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Martyn P Chipperfield, Slimane Bekki

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1 **Opinion: Stratospheric Ozone – Depletion, Recovery and New**

2 **Challenges**

3 Martyn P. Chipperfield^{1,2} and Slimane Bekki³

4 ¹School of Earth and Environment, University of Leeds, LS2 9JT, UK

5 ²National Centre for Earth Observation, University of Leeds, Leeds LS2 9JT, UK

6 ³LATMOS/IPSL Sorbonne Université, UVSQ, CNRS, 75005 Paris, France

7 *Correspondence to:* Martyn P. Chipperfield (M.Chipperfield@leeds.ac.uk)

8 **Abstract.** We give a personal perspective on recent issues related to the depletion of stratospheric ozone and some newly
9 emerging challenges. We first provide a brief review of historic work on understanding the ozone layer where we highlight
10 some work from the late Paul Crutzen as a contribution to the special issue in his honour. We then review the status of ozone
11 recovery from the effects of halogenated source gases and discuss the undoubted effectiveness of the Montreal Protocol and
12 its challenges from renewed production of controlled substances and short-lived uncontrolled substances. We then discuss, in
13 some detail, the recent observations of ozone depletion through injection of smoke particles from Australian fires in early
14 2020. Further unexpected perturbations to the ozone layer are occurring at the moment through injection of very large amounts
15 of water vapour (and some sulphur dioxide) from the Hunga Tonga-Hunga Ha`apai volcano in January 2022. We conclude
16 with some thoughts on the urgent need to ensure continuity in observations and on how to exploit ever more complex and
17 expensive models. Overall, the stratospheric ozone layer continues to produce novel research challenges and reveal more
18 processes that threaten this essential component of the Earth system.

19 **1 Introduction**

20 Depletion of the stratospheric ozone layer has been a major environmental issue of the past few decades, especially since the
21 discovery of the Antarctic ozone hole in 1985 (Farman et al., 1985). The observed depletion at middle and high latitudes has
22 been caused by increasing abundances of chlorine and bromine species, which are derived from long-lived surface-emitted
23 halogenated gases, so-called ozone-depleting substances (ODSs). A primary reason for concern is that the ozone layer prevents
24 harmful, biologically damaging ultraviolet (UV) radiation (wavelengths below about 300 nm) from reaching the surface. This
25 radiation can, among other impacts, cause skin cancer in humans and can be damaging to plants. Ozone not only absorbs UV
26 radiation, heating up the stratosphere, but also interacts with terrestrial infrared (IR) radiation. As such, it plays a key role in
27 determining the temperature structure of the atmosphere. Hence, changes in the ozone layer can also affect surface climate,
28 and moreover the long-lived ODSs, such as chlorofluorocarbons (CFCs), themselves are also potent greenhouse gases (Velders
29 et al., 2007).

30
31 The Montreal Protocol on Substances that Deplete the Ozone Layer was signed in 1987 and ratified two years later. With
32 several subsequent amendments, the Protocol now controls (limits) the production and consumption of all major long-lived
33 ODSs, which are ultimately emitted to the atmosphere. The atmospheric abundances of these species have responded to these
34 controls; the stratospheric levels of chlorine and bromine peaked in the 1990s and are now slowly declining. In consequence,
35 an increase (‘recovery’) of stratospheric ozone has been detected in the upper stratosphere and the Antarctic, although the
36 signal is currently small and is difficult to separate from other atmospheric influences. A common measure of recovery is the
37 date at which stratospheric ozone values are predicted to return to 1980 levels, before the occurrence of large depletion. This



38 return will also be affected by other factors, notably climate change (see **Section 4**). Models predict that this will occur around
39 the middle of this century (e.g. Dhomse et al., 2018), although there are limitations using this simple measure of the timing of
40 a specific event for quantifying the ongoing process of recovery. Accordingly, the Montreal Protocol (MP) is arguably the
41 most successful international environmental treaty to date. However, recent discoveries related to increased emissions of
42 controlled ODSs and uncontrolled shorter-lived halogenated source gases have raised some concerns on the continued success
43 of the treaty and the outlook for ozone recovery.

44

45 This Opinion paper gives our personal view of some selected current and future issues in ozone layer science. It is not a review
46 of the subject; there are many excellent text books and the 4-yearly WMO/UNEP assessments which serve that purpose.
47 Section 2 gives a brief summary of ozone layer research, with emphasis on the contribution of Paul Crutzen, to whom selected
48 papers in this issue are dedicated. Section 3 addresses ozone depletion and the role of halogenated species. Section 4 discusses
49 the new research areas of wildfire smoke and the ozone layer, and the expanding topic of volcanic impacts. Sections 5 and 6
50 give some personal thoughts on issues related to the availability of observations necessary to follow the evolution of the ozone
51 layer and modelling developments that are needed. Finally, a summary is provided in Section 7.

52 **2 A Century of Ozone Layer Research**

53 Active research into stratospheric ozone dates back around 100 years. Dobson pioneered the detection and quantification of
54 ozone in the stratosphere using a UV spectrometer (Dobson and Harrison, 1926) following earlier work by Fabry and Buisson
55 (see historical summary in Brasseur, 2020). A theoretical model for creation of a stratospheric ozone layer, based solely on
56 oxygen chemistry, was first proposed by Chapman (1930). This was formulated on the slow production and destruction of
57 ‘odd oxygen’ ($Ox = O_3 + O(^3P)$) along with fast interconversion of O_3 and $O(^3P)$ within the Ox family. This oxygen-only
58 model appeared to suffice until the 1960s when improved observations and laboratory measurements of key rate coefficients
59 revealed a major quantitative discrepancy. The Chapman cycle included the only significant chemical source of Ox, i.e.
60 photolysis of O_2 , but ignored around 80% of stratospheric Ox loss via catalytic cycles that destroy ozone through reactions
61 involving HOx, NOx and halogen radicals.

62

63 Here we should highlight the contribution of the late Paul Crutzen (1933 – 2021) to ozone layer science. For a comprehensive
64 summary of his whole career please see Müller et al. (2022), and references therein, and Solomon (2021a). Paul Crutzen started
65 contributing to our understanding of the ozone layer very early in his scientific career. In 1965, at Stockholm University,
66 Crutzen helped visiting US scientist J.R. Blankenship to develop a numerical model of different forms of oxygen in the
67 stratosphere, mesosphere and lower thermosphere. This marked the start of his scientific career and gave him his first paper
68 (Blankenship and Crutzen, 1965). Following this work Crutzen chose to study for a PhD in stratospheric ozone as it appeared,
69 at that time, to be a topic of “pure science related to natural processes” rather than one about human impact. Clearly, that
70 situation later changed! In due course Crutzen submitted his PhD thesis ‘On the photochemistry of ozone in the stratosphere
71 and troposphere and pollution of the stratosphere by high-flying aircraft’ to Stockholm University in May 1973.

72

73 In his PhD work (Crutzen 1970, 1971, 1972, 1973), Crutzen was the first to suggest that reactions catalysed by NO and NO_2
74 control the abundance of ozone in the middle stratosphere (around 25-35 km). This is summarised by the cycle:

75



76



77 Where the sum of NO and NO_2 is termed NOx. This discovery was a major achievement and helped to pave the way for a
78 quantitative understanding of stratospheric ozone whereby catalytic cycles due to species from various families (HOx, NOx,



79 Clx, Brx) are added to the original oxygen-only model of Chapman (1930). This work formed part of the basis for Crutzen
80 being awarded the 1995 Nobel Prize for Chemistry jointly with Mario J. Molina and F. Sherwood Rowland "for their work in
81 atmospheric chemistry, particularly concerning the formation and decomposition of ozone".

