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Opinion: Stratospheric Ozone – Depletion, Recovery and New Challenges

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

1 Introduction

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

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

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

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

2 A Century of Ozone Layer Research

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

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

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

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O(^3P) \rightarrow NO + O_2$$

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 quantitative understanding of stratospheric ozone whereby catalytic cycles due to species from various families (HOx, NOx,

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

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

During the 1970s Crutzen's scientific interests extended into other areas, though he did maintain a link with the stratosphere through the study of the impact of NOx produced from solar proton events on the ozone layer (Solomon and Crutzen, 1981). He also addressed the budget of stratospheric NOy (reactive odd nitrogen) from the perspective of surface sources, highlighting the human impact on stratospheric ozone of increased fertilizer and associated increased emissions of N_2O, the main source of NOy (Crutzen and Ehalt, 1977). Following the same reasoning as for N_2O, he also worked out that the dominant non-volcanic source of stratospheric sulfur was the surface emissions of carbonyl sulfide (COS), the long-lived atmospheric sulfur compound (Crutzen, 1976).

Before his works on N_2O and COS, Crutzen had also keenly followed the publication of the seminal paper on chlorofluorocarbons (CFCs) by Molina and Rowland (1974), prompting him to publish a contribution on this topic (Crutzen, 1974). Similarly, following the surprise discovery of the Antarctic Ozone Hole (Farman et al., 1985) Crutzen was quick to think about the possible implications of co-condensation of HNO_3 and H_2O at temperatures above that at which pure ice clouds form as a mechanism for widespread occurrence of polar stratospheric clouds (PSCs) and the initiation of key ozone-destroying halogen chemistry (Solomon et al., 1986) via heterogeneous reactions on PSCs (Crutzen and Arnold, 1986). In this way Crutzen made important scientific contributions to the early research into the causes of polar ozone depletion. His later work on describing the epoch of the Anthropocene still has ongoing relevance to protecting the Earth's ozone layer shield (see Solomon et al., 2021b). His multi-faceted scientific legacy for stratospheric ozone is assured.

3 Ozone Depletion and the Montreal Protocol

3.1 Montreal Protocol

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

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

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

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

3.2 Ozone Recovery

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

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Given that recovery is from the effects of halogen-catalysed chemical loss, the clearest signal of recovery would be expected in regions where this chemistry exerts a strong influence on ozone. Newchurch et al. (2003) first claimed the detection of ozone recovery in the upper stratosphere where the classical ClO + O cycle (Molina and Rowland, 1974) has its maximum efficiency. In this region the contributing effects of ozone increase from stratospheric cooling need to be removed, which can be done by model attribution studies of the different processes (noting that the stratospheric temperature changes can be due both to increased longwave cooling by CO_2 and less shortwave heating by O_3 itself). It proved more elusive to detect recovery in the other atmospheric regions subject to large halogen-catalysed loss - namely the polar lower stratospheres. Solomon et al. (2016) succeeded in detecting Antarctic recovery (or 'healing') by focussing on the period of rapid chemical loss in September, rather than the period of lowest ozone in October. As expected, the larger variability in Arctic ozone loss has made detection of any trends in this region difficult. However, using long-term ground-based UV-visible observations, Pazmino et al. (2023) recently claimed some measure of Arctic ozone recovery.

