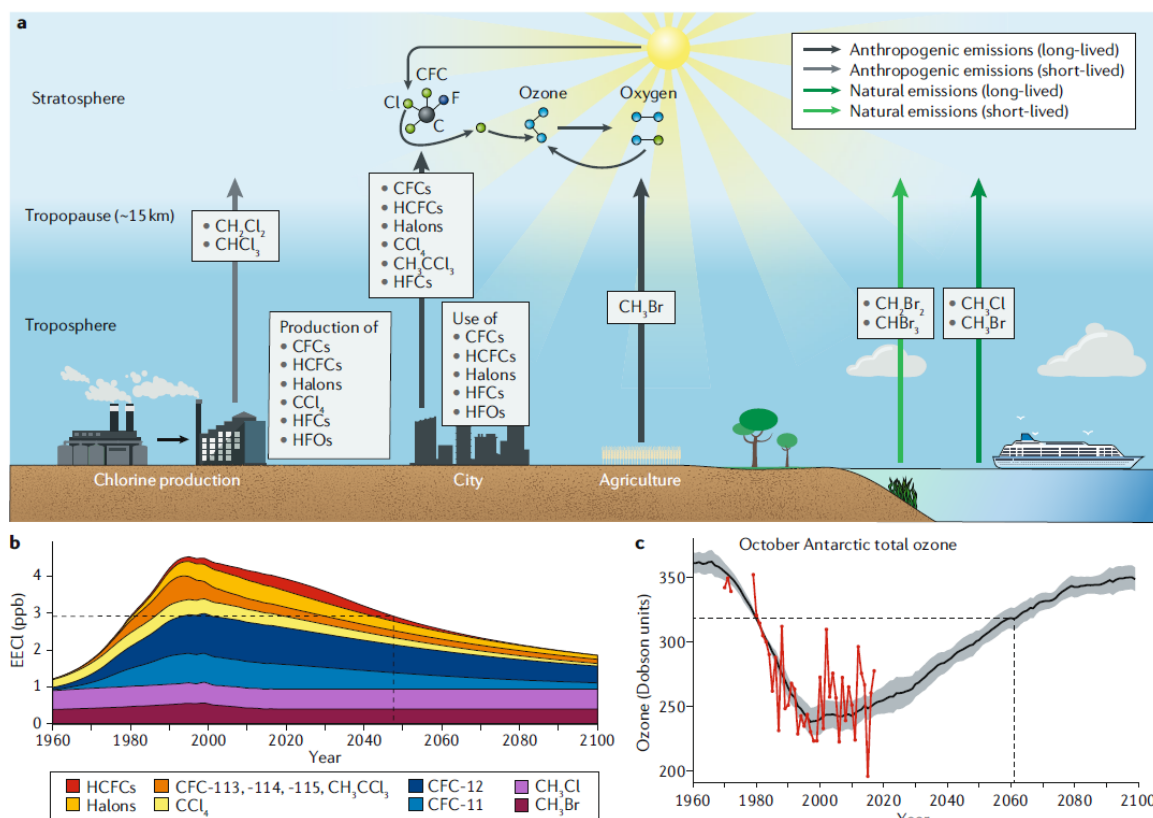
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892 **Supplementary information**

893 Supplementary information is available for this paper at [https://doi.org/10.1038/s415XX-XXX-](https://doi.org/10.1038/s415XX-XXX-XXXX-X)
894 [XXXX-X](https://doi.org/10.1038/s415XX-XXX-XXXX-X)

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898

899 **Figure 1. Halogenated source gases and their impact on stratospheric ozone. a|**

900 Anthropogenic (black and grey arrows) and natural (green arrows) sources of long-lived and

901 short-lived ozone depleting substances. The majority of long-lived Ozone Depleting

902 Substances (ODSs) reach the stratosphere, where they are photochemically decomposed,

903 liberating halogens that destroy ozone (O_3). Short-lived substances largely decompose in the904 troposphere and only a fraction of the emissions reaches the stratosphere. **b|** Past