82

83 Prior to submitting his PhD thesis Crutzen spent two years (1969-1971) as a visitor to the University of Oxford. Here he
84 developed his ideas on the importance of NO_x in controlling ozone in order to address the issue of human-induced perturbations
85 to the ozone layer caused by emissions from high flying supersonic transport (SST) aircraft. The debate on the atmospheric
86 impacts of SST had begun in the early 1970s when it was envisaged that large fleets of around 500 aircraft such as the Anglo-
87 French Concorde might be flown within the lower stratosphere. Through his modelling work Crutzen was aware of inherent
88 model uncertainties which prompted him to make the statement that the "minimum requirement is therefore that extensive
89 supersonic air traffic should not take place in the stratosphere before reliable predictions can be made of the possible
90 environmental consequences of such operations" (Crutzen, 1972). This is an insightful lesson that would be equally applicable
91 to many other past and present areas of atmospheric science and therefore one worth remembering.

92

93 During the 1970s Crutzen's scientific interests extended into other areas, though he did maintain a link with the stratosphere
94 through the study of the impact of NO_x produced from solar proton events on the ozone layer (Solomon and Crutzen, 1981).
95 He also addressed the budget of stratospheric NO_y (reactive odd nitrogen) from the perspective of surface sources, highlighting
96 the human impact on stratospheric ozone of increased fertilizer and associated increased emissions of N₂O, the main source of
97 NO_y (Crutzen and Ehalt, 1977). Following the same reasoning as for N₂O, he also worked out that the dominant non-volcanic
98 source of stratospheric sulfur was the surface emissions of carbonyl sulfide (COS), the long-lived atmospheric sulfur
99 compound (Crutzen, 1976).

100

101 Before his works on N₂O and COS, Crutzen had also keenly followed the publication of the seminal paper on
102 chlorofluorocarbons (CFCs) by Molina and Rowland (1974), prompting him to publish a contribution on this topic (Crutzen,
103 1974). Similarly, following the surprise discovery of the Antarctic Ozone Hole (Farman et al., 1985) Crutzen was quick to
104 think about the possible implications of co-condensation of HNO₃ and H₂O at temperatures above that at which pure ice clouds
105 form as a mechanism for widespread occurrence of polar stratospheric clouds (PSCs) and the initiation of key ozone-destroying
106 halogen chemistry (Solomon et al., 1986) via heterogeneous reactions on PSCs (Crutzen and Arnold, 1986). In this way
107 Crutzen made important scientific contributions to the early research into the causes of polar ozone depletion. His later work
108 on describing the epoch of the Anthropocene still has ongoing relevance to protecting the Earth's ozone layer shield (see
109 Solomon et al., 2021b). His multi-faceted scientific legacy for stratospheric ozone is assured.

110

111 **3 Ozone Depletion and the Montreal Protocol**

112

113 **3.1 Montreal Protocol**

114 The signing of the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987 and its subsequent amendments
115 have had a major impact on the anthropogenic halogen source to the stratosphere. The Protocol now controls (limits) the
116 production and consumption of all major long-lived ODSs, which are ultimately emitted to the atmosphere. This control of
117 ODS production is leading to a net reduction in the tropospheric source gases (**Figure 1a**) which transport chlorine and bromine
118 to the stratosphere.



119

120 A very important recent development in the Montreal Protocol was the inclusion of hydrofluorocarbons (HFCs) in the Kigali
121 Amendment of 2016 (WMO, 2018). HFCs do not contain any chlorine or bromine and hence do not lead directly to ozone
122 depletion. However, they are potent greenhouse gases and are only present in the atmosphere as replacements for CFCs and
123 HCFCs, hence the need to control these gases and to do so within the MP.

124

125 The majority of long-lived halocarbon source gases are now controlled by the Protocol. Further, or more rapid, reductions in
126 stratospheric chlorine (and bromine) would depend on extension of the Protocol to chlorinated very short-lived substances
127 (VSLS), defined as having an atmospheric lifetime of less than 6 months. The prime example of this is dichloromethane
128 (CH_2Cl_2) (Hossaini et al., 2017) which, although largely removed in the troposphere, does deliver a large fraction of the
129 estimated 130 ± 20 pptv of VSLS chlorine to the stratosphere both directly (source gas injection, SGI) and through decay
130 products (product gas injection, PGI) (see WMO, 2022).

131

132 The history of the MP since its signing in 1987 (and ratification in 1989) has been very successful – as evidenced by the
133 decreasing loading of stratospheric chlorine and bromine. Indeed, the former UN Secretary General, Kofi Annan, described
134 the Protocol to be not only “the most successful environmental treaty in history”, but also “perhaps the most successful
135 international agreement to date” of any kind. However, that success appeared to be challenged for the first time by the
136 observation of an unexpected reduction in the atmospheric CFC-11 decay rate (Montzka et al., 2018), which implied renewed
137 emissions. A large fraction of these emissions (at least) were traced to eastern China (Rigby et al., 2019). It should be
138 emphasised that this detection of apparent contravention of the MP was only possible through continued observations by the
139 distributed ground-based monitoring networks (see Section 5). Following this discovery, alarm was raised by policy makers
140 involved in the MP. Updates to these observations three years later (Montzka et al., 2021; Park et al., 2021) show that these
141 renewed emissions of CFC-11 appeared to have greatly declined. Therefore, we can argue that this episode has been further
142 evidence of the success of the MP and of the effective combination of monitoring observations, science and policy. It is
143 important to note that persistent uncertainties remain in the budget of carbon tetrachloride (CCl_4) another of the major
144 controlled ODS (Sherry et al., 2018). CCl_4 is produced in large quantities for feedstock use (e.g. Chipperfield et al., 2020) and
145 it also has soil and oceanic sinks (e.g. Butler et al., 2016). Therefore, it has proved challenging to pin down the atmospheric
146 budget of this species and explain the apparently slower atmospheric decay than expected based on its estimated lifetime (e.g.
147 Park et al., 2018). Continued observations of these controlled ODSs, and further improved understanding of their atmospheric
148 budgets, is important to ensure the continued success of the MP.

149

150 **3.2 Ozone Recovery**

151 The undoubted success of the Montreal Protocol in halting and turning around the increasing trend in stratospheric chlorine
152 and bromine is clearly expected to lead to ozone recovery, e.g. an increase in global ozone. However, the detection of ozone
153 recovery, and even the definition of what recovery is, has proven difficult. There is now a general consensus that recovery
154 means ‘recovery from the effects of depletion caused by halogen (chlorine and bromine) species’ (e.g. WMO, 2011).
155 Stratospheric ozone amounts clearly depend on many other varying factors (e.g. solar radiation, temperature, dynamics) which
156 can also lead to an increase or a decrease in ozone. These influences need to be removed if the ozone recovery is to be
157 quantified. Therefore, recovery cannot generally be detected from observations of ozone alone; a statistical or physical model
158 is needed to isolate the effects of halogen chemistry from other effects.