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

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

3.3 Other Issues related to Halogen Chemistry

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

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

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

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

4 Other Challenges

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

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

More recently, other new challenges have emerged. The stratosphere contains aerosol particles which are mostly found in its lower altitude region. This stratospheric aerosol load is overwhelmingly dominated by supercooled sulfuric acid particles whose main sources are stratospheric oxidation of volcanic SO_2 and of OCS, a long-lived sulfur species emitted at the surface (Crutzen, 1976). Sulfuric acid aerosols play an important role in stratospheric chemistry and in the radiative balance of the atmosphere, notably when it is enhanced volcanically. They provide surfaces for key heterogeneous reactions (Hofmann and Solomon, 1989). They also cool the surface by scattering incident sunlight back to space and can heat the stratosphere by absorbing near-infrared radiation (Stenchikov et al., 1998; Robock, 2000). Until quite recently, almost all the observed global enhancements in stratospheric aerosols and resulting ozone perturbations were linked to sulfur injections by large volcanic eruptions (e.g. El Chichon in 1983, Mt Pinatubo in 1991). As the stratospheric aerosol variability appeared to be essentially driven by volcanic sulfur inputs, only sulfur-induced perturbations of stratospheric aerosols have usually been considered significant for the global stratosphere and climate. This focus on sulfur has also led to the development of sophisticated stratospheric sulfate aerosol microphysical modules which are now implemented in several global climate models (e.g. Zanchettin et al., 2016). These models are able to reproduce observed features of the stratospheric aerosol layer rather well, especially the large enhancements by volcanic eruptions (Zanchettin et al., 2022) and associated ozone losses (Bekki and Pyle, 1994; Mills et al., 2017). These models are also used to assess the impacts of other stratospheric sulfur injections on stratospheric ozone, for example from aircraft or potential stratospheric geoengineering (Pitari et al., 2014).

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

4.2 Australian Wildfires

4.2.1 Injections of Carbonaceous Particles

Wildfires can trigger the formation of pyrocumulonimbus (PyroCb) towers that can rise high depending on meteorological conditions and intensity of the fires, and transport biomass-burning material into the UTLS (Peterson et al., 2018). The Australian 'Black Summer' wildfires of 2019–2020 were exceptional in terms of scale, intensity and stratospheric impacts according to historical records (Damany-Pearce et al., 2022). The strongest set of PyroCb outbreaks occurred at the turn of 2020, injecting massive amounts of gaseous and particulate biomass-burning products above the tropopause, resulting in a sharp increase in global stratospheric aerosol optical depth (SAOD) which was on a par with the SAOD increases observed after the strongest volcanic eruptions in the last 27 years, Calbuco in 2015 and Raikoke in 2019 (see **Figure 3**). For example, of the order of 1 Tg of carbonaceous aerosols and ~25 Tg of H_2O were released into the lower stratosphere during the ANY

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

4.2.2 Aerosol Changes

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

4.2.3 Gaseous Composition Changes

ANY stratospheric aerosol changes were accompanied by very unusual large-scale perturbations in gaseous composition. For example, in the months following the ANY aerosol dispersion, unexpected partitioning between radicals and reservoir species in the chlorine and nitrogen families were observed at southern mid-latitudes at relatively warm stratospheric temperatures (Santee et al., 2022). The main stratospheric chlorine reservoir species HCl was found to be largely depleted while the other chlorine reservoir, $ClONO_2$, and the ozone–destroying chlorine radical ClO, were enhanced. The anomalous partitioning is somewhat reminiscent of the effects of ozone-destroying heterogeneous chemistry on other stratospheric aerosols (sulfuric acid particles, PSCs) and is likely caused by some heterogeneous processing on the particles (Bernarth et al., 2022; Solomon et al., 2023). However, the physical state and chemical reactivity of such wildfire carbonaceous particles in the conditions prevailing in the stratosphere needs to be characterised, notably through laboratory studies and field campaigns.

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

4.2.4 Dynamics and Radiative Forcing

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

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

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the so-called brown carbon (BrC) component) (Liu et al., 2022). BC absorbs across the entire solar spectrum and hence is by far the most efficient source of heating. Most OM compounds absorb strongly in the IR and UV wavelengths, but are relatively 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 spectral regions, albeit with a much weaker efficiency than BC (Laskin et al., 2015; Yu et al., 2021). Since the exact composition, mixture state, and size of ANY carbonaceous aerosols are poorly constrained, the ANY radiative impact remains difficult to quantify. Estimations of ANY aerosol surface radiative forcing (RF) vary from negligible to about -1 Wm^{-2}; this range can be compared to the RF of small to moderate volcanic eruptions during the last 3 decades, estimated at between −0.1 and −0.2 Wm^{-2} (Sellitto et al., 2022a; Liu et al., 2022). An additional complication in the ANY RF estimation is the effect of the aerosol-driven stratospheric warming on the longwave radiation budget (Liu et al., 2022).