905 observations and projections of equivalent effective chlorine (EECl; total chlorine + 65xtotal

906 bromine at surface, ppb) from different long-lived ODSs between 1960 and 2100. After the

907 signing of the Montreal Protocol and subsequent phase-out of many long-lived ODSs, EECl

908 began to decline and is expected to return to 1980 levels by around 2050, as indicated by the

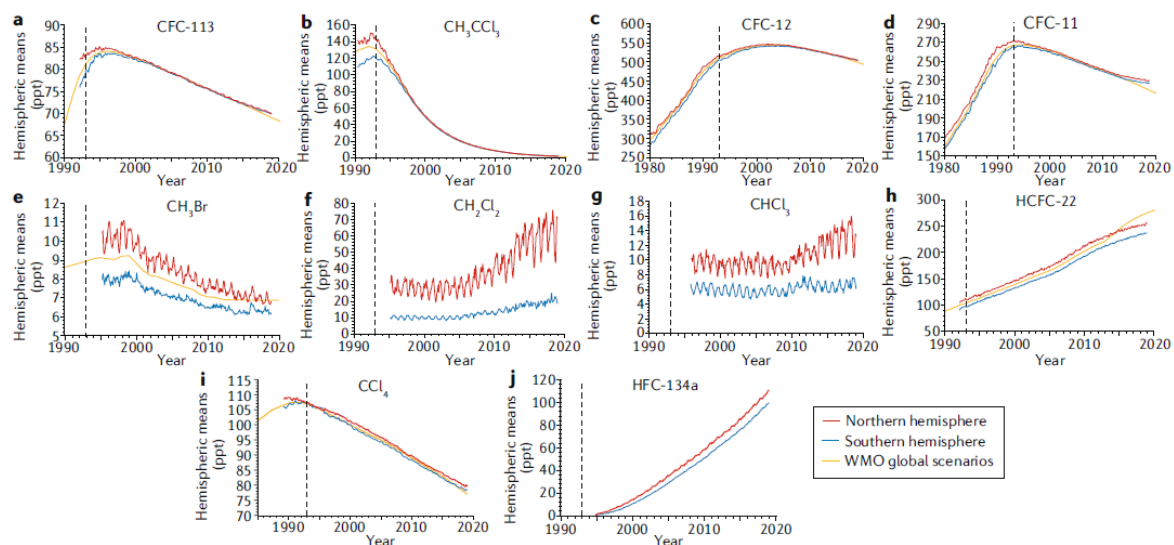
909 horizontal and vertical dashed lines. **c|** Measured (red line) and predicted (black line, with

910 uncertainty shown as grey shading) for Antarctic October column ozone (Dobson Units; DU)

911 between 1960 and 2100. The Antarctic ozone layer is expected to return to 1980 levels around

912 2060, around a decade later than EECl (horizontal and vertical dashed lines).