159



160 Given that recovery is from the effects of halogen-catalysed chemical loss, the clearest signal of recovery would be expected
161 in regions where this chemistry exerts a strong influence on ozone. Newchurch et al. (2003) first claimed the detection of
162 ozone recovery in the upper stratosphere where the classical ClO + O cycle (Molina and Rowland, 1974) has its maximum
163 efficiency. In this region the contributing effects of ozone increase from stratospheric cooling need to be removed, which can
164 be done by model attribution studies of the different processes (noting that the stratospheric temperature changes can be due
165 both to increased longwave cooling by CO₂ and less shortwave heating by O₃ itself). It proved more elusive to detect recovery
166 in the other atmospheric regions subject to large halogen-catalysed loss - namely the polar lower stratospheres. Solomon et al.
167 (2016) succeeded in detecting Antarctic recovery (or 'healing') by focussing on the period of rapid chemical loss in September,
168 rather than the period of lowest ozone in October. As expected, the larger variability in Arctic ozone loss has made detection
169 of any trends in this region difficult. However, using long-term ground-based UV-visible observations, Pazmino et al. (2023)
170 recently claimed some measure of Arctic ozone recovery.

171

172 At extrapolar latitudes, observations confirm that the ozone decline in 1990s and earlier, caused by increasing atmospheric
173 concentrations of ODSs, has now transitioned to a slow ozone increase in both hemispheres (**Figure 2**, WMO (2022)). This is
174 consistent among the ground- and satellite-based measurements and chemistry-climate model simulations in the middle and
175 upper stratosphere, despite the larger variability of the ground-based measurements. This is apparent in the evolution of
176 observed and modelled annual mean deseasonalized ozone anomalies, relative to the 1998–2008 climatology of each individual
177 dataset in **Figure 2**, in the upper stratosphere (42 km or 2 hPa) and in the lower stratosphere (19 km or 70 hPa). Ozone
178 anomalies over 2017–2020 in the upper stratosphere from most datasets are positive relative to the 1998–2008 average,
179 consistent with expectations from the CCM simulations. In contrast, lower-stratospheric ozone anomalies over 2017–2020
180 continue to be about the same as for the 1998–2008 average. In 2019 and 2020, stratospheric ozone values were lower than in
181 previous years and below the level expected from model simulations (Weber et al., 2020). The particularly low 2020 annual
182 mean is the result of a very weak BDC and a large and stable Antarctic ozone hole (Klekociuk et al., 2021; Weber et al., 2021).
183 Such large variability, driven by variations in meteorology and transport (e.g. Chipperfield et al., 2018), is typical for the lower
184 stratosphere and limits our ability to drawing definite conclusions about long-term trends, especially for the mid-latitudes (30°–
185 60°) in both hemispheres (see WMO, 2022). Evidently, longer observational time series are needed to reduce the uncertainty
186 due to this variability.

187

188 While we can see that stratospheric halogen levels are decreasing, and therefore their impact on ozone is decreasing, there are
189 a number of concerns about the extent and rate of ozone recovery. Clearly, ongoing emissions of chlorine and bromine from
190 ODSs or VSLS will act to slow down this recovery (Sections 3.1 and 3.3). However, there are other factors which are not
191 controlled by the MP and which may also lead to decreases in column ozone, ultimately the parameter of primary concern for
192 protecting the biosphere. There are many studies (e.g. Ball et al., 2018, see also **Figure 2**) which point to an ongoing decrease
193 in ozone in the mid-latitude lower stratosphere. This may be related to dynamical changes, which are predicted to decrease
194 tropical column ozone in the future (Section 6). In contrast, Villemayor et al. (2023) have suggested a role for the combined
195 effects of chlorine, bromine and iodine VSLS acting together. This is a region where further work is needed to determine the
196 extent of ozone depletion/recovery and to quantify its driving factors.

197

198 3.3 Other Issues related to Halogen Chemistry

199 As noted in Section 2.2, VSLS deliver important amounts of chlorine and bromine to the stratosphere. VSLS bromine is largely
200 of natural oceanic origin and contributes 5 ± 2 pptv to stratospheric bromine, which is around 27% of the total (WMO, 2022).
201 There is currently no suggestion of a trend in this VSLS bromine contribution but this could potentially occur due to climate



202 feedbacks on the strengths of the emission sources. In contrast, VLSL chlorine is largely of anthropogenic origin. Although
203 the total VLSL chlorine injection of 130 ± 20 pptv is only 4% of the total stratospheric chlorine (WMO, 2022), it is showing a
204 small increasing trend notably through increases in the atmospheric abundance of CH_2Cl_2 and CHCl_3 (e.g. Fang et al., 2019;
205 Claxton et al., 2020). Far larger local stratospheric chlorine inputs from VLSL have recently been observed in regions where
206 strong convection and emissions co-locate, notably the Asian Summer Monsoon (Adcock et al., 2020).

207
208 Solomon et al. (1994) pointed out that iodine depletes ozone more efficiently than chlorine, and thus could be responsible for
209 significant contribution to past and future ozone changes. However, there are still large uncertainties in the main gas- and
210 condensed-phase iodine photochemical processes (see e.g. Saiz-Lopez et al., 2012; Feng et al. 2023) and observations of
211 inorganic iodine (Iy) species in the upper troposphere – lower stratosphere (UTLS) are sparse. So far, only a few global 3-D
212 models have included iodine chemistry (e.g., atmospheric chemistry-climate models such as CAM by Ordóñez et al., 2012;
213 SOCOL-AERv2-I by Karagodin-Doyennel et al., 2021; WACCM by Cuevas et al., 2022; LMDZ-INCA by Caramet et al., 2023;
214 Chemical transport models MOZART by Youn et al., 2010; TOMCAT/SLIMCAT by Hossaini et al., 2015 and GEOS-Chem
215 by Sherwen et al., 2016). These models have included the major sources of iodine from the ocean, including short-lived
216 iodocarbons (e.g. CH_3I , CH_2I_2) and primary HOI and I_2 emissions (e.g., Carpenter, 2003; Jones et al., 2010, Saiz-Lopez et al.,
217 2012; Carpenter et al., 2013). Recent measurements have indicated that up to 0.77 ± 0.10 parts per trillion by volume (pptv)
218 total inorganic iodine is injected to the stratosphere from the oceans (Koenig et al., 2020). These studies have indicated that
219 iodine may play an important role in stratospheric ozone depletion. However, significant uncertainties remain over the
220 magnitude and impact of iodine on stratospheric ozone, ranging from a few percent (e.g., Hossaini et al., 2015; Karagodin-
221 Doyennel et al., 2021) to 10% (Cuevas et al., 2022) and up to 30% (e.g., Ordóñez et al., 2012). Indeed, the contribution of
222 iodine could become more important (Cuevas et al., 2022; Villemayor et al., 2023) due to the decreasing amounts of
223 stratospheric chlorine and bromine brought about by the Montreal Protocol (Feng et al., 2021).

224
225 It is worth pointing out that volcanoes are also a potentially significant source of halogens to the atmosphere (Bobrowski et
226 al., 2003; Pyle and Mather, 2009). Large halogen-rich eruptions could in principle inject large amounts of halogens, notably
227 bromine, directly into the stratosphere, causing massive ozone destruction (Kutterolf et al., 2013; Cadoux et al., 2015).
228 However, this phenomenon has not been observed during the satellite era.