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

4.3.1 Injection of H_2O and Sulfur

The eruption of the Hunga Tunga – Hunga Ha'apai volcano with an underwater caldera occurred on January 15th 2022. Several features of this eruption were unique in the record of stratospheric observations. First, it generated a very powerful blast that injected volcanic material up to an altitude of nearly 58 km (Proud et al., 2022; Carr et al., 2022). A plume from a moderate eruption reaching the lower mesosphere was barely conceivable until this event, especially when the plume of the Mt Pinatubo eruption in 1991 with an explosivity index larger than the HTHH eruption reached at most an altitude of ~40 km (McCormick et al., 1995). Second, the HTHH eruption injected a very small amount of SO_2 (0.4-0.5 Tg) but a very large quantity of H_2O into the middle atmosphere, between 120 and 150 Tg (Carn et al., 2022; Millan et al., 2022; Xu et al., 2022; Khaykin et al., 2022), resulting in unprecedented increases in stratospheric water vapour (see **Figure 4**). Again, such a volcanic emission scenario had not been generally considered previously. H_2O isotopic ratio data strongly suggest that sea water was a major source of stratospheric hydration by the HTHH eruption (Khaykin et al., 2022).

4.3.2 H_2O and Sulfate Aerosol Changes

Following the HTHH eruption, the global stratospheric water content increased by approximately 10%, which is unprecedented in the entire observational record dating back to 1985. Note that, as there are no significant sinks of H_2O within the stratosphere, this excess H_2O is expected to last over several years. In contrast, volcanic sulfate particles have a shorter residence time in the stratosphere, typically a year, because of the effect of gravitational sedimentation.

Most of the SO_2 was oxidised to sulfate aerosols within a month because of the H_2O-driven OH enhancement (Zhu et al., 2022). As a result, the SAOD (averaged between 60°S and 60°N above 380 K) increased rapidly and reached a peak 5 months after the eruption (Khaykin et al., 2022). Surprisingly, the magnitude of the SAOD increment did not follow at all the usual relationship between SAOD and volcanic SO_2 mass. The ANY SAOD peak exceeded by about a factor 2 the SAOD perturbations caused by all the volcanic or wildfire events in the last three decades, including the 2019 Raikoke eruption that injected two times more SO_2 than the Toga eruption. This 4-fold enhancement in SAOD for the HTHH eruption compared to the SAOD expected for a 0.4-0.5 Tg SO_2 injection, such as the 2015 Calbuco eruption, could not be due to the possible presence of volcanic ash because that was apparently removed within days after the eruption and, according to satellite data, ANY aerosols were essentially liquid sulfate droplets (Legras et al., 2022; Bernath et al., 2023). The highly enhanced SAOD must have its origin in the excess humidity in the stratosphere, possibly through aerosol hygroscopic growth or coagulation. Indeed,

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in sulfate aerosol microphysical model simulations of the HTHH eruption, the SAOD generated by the ~0.4 Tg SO_2 injection is approximately doubled by the co-injection of 150 Tg of water (Zhu et al., 2022). However, the model still underestimates observed SAOD by a factor 2, suggesting that the effect of water vapour on sulfate aerosols is yet not fully understood. Model simulations indicate that stratospheric ozone has been significantly impacted by the eruption following several mechanisms (e.g. heterogeneous chemistry on diluted sulfate aerosols, H_2O-enhanced gas-phase radical chemistry, and circulation changes).

4.3.3 Dynamics and Radiative Forcing

It is worth recalling that an increased lower stratospheric H_2O and enhanced stratospheric sulfate aerosols generally have opposite radiative impacts. The H_2O increment tends to cool the stratosphere and warm the surface while a sulfate aerosol increment tends to warm the stratosphere and cool the surface.