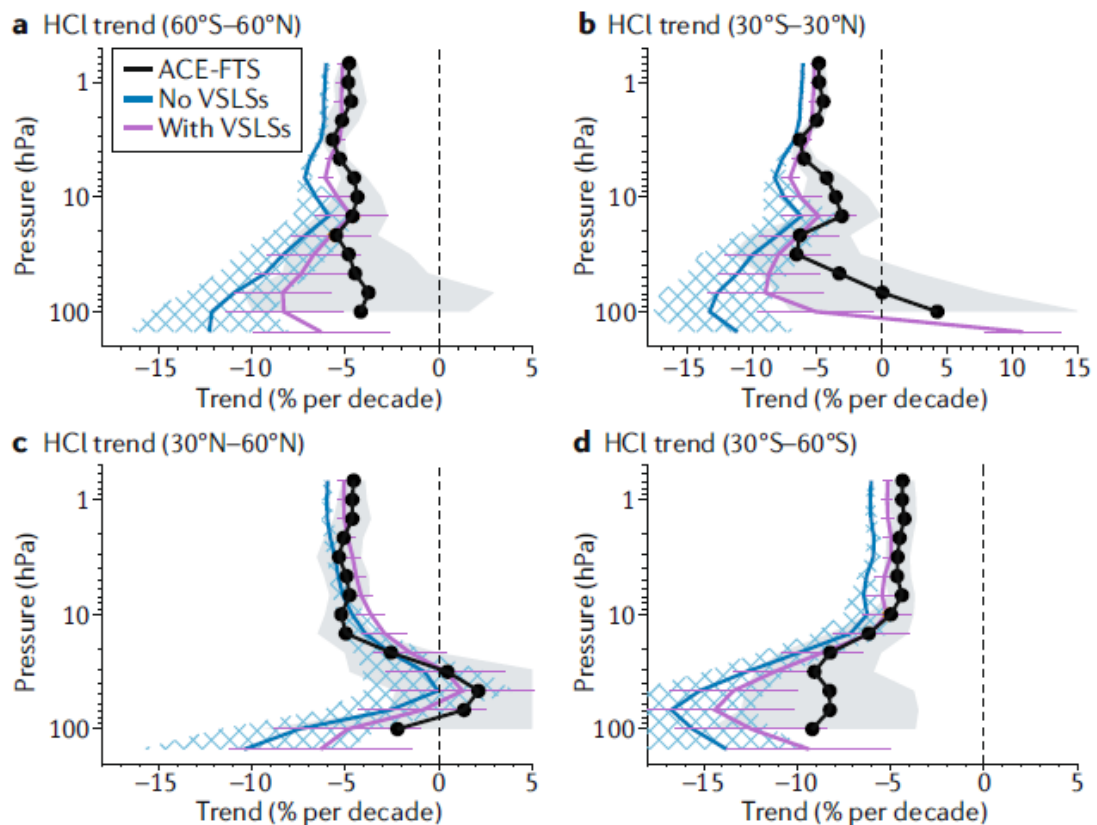
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915 **Figure 2. Atmospheric concentrations of selected halogenated gases over time.**

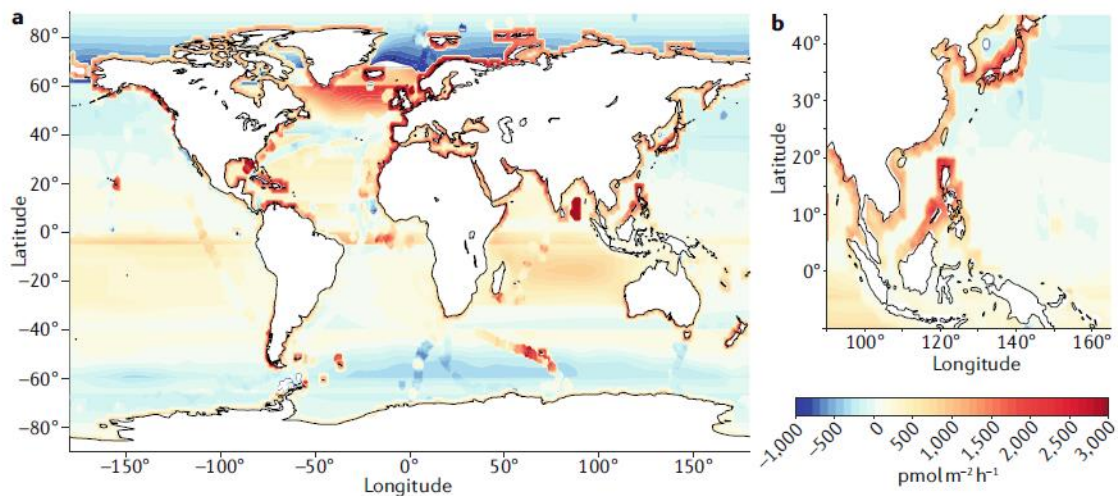
916 Hemispheric mean concentrations (or mole fractions, as parts per trillion, or ppt; northern
 917 hemisphere in red, southern hemisphere in blue) of long-lived ozone-depleting substances
 918 (ODSs; a-e, h, i), two very short-lived substances (VSLs; f, g), and a substitute HFC (j). a-j
 919 CFC-113, methyl chloroform (CH_3CCl_3), CFC-12, CFC-11, methyl bromide (CH_3Br),
 920 dichloromethane (DCM, CH_2Cl_2), chloroform (CHCl_3), HCFC-22, carbon tetrachloride (CCl_4),
 921 and HFC-134a concentrations through time. All surface means are derived from NOAA
 922 measurements at 4 to 12 remote sites using in-situ and flask collection techniques^{11,27,44}.
 923 These results, along with those from an independent global network¹², form the basis for WMO
 924 scenario records of global concentration changes for Montreal Protocol-controlled substances
 925 for years prior to 2014 (yellow lines on long-lived ODS panels; REF³⁴). These scenario results
 926 are projected into the future based on historical data for production, emissions, and bank
 927 reservoirs, and existing production controls. Although an updated scenario analysis is
 928 available⁹⁴, the older scenario is used here to understand observed vs expected concentration
 929 changes since 2014. The year that tropospheric chlorine from long-lived ozone-depleting
 930 gases peaked¹¹ (dashed black line) is provided for reference given that the time-scale differs
 931 in the panels. Most ODSs are decreasing over time due to phase out. However, the very short-
 932 lived species, DCM and chloroform, both increased during this time period, as did HCFC-22.
 933