230 **4 Other Challenges**

231 The MP has been focused on reducing ozone depletion by anthropogenic halogens. However, there are other well-known
232 causes of global ozone perturbations, notably natural ones such as the 11-year solar variability (for which the recent solar cycle
233 23 showed decreased flux) and stratospheric sulfur injections by large volcanic eruptions (e.g. El Chichon in 1982 and Pinatubo
234 eruption in 1991) (WMO, 2022). So far, since the start of satellite observations around 1980, these natural factors have had a
235 relatively limited impact on global ozone and, unlike the anthropogenic halogen threat, are only expected to cause short-term
236 (decadal timescales at most) fluctuations in stratospheric ozone. Climate change represents a pressing and long-term issue for
237 stratospheric ozone. The overall impacts of climate change (largely driven by the increase in CO_2 levels) on stratospheric ozone
238 are complex, ranging from transport to chemistry effects (e.g. changes in the strength of the stratospheric general circulation,
239 changes in the tropospheric water flux into the stratosphere, temperature-dependent chemistry effects, chemistry changes
240 linked to the increasing levels in stratospheric source gases such as CH_4 and N_2O that are also major the greenhouse gases)
241 (e.g. WMO, 2018; 2022). Many of these effects are coupled and some of the resulting stratospheric perturbations can, in return,



242 influence the surface climate. Understanding and forecasting the effects of climate change on stratospheric ozone has been a
243 major challenge for several decades now.

244

245 More recently, other new challenges have emerged. The stratosphere contains aerosol particles which are mostly found in its
246 lower altitude region. This stratospheric aerosol load is overwhelmingly dominated by supercooled sulfuric acid particles
247 whose main sources are stratospheric oxidation of volcanic SO₂ and of OCS, a long-lived sulfur species emitted at the surface
248 (Crutzen, 1976). Sulfuric acid aerosols play an important role in stratospheric chemistry and in the radiative balance of the
249 atmosphere, notably when it is enhanced volcanically. They provide surfaces for key heterogeneous reactions (Hofmann and
250 Solomon, 1989). They also cool the surface by scattering incident sunlight back to space and can heat the stratosphere by
251 absorbing near-infrared radiation (Stenchikov et al., 1998; Robock, 2000). Until quite recently, almost all the observed global
252 enhancements in stratospheric aerosols and resulting ozone perturbations were linked to sulfur injections by large volcanic
253 eruptions (e.g. El Chichon in 1983, Mt Pinatubo in 1991). As the stratospheric aerosol variability appeared to be essentially
254 driven by volcanic sulfur inputs, only sulfur-induced perturbations of stratospheric aerosols have usually been considered
255 significant for the global stratosphere and climate. This focus on sulfur has also led to the development of sophisticated
256 stratospheric sulfate aerosol microphysical modules which are now implemented in several global climate models (e.g.
257 Zanchettin et al., 2016). These models are able to reproduce observed features of the stratospheric aerosol layer rather well,
258 especially the large enhancements by volcanic eruptions (Zanchettin et al., 2022) and associated ozone losses (Bekki and Pyle,
259 1994; Mills et al., 2017). These models are also used to assess the impacts of other stratospheric sulfur injections on
260 stratospheric ozone, for example from aircraft or potential stratospheric geoengineering (Pitari et al., 2014).

261

262 Two recent events have challenged the dominant view that sulfur is the only aerosol component relevant for the global
263 stratosphere, ozone layer and climate. The first event was the massive Australian wildfires at the turn of 2020, the so-called
264 Australian New Year's (ANY) event (Khaykin et al., 2020; Peterson et al., 2021), and the second event was the eruption of the
265 Hunga Tonga – Hunga Ha'apai (HTHH) volcano in January 2022 (Carr et al., 2022; Zuo et al., 2022). The nature and
266 magnitude of the various stratospheric impacts of these two events have been unexpected and sometimes unprecedented in the
267 historical records. After intensive research on the stratosphere since the discovery of the Antarctic ozone hole phenomenon in
268 1985, these two recent events have represented extreme but valuable testbeds of our understanding and modelling of
269 stratospheric physics and chemistry.

270

271 **4.2 Australian Wildfires**

272

273 **4.2.1 Injections of Carbonaceous Particles**

274 Wildfires can trigger the formation of pyrocumulonimbus (PyroCb) towers that can rise high depending on meteorological
275 conditions and intensity of the fires, and transport biomass-burning material into the UTLS (Peterson et al., 2018). The
276 Australian 'Black Summer' wildfires of 2019–2020 were exceptional in terms of scale, intensity and stratospheric impacts
277 according to historical records (Damany-Pearce et al., 2022). The strongest set of PyroCb outbreaks occurred at the turn of
278 2020, injecting massive amounts of gaseous and particulate biomass-burning products above the tropopause, resulting in a
279 sharp increase in global stratospheric aerosol optical depth (SAOD) which was on a par with the SAOD increases observed
280 after the strongest volcanic eruptions in the last 27 years, Calbuco in 2015 and Raikoke in 2019 (see **Figure 3**). For example,
281 of the order of 1 Tg of carbonaceous aerosols and ~25 Tg of H₂O were released into the lower stratosphere during the ANY



282 event (Khaykin et al., 2020; Damany-Pearce et al., 2022). Most of the impacts of ANY on the stratosphere resulted from
283 aerosol perturbations.

284

285 **4.2.2 Aerosol Changes**

286 A very peculiar effect of the strong solar heating by the highly absorptive ANY aerosol plumes was the generation of self-
287 maintained anticyclonic vortices, including one with a diameter of ~1000 km, which contained extremely high concentrations
288 of wildfire gases and aerosols. The massive and remarkably compact vortex persisted for several months while rising to ~35
289 km (Khaykin et al., 2020). The aerosol lofting opposed the effect of gravitational settling, extending the residence time of
290 ANY aerosols in the stratosphere. Stratospheric aerosol levels remained enhanced in the southern hemisphere throughout 2020.
291 The increase in stratospheric aerosol optical depth (SAOD) was comparable to the increase produced by the Raikoke volcanic
292 eruption in 2019 which was then the greatest aerosol increments since the massive volcanic eruption of Mt Pinatubo in 1991.

293

294 **4.2.3 Gaseous Composition Changes**

295 ANY stratospheric aerosol changes were accompanied by very unusual large-scale perturbations in gaseous composition. For
296 example, in the months following the ANY aerosol dispersion, unexpected partitioning between radicals and reservoir species
297 in the chlorine and nitrogen families were observed at southern mid-latitudes at relatively warm stratospheric temperatures
298 (Santee et al., 2022). The main stratospheric chlorine reservoir species HCl was found to be largely depleted while the other
299 chlorine reservoir, ClONO₂, and the ozone-destroying chlorine radical ClO, were enhanced. The anomalous partitioning is
300 somewhat reminiscent of the effects of ozone-destroying heterogeneous chemistry on other stratospheric aerosols (sulfuric
301 acid particles, PSCs) and is likely caused by some heterogeneous processing on the particles (Bernarth et al., 2022; Solomon
302 et al., 2023). However, the physical state and chemical reactivity of such wildfire carbonaceous particles in the conditions
303 prevailing in the stratosphere needs to be characterised, notably through laboratory studies and field campaigns.