The water vapour content within the plume was initially so large that the H_2O radiative cooling led to a descent of the plume during the first weeks after the eruption (Sellitto et al., 2022b). After this initial phase, negative temperature anomalies were found to be correlated with H_2O-rich layers and cooling rate (Schoeberl et al., 2022). The decrease in global temperatures were rather extreme in the mid-stratosphere during 2022, deviating markedly from the previous 42 years of meteorological data (Coy et al., 2022). The sign of the stratospheric temperature response confirms that the H_2O cooling clearly dominated the sulfate aerosol warming in the stratosphere. These temperature perturbations were also accompanied by circulation adjustments.

The effect of the HTHH event on surface climate is not as clear-cut as in the stratosphere. RF model calculations suggest that ultimately the eruption warmed the surface; i.e. that the H_2O warming was slightly dominant over sulfate cooling (Sellitto et al., 2022b; Jenkins et al., 2023). Interestingly, the initial RF model calculations only took into account the amount of sulfur injected and hence concluded that the HTHH eruption would slightly cool the surface (Zuo et al., 2022). It is also worth pointing out that, as global warming intensifies, massive wildfires and of pyro-convective injections of carbonaceous particles in the stratosphere are expected to become more frequent. Pyro-convection could turn into a significant source of large-scale perturbations for stratospheric ozone and climate. As such, it will be necessary to account for it in Earth system models (ESMs) in the future.

5 Maintaining Observational Capacity

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

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

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for studies of stratospheric chemistry and dynamics will no longer be available. These trace gases include reactive (ClO) and reservoir (HCl, $ClONO_2$) chlorine species, water vapour, nitric acid (HNO_3), and long-lived transport tracers (e.g., nitrous oxide, N_2O; methane, CH_4; carbon monoxide, CO). As noted in WMO (2022), the 2021 Report of the Ozone Research Managers of the Parties to the Vienna Convention identified the need to "continue limb emission and infrared solar occultation observations from space" that are "necessary for global vertical profiles of many ozone- and climate-related trace gases" as one of the "key systematic observations recommendations." Indeed, the impending loss of these measurements, many of which have been taken continuously over the last several decades, will hamper our ability to reduce key uncertainties in our understanding of stratospheric ozone depletion, including the lack of emergence of a clear signature of recovery in the Arctic, the potential influence of volcanic and wildfire emissions, the role of VSLS, and the impact of strengthening of the Brewer-Dobson circulation. It may take many years for the next generation of improved limb sounders to become operational and provide us with the observational capacity that we have been used to over the past three decades. For example, the novel, high resolution Changing Atmosphere Infra-Red Tomography Explorer (CAIRT) (https://www.cairt.eu/) is currently a candidate mission for a European Space Agency Earth Explorer mission.

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

6 Chemistry-Climate Modelling and Ozone Projections

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

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

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

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

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

7 Summary

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

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List of Acronyms

ANY – Australia New Year
CCM – Chemistry-climate model
EECl – Equivalent effective chlorine
ESM – Earth system model
GHG – Greenhouse gas
HTHH – Hunga Tunga – Hunga Ha'apai
IOD – Integrated ozone depletion
MP – Montreal Protocol
ODP – Ozone depletion potential
ODS – Ozone depleting substance
PGI – Product gas injection
PSC – Polar stratospheric cloud
RF – Radiative forcing
SAOD – Stratospheric aerosol optical depth
SGI – Source gas injection
SODP – Stratospheric ODP
UTLS – Upper troposphere – lower stratosphere
UV – Ultraviolet
VSLS – Very short-lived substance
WMO – World Meteorological Organisation

Author Contributions

Both authors contributed to the writing of this article.

Competing Interests

The authors declare that they have no conflicts of interest.

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Preprint. Discussion started: 30 June 2023

References

Adcock, K. E., Fraser, P. J., Hall, B. D., Langenfelds, R. L., Lee, G., Montzka, S. A., et al.: Aircraft-based observations of ozone-depleting substances in the upper troposphere and lower stratosphere in and above the Asian summer monsoon, J. Geophys. Res., 126, e2020JD033137. https://doi.org/10.1029/2020JD033137, 2020.