935

936 **Figure 3. Impact of chlorinated VSLs on stratospheric HCl trends. a-d|** Mean HCl trends
 937 (2004-2017) calculated for latitude bands 60°S-60°N, 30°S-30°N, 30°N-60°N, and 30°S-60°S.
 938 Modelled HCl trends (% decade⁻¹) with and without very short-lived substances (VSLs) are
 939 from the TOMCAT 3-D chemical transport model⁹⁵. For the long-lived chlorine source gases
 940 the model used global mean surface mixing ratios based on observations⁹⁶. Observed HCl
 941 trends are derived from the ACE-FTS satellite instrument⁶¹. 2 σ trend errors denoted by
 942 horizontal bars, shading and grating. The panels show that the inclusion of VSLs increases
 943 the HCl trend, especially in the lower stratosphere, bringing the model into better agreement
 944 with the observations. The observed HCl trend is also affected by atmospheric dynamical
 945 variability, leading to a positive trend in northern mid-latitudes and tropics, compared to the
 946 expected negative trend elsewhere⁹⁷.

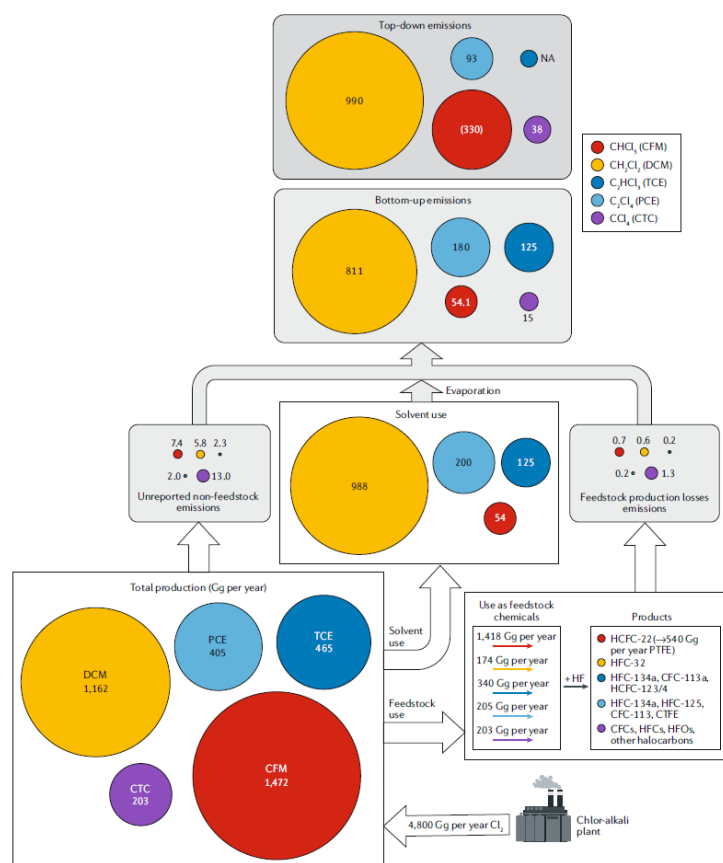
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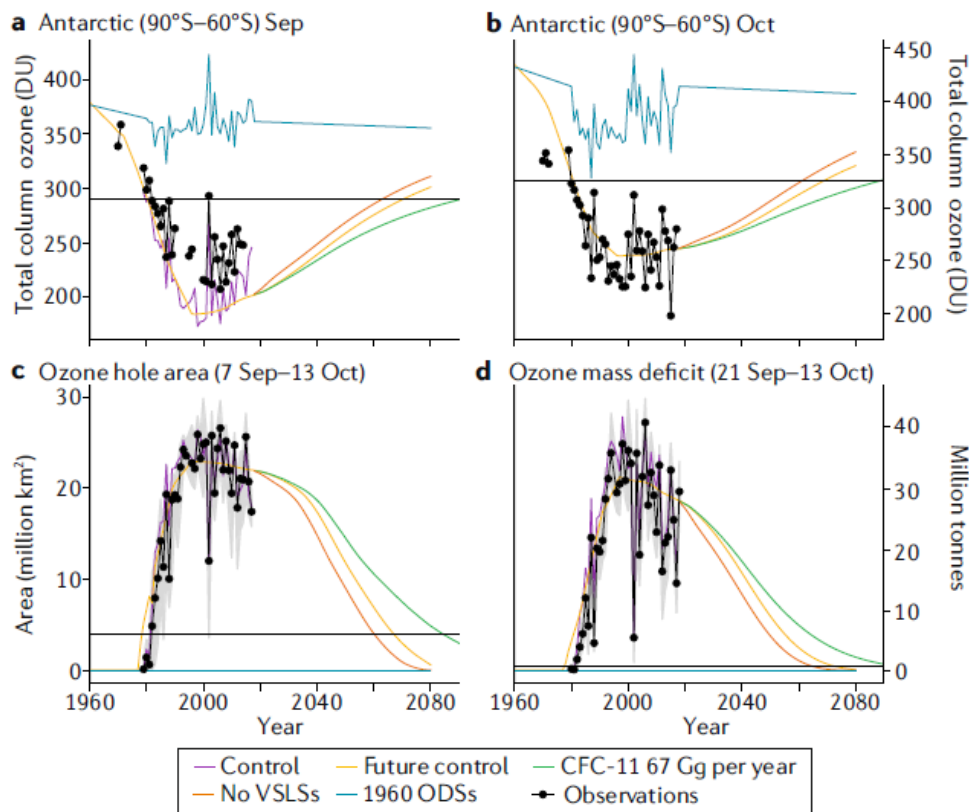
950 **Figure 4. Total and anthropogenic bromoform emissions from the oceans. a,b)** Global
 951 bromoform (CHBr_3) emissions are shown for global and East and South-East Asia regions⁷⁴
 952 based on a recent update of measurement-based emission estimates⁷⁵. Both panels use the
 953 same colour scale. In addition to the known elevated emissions along the coastlines and in
 954 upwelling regions, enhanced emissions in the tropical Indian Ocean and subtropical northern
 955 Atlantic have been identified. For the west Indian Ocean, updated bromoform emissions
 956 almost double and can reach the stratosphere via two transport pathways; locally through
 957 convection and in the south-eastern part of the Asian monsoon anticyclone⁷¹ highlighting this
 958 area as a potentially important source region.