304

305 Overall, the enhanced ClO concentrations must have resulted in some, albeit weak, chemical ozone depletion. A mini ozone
306 hole (depletion of up to 100 DU) was also apparent within the largest vortex early on (Khaykin et al., 2020) and the Antarctic
307 ozone hole was particularly long-lasting in 2020. Different aerosol-driven mechanisms have been proposed to explain ozone
308 changes, invoking changes in stratospheric dynamics and/or heterogeneous chemistry.

309

310 **4.2.4 Dynamics and Radiative Forcing**

311 In the early phase when aerosol concentrations within the ANY plumes were extremely high, the intense solar heating by ANY
312 aerosols led to the formation of rising, confined vortex-like plumes through dynamical feedbacks. Once the ANY aerosol
313 plumes were dispersed and spread, the aerosol heating led to a pronounced large-scale warming of the southern lower
314 stratosphere (Stocker et al., 2021; Damany-Pearce et al., 2022) which was stronger than any warmings from recent volcanic
315 eruptions.

316

317 The radiative forcing of ANY aerosols is difficult to estimate by comparison to that from sulfate aerosols. Sulfate aerosols
318 cool the surface by efficiently scattering incoming sunlight back to space which dominates the surface warming tendency from
319 their absorption of longwave radiation. Carbonaceous aerosols not only scatter solar radiation but also absorb it, and this
320 absorption is strongly dependent on the aerosol composition. ANY aerosols are thought to have been mostly composed of a
321 small fraction of black carbon (BC, soot-like component) and a vastly dominant fraction of organic material (OM, including



322 the so-called brown carbon (BrC) component) (Liu et al., 2022). BC absorbs across the entire solar spectrum and hence is by
323 far the most efficient source of heating. Most OM compounds absorb strongly in the IR and UV wavelengths, but are relatively
324 transparent in the visible and near-IR wavelengths. This is not the case for BrC which can also absorb in the blue and near-UV
325 spectral regions, albeit with a much weaker efficiency than BC (Laskin et al., 2015; Yu et al., 2021). Since the exact
326 composition, mixture state, and size of ANY carbonaceous aerosols are poorly constrained, the ANY radiative impact remains
327 difficult to quantify. Estimations of ANY aerosol surface radiative forcing (RF) vary from negligible to about -1 W m^{-2} ; this
328 range can be compared to the RF of small to moderate volcanic eruptions during the last 3 decades, estimated at between -0.1
329 and -0.2 W m^{-2} (Sellitto et al., 2022a; Liu et al., 2022). An additional complication in the ANYRF estimation is the effect of
330 the aerosol-driven stratospheric warming on the longwave radiation budget (Liu et al., 2022).

331

332 **4.3 Hunga Tonga – Hunga Ha`apai volcanic eruption of the January 15th, 2022**

333

334 **4.3.1 Injection of H₂O and Sulfur**

335 The eruption of the Hunga Tonga – Hunga Ha`apai volcano with an underwater caldera occurred on January 15th 2022. Several
336 features of this eruption were unique in the record of stratospheric observations. First, it generated a very powerful blast that
337 injected volcanic material up to an altitude of nearly 58 km (Proud et al., 2022; Carr et al., 2022). A plume from a moderate
338 eruption reaching the lower mesosphere was barely conceivable until this event, especially when the plume of the Mt Pinatubo
339 eruption in 1991 with an explosivity index larger than the HTHH eruption reached at most an altitude of ~ 40 km (McCormick
340 et al., 1995). Second, the HTHH eruption injected a very small amount of SO₂ (0.4-0.5 Tg) but a very large quantity of H₂O
341 into the middle atmosphere, between 120 and 150 Tg (Carn et al., 2022; Millan et al., 2022; Xu et al., 2022; Khaykin et al.,
342 2022), resulting in unprecedented increases in stratospheric water vapour (see **Figure 4**). Again, such a volcanic emission
343 scenario had not been generally considered previously. H₂O isotopic ratio data strongly suggest that sea water was a major
344 source of stratospheric hydration by the HTHH eruption (Khaykin et al., 2022).

345

346 **4.3.2 H₂O and Sulfate Aerosol Changes**

347 Following the HTHH eruption, the global stratospheric water content increased by approximately 10%, which is unprecedented
348 in the entire observational record dating back to 1985. Note that, as there are no significant sinks of H₂O within the stratosphere,
349 this excess H₂O is expected to last over several years. In contrast, volcanic sulfate particles have a shorter residence time in
350 the stratosphere, typically a year, because of the effect of gravitational sedimentation.

351

352 Most of the SO₂ was oxidised to sulfate aerosols within a month because of the H₂O-driven OH enhancement (Zhu et al.,
353 2022). As a result, the SAOD (averaged between 60°S and 60°N above 380 K) increased rapidly and reached a peak 5 months
354 after the eruption (Khaykin et al., 2022). Surprisingly, the magnitude of the SAOD increment did not follow at all the usual
355 relationship between SAOD and volcanic SO₂ mass. The ANY SAOD peak exceeded by about a factor 2 the SAOD
356 perturbations caused by all the volcanic or wildfire events in the last three decades, including the 2019 Raikoke eruption that
357 injected two times more SO₂ than the Toga eruption. This 4-fold enhancement in SAOD for the HTHH eruption compared to
358 the SAOD expected for a 0.4-0.5 Tg SO₂ injection, such as the 2015 Calbuco eruption, could not be due to the possible presence
359 of volcanic ash because that was apparently removed within days after the eruption and, according to satellite data, ANY
360 aerosols were essentially liquid sulfate droplets (Legras et al., 2022; Bernath et al., 2023). The highly enhanced SAOD must
361 have its origin in the excess humidity in the stratosphere, possibly through aerosol hygroscopic growth or coagulation. Indeed,



362 in sulfate aerosol microphysical model simulations of the HTHH eruption, the SAOD generated by the ~0.4 Tg SO₂ injection
363 is approximately doubled by the co-injection of 150 Tg of water (Zhu et al., 2022). However, the model still underestimates
364 observed SAOD by a factor 2, suggesting that the effect of water vapour on sulfate aerosols is yet not fully understood. Model
365 simulations indicate that stratospheric ozone has been significantly impacted by the eruption following several mechanisms
366 (e.g. heterogeneous chemistry on diluted sulfate aerosols, H₂O-enhanced gas-phase radical chemistry, and circulation changes).
367

368 **4.3.3 Dynamics and Radiative Forcing**

369 It is worth recalling that an increased lower stratospheric H₂O and enhanced stratospheric sulfate aerosols generally have
370 opposite radiative impacts. The H₂O increment tends to cool the stratosphere and warm the surface while a sulfate aerosol
371 increment tends to warm the stratosphere and cool the surface.

372

373 The water vapour content within the plume was initially so large that the H₂O radiative cooling led to a descent of the plume
374 during the first weeks after the eruption (Sellitto et al., 2022b). After this initial phase, negative temperature anomalies were
375 found to be correlated with H₂O-rich layers and cooling rate (Schoeberl et al., 2022). The decrease in global temperatures were
376 rather extreme in the mid-stratosphere during 2022, deviating markedly from the previous 42 years of meteorological data
377 (Coy et al., 2022). The sign of the stratospheric temperature response confirms that the H₂O cooling clearly dominated the
378 sulfate aerosol warming in the stratosphere. These temperature perturbations were also accompanied by circulation
379 adjustments.