Arosio, C., A. Rozanov, E. Malinina, K.-U. Eichmann, T. von Clarmann, and J.P. Burrows, Retrieval of ozone profiles from OMPS limb scattering observations, Atmos. Meas. Tech., 11, 2135–2149, doi:10.5194/amt-11-2135-2018, 2018.

Ball, W.T., Alsing, J., Mortlock, D.J., Staehelin, J., Haigh, J.D., Peter, T., Tummon, F., Stuebi, R., Stenke, A., Anderson, J., Bourassa, A., Davis, S., Degenstein, D., Frith, S., Froidevaux, L., Roth. C, Sofieva, V., Wang, R., Wild, P. Yu, J., Ziemke, J., Rozanov, E.V., Evidence for a continuous decline in lower stratospheric ozone offsetting ozone layer recovery, Atmos. Chem. Phys., 18, 1379-1394, 10.5194/acp-18-1379-2018, 2018.

Bekki, S., and Pyle, J. A.: A two-dimensional study of the volcanic eruption of Mount Pinatubo, Geophys. Res. Lett., 99, 18861-18869, https://doi.org/10.5194/acp-17-2229-2017, 1994.

Bernath, P., Boone, C., and Crouse, J.: Wildfire smoke destroys stratospheric ozone. Science, 375(6586), 1292–1295. https://doi.org/10.1126/science.abm5611, 2022.

Bernath, P., Boone, C., Pastorek, A., Cameron, D., and Lecours, M.: Satellite characterization of global stratospheric sulfate aerosols released by Tonga volcano, J. Quant. Spectrosc. Rad. Transf., 299, 108520, https://doi.org/10.1016/j.jqsrt.2023.108520, 2023.

Blankenship, J.R, and Crutzen P.J: A photochemical model for the space-time variations of the oxygen allotropes in the 20 to 100 km later, Tellus 18, 160-176, 1965.

Bobrowski, N., Hönninger, G., Galle, B., and Platt, U.: Detection of bromine monoxide in a volcanic plume, Nature, 423, 273–276, https://doi.org/10.1038/nature01625, 2003.

Brasseur, G., The ozone layer from discovery to recovery, American Meteorological Society, ISBN 1944970541, 9781944970543, 2020.

Butler, J. H., Yvon-Lewis, S. A., Lobert, J. M., King, D. B., Montzka, S. A., Bullister, J. L., Koropalov, V., Elkins, J. W., Hall, B. D., Hu, L., and Liu, Y.: A comprehensive estimate for loss of atmospheric carbon tetrachloride (CCl4) to the ocean, Atmos. Chem. Phys., 16, 10899–10910, https://doi.org/10.5194/acp-16-10899-2016, 2016.

Cadoux, A., Scaillet, B., Bekki, S., Oppenheimer, C., and Druitt,T. H.: Stratospheric Ozone destruction by the Bronze-Age Minoan eruption (Santorini Volcano, Greece), Sci. Rep.-UK, 5, 12243, https://doi.org/10.1038/srep12243, 2015.

Caram, C., Szopa, S., Cozic, A., Bekki, S., Cuevas, C.A., and Saiz-Lopez, A.: Sensitivity of tropospheric ozone to halogen chemistry in the chemistry-climate model LMDZ-INCA-vNMHC, Atmos. Chem. Phys., https://doi.org/10.5194/gmd-2021-388, in press, 2023.

Carpenter, L. J.: Iodine in the marine boundary layer. Chemical Reviews, 103(12), 4953–4962. doi:10.1021/cr0206465, 2003.

Carpenter, L. J., MacDonald, S. M., Shaw, M. D., Kumar, R., Saunders, R. W., Parthipan, R., et al., Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine. Nature Geoscience, 6(2), 108–111. https://doi.org/10.1038/ngeo1687, 2013.