959



961
 962 **Figure 5. Production of chlorine-containing compounds.** Chlorine (Cl₂) from chlor-alkali
 963 plants is combined with methanol (CH₃OH) to produce various chlorocarbons. Emissions of
 964 these chemicals can occur during their production (unreported non-feedstock emissions); their
 965 use as solvents; and their use as feedstock chemicals for chlorofluorocarbons (CFCs; no
 966 longer permitted), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs),
 967 hydrofluoroolefins (HFOs) and other halogenated chemicals. Production or emissions
 968 processes are shown as arrows, with estimated amounts (Gg yr⁻¹) for 2016 shown when
 969 available. White-filled arrows indicate use; grey-filled arrows indicate emissions. Circles are
 970 colour coded by chlorocarbon type and show either total production numbers or emissions.
 971 Grey background shading denotes emissions. Global bottom-up emissions estimates for 2016
 972 are derived from production magnitudes, and top-down emission values for 2016 are derived
 973 from global atmospheric measurements. Note that total bottom-up emissions do not equal the
 974 sum of all contributions because many countries enforce incineration of spent solvents,
 975 especially in pharmaceutical uses, leading to lower reported emissions. This figure excludes
 976 an additional 10 Gg yr⁻¹ carbon tetrachloride (CCl₄) suspected to arise from legacy emissions
 977 and from other industrial chlorination processes such as ethylene dichloride and allyl chloride
 978 production.

979



981

982 **Figure 6. Antarctic ozone and metrics quantifying ozone loss as a function of additional**
 983 **CFC-11 and VSLs emissions. a,b|** Mean column ozone (in Dobson Units, DU) averaged
 984 from 90°S – 60°S for September and October from five TOMCAT 3-D model^{95,98,99} simulations:
 985 Control (varying meteorology), future control (2000 meteorology), with constant 67 Gg yr⁻¹
 986 emissions of CFC-11, with no chlorinated very short-lived substances (VSLs) and with 1960
 987 levels of ozone-depleting substances (ODS), as well as NASA Solar Backscatter Ultraviolet
 988 instrument observations from 1960 to 2090. **c,d|** Estimates of the size of the Antarctic ozone
 989 hole under control, future control, 67 Gg yr⁻¹ CFC-11 emissions, no VSLs, and 1960 levels of
 990 ODS simulations, and observations (based on NASA Ozone Watch information) using **(c)** the
 991 area contained within the 220 DU contour ($\times 10^6$ km²) (averaged September 7 – October 13),
 992 and **(d)** ozone mass deficit ($\times 10^6$ tonnes) (averaged September 21 – October 13). The panels
 993 show that additional emission of CFC-11 at the level assumed will delay recovery of the
 994 Antarctic ozone hole, meaning a delay in the date of return to 1980 values of around 10 years.
 995 Similarly, elimination of chlorinated VSLs emissions will speed up the ozone return by around
 996 6 years.

997

998 **Glossary**

999

1000 Bank Reservoir of produced ODSs stored in equipment or materials and not
1001 yet released to atmosphere.

1002 Controlled ODS included in the Montreal Protocol for limits on consumption and
1003 production

1004 Fluorination Reaction of a feedstock with a fluorine-containing compound to
1005 produce a required substance.

1006 Lifetime Measure of the removal rate (e-folding time) of emitted species by
1007 atmospheric processes.

1008 Non-emissive Application that does not lead to the immediate and direct emission of
1009 ODS.

1010 Ozone-depleting substance (ODS) A man-made gas that causes ozone depletion once it
1011 reaches the stratosphere.

1012 Ozone depletion potential (ODP) Relative amount of ozone loss caused by emission of
1013 1 kg of a substance compared to emission of 1 kg of CFC-11.

1014 Stratosphere Layer of atmosphere (approximately 15–50 km).

1015 Troposphere Layer of atmosphere (surface to approximately 15 km).

1016 Uncontrolled ODS not included in Montreal Protocol for limits on production and
1017 consumption.

1018 Very short-lived substance (VSLS) Substance with an atmospheric lifetime of <0.5 year.

1019