380

381 The effect of the HTHH event on surface climate is not as clear-cut as in the stratosphere. RF model calculations suggest that
382 ultimately the eruption warmed the surface; i.e. that the H₂O warming was slightly dominant over sulfate cooling (Sellitto et
383 al., 2022b; Jenkins et al., 2023). Interestingly, the initial RF model calculations only took into account the amount of sulfur
384 injected and hence concluded that the HTHH eruption would slightly cool the surface (Zuo et al., 2022). It is also worth
385 pointing out that, as global warming intensifies, massive wildfires and of pyro-convective injections of carbonaceous particles
386 in the stratosphere are expected to become more frequent. Pyro-convection could turn into a significant source of large-scale
387 perturbations for stratospheric ozone and climate. As such, it will be necessary to account for it in Earth system models (ESMs)
388 in the future.

389

390 **5 Maintaining Observational Capacity**

391 Our understanding of the ozone layer, and the processes which control its evolution including those outlined here, depend on
392 the availability of high-quality observations. In recent years we have benefitted from a wealth of observations from ground-
393 based networks, balloon and aircraft flights and satellites. However, there are several indications that we will be hampered by
394 fewer observations in the future.

395

396 Several currently operational spaceborne instruments are well beyond their design lifetimes, and some are scheduled to be
397 decommissioned in the next few years. Instruments whose data have been cited here or regularly used as part of the 4-yearly
398 WMO/UNEP Ozone Assessments (e.g. WMO, 2022) will likely cease operations within the next few years, including the Aura
399 Microwave Limb Sounder (MLS), the SciSat Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-
400 FTS), the Odin Optical Spectrograph and Infrared Imager System (OSIRIS), and the Odin Sub-Millimetre Radiometer (SMR).
401 With the loss of these current limb-viewing capabilities, vertically resolved global measurements of many trace gases relevant



402 for studies of stratospheric chemistry and dynamics will no longer be available. These trace gases include reactive (ClO) and
403 reservoir (HCl, ClONO₂) chlorine species, water vapour, nitric acid (HNO₃), and long-lived transport tracers (e.g., nitrous
404 oxide, N₂O; methane, CH₄; carbon monoxide, CO). As noted in WMO (2022), the 2021 Report of the Ozone Research
405 Managers of the Parties to the Vienna Convention identified the need to “continue limb emission and infrared solar occultation
406 observations from space” that are “necessary for global vertical profiles of many ozone- and climate-related trace gases” as
407 one of the “key systematic observations recommendations.” Indeed, the impending loss of these measurements, many of which
408 have been taken continuously over the last several decades, will hamper our ability to reduce key uncertainties in our
409 understanding of stratospheric ozone depletion, including the lack of emergence of a clear signature of recovery in the Arctic,
410 the potential influence of volcanic and wildfire emissions, the role of VSLS, and the impact of strengthening of the Brewer-
411 Dobson circulation. It may take many years for the next generation of improved limb sounders to become operational and
412 provide us with the observational capacity that we have been used to over the past three decades. For example, the novel, high
413 resolution Changing Atmosphere Infra-Red Tomography Explorer (CAIRT) (<https://www.cairt.eu/>) is currently a candidate
414 mission for a European Space Agency Earth Explorer mission.

415

416 Ground-based networks have also proved essential for our continued study of the ozone layer and processes that affect it.
417 Examples are the Network for the Detection of Atmospheric Composition Change (NDACC, De Mazière et al., 2018), and the
418 National Oceanic and Atmospheric Administration (NOAA, e.g. Montzka et al., 2018) and Advanced Global Atmospheric
419 Gases Experiment (AGAGE, e.g. Rigby et al., 2019) surface networks. While these networks have an important monitoring
420 function, the data acquired have proved central to the validation of satellite measurements and to the identification of many of
421 the new scientific challenges discussed here. The benefit of these data sets increases greatly as the time series extend so that
422 longer term variations can be characterised and studied. Therefore it is very important to maintain their continuity.

423

424 **6 Chemistry-Climate Modelling and Ozone Projections**

425 Our understanding of the chemical, dynamic and radiative processes and of their couplings which control stratospheric ozone
426 is encapsulated in mathematical form in numerical models. These models are powerful tools and simulators in tackling a range
427 of scientific and societal challenges. Obviously, they can only include known processes (as the discovery of the Antarctic
428 ozone hole demonstrated) and even for these there can be significant uncertainties. Overall, progress in our understanding of
429 the ozone layer will depend on the improvement and careful application of a hierarchy of models from detailed chemical-
430 aerosol box models to complex chemistry-climate models (CCMs).

431

432 Regarding CCMs, these models can be very computationally expensive to run. Huge advances in computing resources allow
433 ever more complex processes to be added to models which can help understanding of feedback pathways but can mean that
434 simulations are often at the limit of what is practical. A set of ensemble simulations (needed to characterise the model internal
435 variability) can take many months of real time even on a powerful High Performance Computing (HPC) system. The costs
436 increase as other modules, such as ocean and biosphere, are added to build an ESM. Therefore, simulations need to be planned
437 carefully. Results from any given CCM (or ESM) will have various causes of uncertainty: (1) scenario uncertainty – related for
438 example to the ODS and GHG scenarios used to force the model; (2) structural uncertainty – related to the model grid and
439 parameterisations used to represent known processes and (3) internal variability. To address (3) CCMs need to perform an
440 ensemble of simulations. To address (2) a selection of models are needed to perform a given experiment in order to obtain a
441 robust result (in the sense that the result is not, or at least only weakly, model-dependent). For example, an important use of
442 CCMs is to predict recovery of the ozone layer from chlorine and bromine-catalysed loss, and the dependence of that recovery



443 on climate change. These results are obtained from projects such as the Chemistry-Climate Modelling Initiative (CCMI,
444 <https://igacproject.org/activities/CCMI>) and feed into the WMO/UNEP Assessments. It is important that the participating
445 models have been thoroughly evaluated and that they perform sufficient experiments (with ensemble members). For example,
446 as noted by Dhomse et al. (2018), robust estimates of sensitivity to GHG scenarios are better achieved when all (well evaluated)
447 models perform all experiments.

448

449 Given the increasing computational cost of the CCM (or ESM) simulations then it seems desirable that some other approaches
450 are used to update projections of ozone layer recovery. A commonly used metric is the ‘ozone return date’ (see **Figure 1b**).
451 This is the date at which modelled ozone levels return to a reference value, which is often taken to be 1960 or 1980. These
452 return dates are, for example, typically around 2040 for global mean column ozone and 2066 for the Antarctic in October, but
453 with large uncertainty due to e.g. GHG scenarios (WMO, 2022). Performing simulations to update these estimates is expensive
454 with possibly only a small benefit if the ODS and GHG scenarios have only changed slightly. Therefore, alternative approaches
455 should be investigated for estimating, for example, the dependence of the ozone return date on the chlorine and bromine return
456 dates, and the sensitivity of this to different GHGs.

457

458 Recently, Pyle et al. (2022) proposed the Integrated Ozone Depletion (IOD) metric and showed how it applies to similar long-
459 lived ODSs. IOD is an absolute measure of the time-integrated column ozone depletion for different halocarbon scenarios
460 which, for long-lived ODSs, reduces to a simple empirical formula with a model-derived scaling factor. As noted above,
461 application of ODPs to VSLs depends on the distribution of the surface emissions, which leads to a range of IOD values.
462 Because VSLs can cause ozone changes in the troposphere, Zhang et al. (2020) proposed the use of ‘stratospheric ODP’
463 (SODP) as a simpler and more direct measure of only stratospheric column changes. Further work from the modelling
464 community is needed to derive a robust range of (S)ODPs for VSLs, and to also extend the work of Pyle et al. (2022) to
465 investigate how to apply the IOD metric to VSLs. In particular, we need to test the sensitivity of modelled ozone depletion to
466 emissions (i.e. IOD scaling factor).