Carr, J. L., Horváth, Á., Wu, D. L. & Friberg, M. D. Stereo plume height and motion retrievals for the record-setting Hunga Tonga-Hunga Ha'apai eruption of 15 January 2022, Geophys. Res. Lett., 49, e2022GL098131, 2022.

Carn, S.A., Krotkov, N.A., Fisher, B.L., and Li C.: Out of the blue: Volcanic SO2 emissions during the 2021–2022 eruptions of Hunga Tonga-Hunga Ha'apai (Tonga), Front. Earth Sci., 10:976962, doi: 10.3389/feart.2022.976962, 2022.

Chapman, S.: A theory of upper-atmospheric ozone, Memoirs of the Royal Meteorological Society, 3, 103-125, 1930.

Chipperfield, M.P., S. Bekki, S. Dhomse, N.R.P. Harris, B. Hassler, R. Hossaini, W. Steinbrecht, R. Thieblemont and M. Weber: Detecting recovery of the stratospheric ozone layer, Nature, 549, 211-218, doi:10.1038/nature23681, 2017.

https://doi.org/10.5194/egusphere-2023-1409
Preprint. Discussion started: 30 June 2023

559 Chipperfield, M.P., S.S. Dhomse, W. Feng, R.L. McKenzie, G. Velders, and J.A. Pyle: Quantifying the ozone and UV benefits
560 already achieved by the Montreal Protocol, Nat. Commun., 6, 7233, doi:10.1038/ncomms8233, 2015.
561 Chipperfield, M.P., S. Dhomse, R. Hossaini, W. Feng, M.L. Santee, M. Weber, J.P. Burrows, J.D. Wild, D. Loyola, and M.
562 Coldewey-Egbers, On the cause of recent variations in lower stratospheric ozone, Geophys. Res. Lett., 45, 5718–5726,
563 doi:10.1029/2018gl078071, 2018.
564 Chipperfield, M.P., R. Hossaini, S.A. Montzka, S. Reimann, D. Sherry, and S. Tegtmeier: Renewed and emerging concerns
565 over the production and emission of ozone-depleting substances, Nat. Rev. Earth Environ., 1 (5), 251–263,
566 doi:10.1038/s43017-020-0048-8, 2020.
567 Claxton, T., R. Hossaini, C. Wilson, S.A. Montzka, M.P. Chipperfield, O. Wild, E.M. Bednarz, L.J. Carpenter, S.J. Andrews,
568 S.C. Hackenberg, J. Mühle, D. Oram, S. Park, M. Park, E. Atlas, M. Navarro, S. Schauffler, D. Sherry, M. Vollmer, T.
569 Schuck, A. Engel, P.B. Krummel, M. Maione, J. Arduini, T. Saito, Y. Yokouchi, S. O'Doherty, D. Young, and C. Lunder,
570 A synthesis inversion to constrain global emissions of two very short lived chlorocarbons: dichloromethane, and
571 perchloroethylene, J. Geophys. Res. Atmos., 125, e2019JD031818, doi:10.1029/2019JD031818, 2020.
572 Coy, L., Newman, P. A., Wargan, K., Partyka, G., Strahan, S., and Pawson, S.: Stratospheric Circulation Changes Associated
573 with the Hunga Tonga-Hunga Ha'apai Eruption, Geophys. Res. Lett., 49, e2022GL100982,
574 https://doi.org/10.1029/2022GL100982, 2022.
575 Crutzen, P.J.: The influence of nitrogen oxides on the atmospheric ozone content, Q. J. R. Meteorol. Soc., 96, 320-325, 1970.
576 Crutzen, P.J.: Ozone production rates in oxygen-hydrogen-nitrogen oxide atmosphere, J. Geophys. Res. 76, 7311–7327,
577 doi:10.1029/JC076i030p07311, 1971.
578 Crutzen, P.J.: SSTs: a threat to the Earth's ozone shield, Ambio 1, 41–51, http://www.jstor.org/stable/4311946, 1972.