467

468 **7 Summary**

469 This Opinion article demonstrates that after 100 years of research, and nearly 4 decades after the discovery of the Antarctic
470 ozone hole, the stratospheric ozone layer is still throwing up surprises and new research challenges, showing that we cannot
471 lower our guard on this global environmental issue. The great progress that we have made in ozone layer science has been
472 achieved through the combination of laboratory studies, observations from a range of platforms, and modelling. All of these
473 components are essential for continued progress in research and policymaking concerning the preservation of the ozone layer.
474 Our personal experience has also convinced us of the great importance of collaborative international programmes and
475 campaigns which have been truly instrumental in advancing our knowledge on the topic. Ultimately, society’s interest in the
476 ozone layer is due to the impact of ozone depletion on surface UV and climate. As this article has shown, although the ozone
477 layer is demonstrating recovery from the effects of long-lived ODSs, other processes such as uncontrolled short-lived species,
478 changing dynamics, and wildfire smoke, threaten further depletion. We need to continue to observe, understand and model
479 these processes; *Atmospheric Chemistry and Physics* will continue to provide a primary journal for our community’s major
480 advances in these areas.

481



482 **List of Acronyms**

483 ANY – Australia New Year
484 CCM – Chemistry-climate model
485 EECL – Equivalent effective chlorine
486 ESM – Earth system model
487 GHG – Greenhouse gas
488 HTHH – Hunga Tunga – Hunga Ha’apai
489 IOD – Integrated ozone depletion
490 MP – Montreal Protocol
491 ODP – Ozone depletion potential
492 ODS – Ozone depleting substance
493 PGI – Product gas injection
494 PSC – Polar stratospheric cloud
495 RF – Radiative forcing
496 SAOD – Stratospheric aerosol optical depth
497 SGI – Source gas injection
498 SODP – Stratospheric ODP
499 UTLS – Upper troposphere – lower stratosphere
500 UV – Ultraviolet
501 VSLS – Very short-lived substance
502 WMO – World Meteorological Organisation
503

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505 Both authors contributed to the writing of this article.
506

507 **Competing Interests**

508 The authors declare that they have no conflicts of interest.
509

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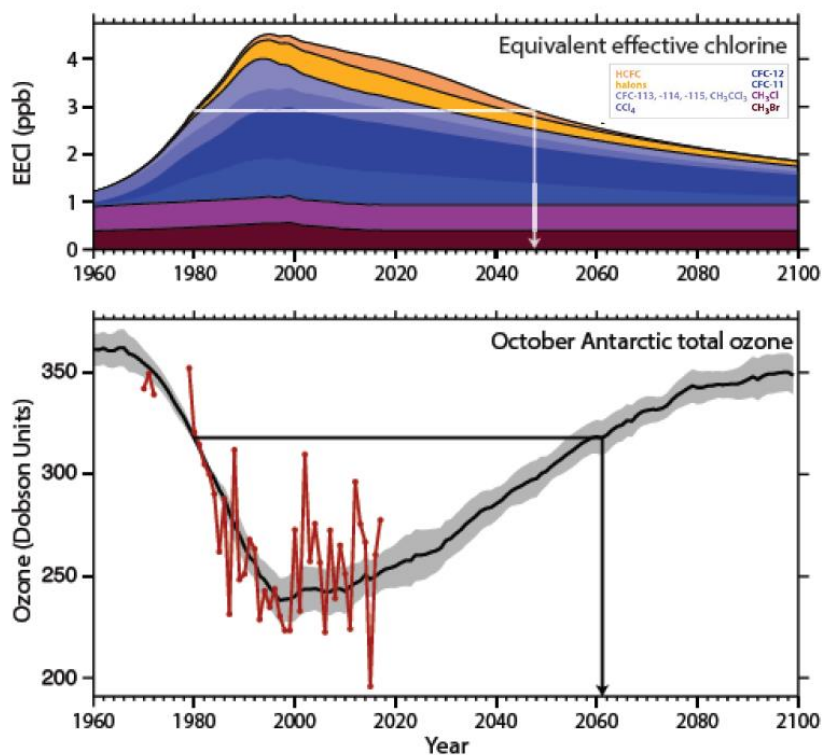


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810 **Figures**

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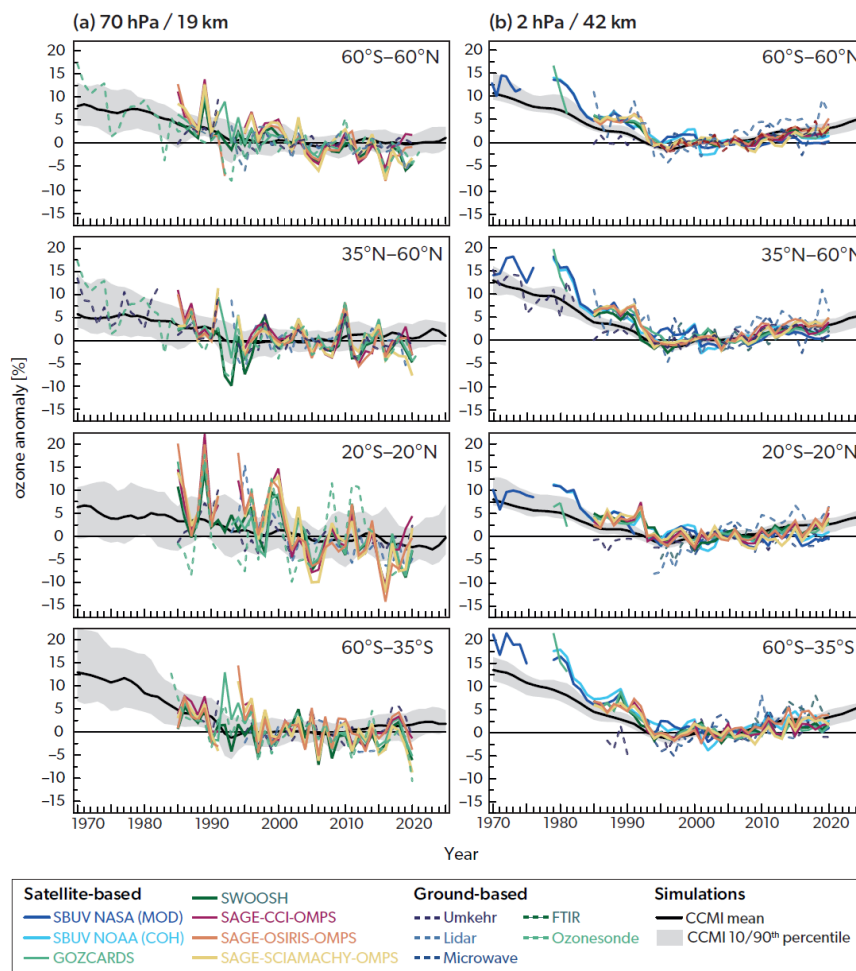
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814 **Figure 1:** (a) Past observations and projections of the equivalent effective chlorine (EECI; total chlorine + 65 × total bromine
 815 at surface, ppb) from different long-lived ODSs between 1960 and 2100. After the signing of the Montreal Protocol and
 816 subsequent phase-out of many long-lived ODSs, the EECI began to decline and is expected to return to 1980 levels by around
 817 2050, as indicated by the horizontal and vertical dashed lines. (b) Measured (red line) and predicted (black line, with uncertainty
 818 shown as grey shading) October Antarctic column ozone (Dobson units) between 1960 and 2100. In this simulation the
 819 Antarctic ozone layer is expected to return to 1980 levels around 2061, around a decade later than the EECI (horizontal and
 820 vertical dashed lines). CFC, chlorofluorocarbon; HCFC, hydrochlorofluorocarbon. Note that this Antarctic October return date
 821 is slightly earlier than the most recent estimate given in WMO (2022) but still within the model uncertainty range. Figure
 822 adapted from WMO (2018) and Chipperfield et al. (2020).



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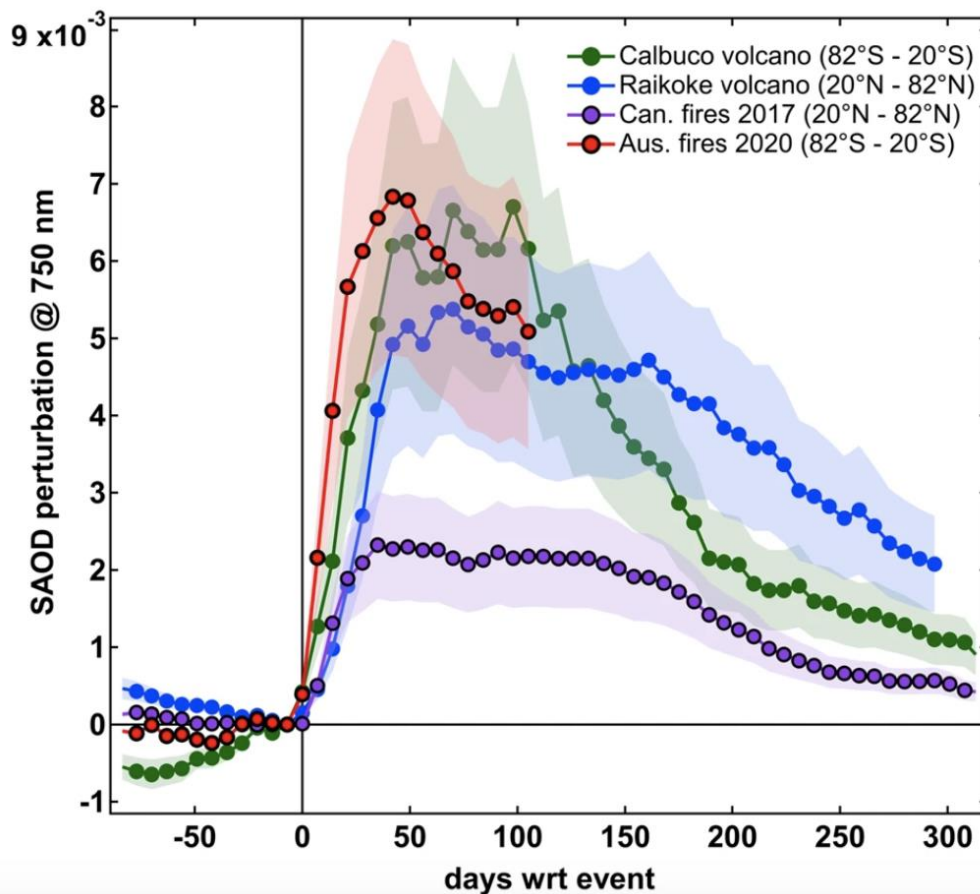
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826 **Figure 2.** Annual mean anomalies of ozone in (a) the lower stratosphere, near 19 km altitude (70 hPa pressure) and (b) the
 827 upper stratosphere, near 42 km (2 hPa), for four latitude bands: 60°S–60°N, 35–60°N, 20°S–20°N (tropics), and 60–35°S.
 828 Anomalies are referenced to a 1998–2008 baseline. Coloured lines are long-term records obtained by merging data from
 829 different nadir (SBUV NASA (MOD) and SBUV NOAA (COH)) or limb-viewing (GOZCARDS, SWOOSH, SAGE-CCI-
 830 OMPS, SAGE-OSIRIS-OMPS, SAGE-SCIAMACHY-OMPS) satellite instruments. Dashed coloured lines are long-term
 831 records from ground-based observations (Umkehr, lidar, microwave, FTIR and ozonesondes); see Steinbrecht et al. (2017),
 832 WMO (2018), and Arosio et al. (2018) for details on the various datasets. The gray shaded areas show the range (10th and
 833 90th percentiles) of 16 CCM simulations performed as part of the CCMI-1 REF-C2 experiment (see Morgenstern et al., 2017)
 834 with the black line indicating the median. Taken from Figure 3-9 in WMO (2022).



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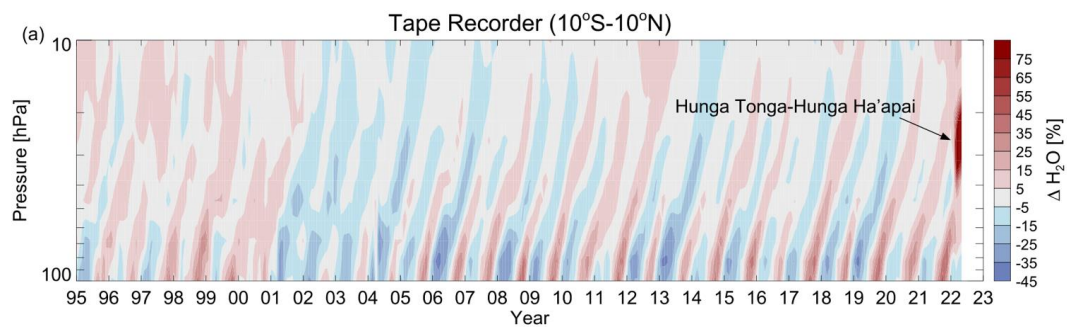
838 **Figure 3.** Perturbation of the stratospheric aerosol optical depth (SAOD) due to Australian fires and the strongest events since
 839 1991. The curves represent the SAOD perturbation at 746 nm following the Australian wildfires, the previous record-breaking
 840 Canadian wildfires in 2017, and the strongest volcanic eruptions in the last 29 years (eruptions of Calbuco volcano in 2015
 841 and Raikoke volcano in 2019). The time series are computed from OMPS-LP aerosol extinction profiles as weekly-mean
 842 departures of aerosol optical depth above 380 K isentropic level from the levels on the week preceding the ANY event. The
 843 weekly averages are computed over equivalent-area latitude bands roughly corresponding to the meridional extent of
 844 stratospheric aerosol perturbation for each event. The shading indicates a 30% uncertainty in the calculated SAOD, as estimated
 845 from SAGE III coincident comparisons. See Khaykin et al. (2020) for more details.

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851 **Figure 4.** Zonal mean H₂O anomalies in the tropics, between 10°S and 10°N (the so-called atmospheric tape recorder). H₂O

852 abundances are based on GOZCARDS (Froidevaux et al., 2015) and Microwave Limb Sounder data. See Millan et al. (2022)

853 for more details.