579 Crutzen, P.J.: A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, Pure App Geophys,
580 106-10, 1385-1399, 1973.
581 Crutzen, P.J.: Estimates of possible future ozone reductions from continued use of fluorochloromethanes (CF_2Cl_2, $CFCl_3$),
582 Geophys. Res. Lett., 1, 205–208, doi:10.1029/GL001i005p00205, 1974.
583 Crutzen, P.J.: The possible importance of CSO for the sulphate layer of the stratosphere, Geophys. Res. Lett., 3(2), 73– 76,
584 doi:10.1029/GL003i002p00073, 1976.
585 Crutzen, P.J. and Arnold, F.: Nitric acid cloud formation in the cold Antarctic stratosphere: a major cause for the springtime
586 'ozone hole', Nature, 324, 651–655, doi:10.1038/324651a0, 1986.
587 Crutzen, P.J. and Ehalt D.H.: Effects of nitrogen fertilizers and combustion on the stratospheric ozone layer, Ambio, 6, 1-3,
588 112-117, 1977.
589 Cuevas, C.A., Fernandez, R.P., Kinnison, D.E., Li, Q., Lamarque, J.-F., Trabelsi, T., Francisco, J.S., Solomon, S., and Saiz-
590 Lopez, A., The influence of iodine on the Antarctic stratospheric ozone hole, *Proceedings of the National Academy of*
591 *Sciences*, 119, doi:10.1073/pnas.2110864119, 2022.
592 Damany-Pearce, L., Johnson, B., Wells, A., Osborne, M., Allan, J., Belcher, C., et al.: Australian wildfires cause the largest
593 stratospheric warming since Pinatubo and extends the lifetime of the Antarctic ozone hole, Nat. Sci. Rep., 12(1), 1-15.
594 https://doi.org/10.1038/s41598-022-15794-3, 2022.
595 De Mazière, M., Thompson, A. M., Kurylo, M. J., Wild, J. D., Bernhard, G., Blumenstock, T., Braathen, G. O., Hannigan, J.
596 W., Lambert, J.-C., Leblanc, T., McGee, T. J., Nedoluha, G., Petropavlovskikh, I., Seckmeyer, G., Simon, P. C., Steinbrecht,
597 W., and Strahan, S. E.: The Network for the Detection of Atmospheric Composition Change (NDACC): history, status and
598 perspectives, Atmos. Chem. Phys., 18, 4935–4964, doi:10.5194/acp-18-4935-2018, 2018.
599 Dhomse, S.S., W. Feng, S.A. Montzka, R. Hossaini, J. Keeble, J.A. Pyle, J.S. Daniel and M.P. Chipperfield, Delay in recovery
600 of the Antarctic ozone hole from unexpected CFC-11 emissions, Nature Communications, 10, 5781, doi:10.1038/s41467-
601 019-13717-x, 2019.

https://doi.org/10.5194/egusphere-2023-1409
Preprint. Discussion started: 30 June 2023

Dhomse, S.S., D. Kinnison, M.P. Chipperfield, R.J. Salawitch, I. Cionni, M. Hegglin, N.L. Abraham, H. Akiyoshi, A.T. Archibald, E.M. Bednarz, S. Bekki, P. Braesicke, N. Butchart, M. Dameris, M. Deushi, S. Frith, S.C. Hardiman, B. Hassler, L.W. Horowitz, R.-M. Hu, P. Joeckel, B. Josse, O. Kirner, S. Kremser, U. Langematz, J. Lewis, M. Marchand, M. Lin, E. Mancini, V. Marecal, M. Michou, O. Morgenstern, F. O'Connor, L. Oman, G. Pitari, D.A. Plummer, J.A. Pyle, L.E. Revell, E. Rozanov, R. Schofield, A. Stenke, K. Stone, K. Sudo, S. Tilmes, D. Visioni, Y. Yamashita and G. Zeng, Estimates of ozone return dates from Chemistry-Climate Model Initiative simulations, *Atmos. Chem. Phys.*, **18**, 8409-8438, doi:10.5194/acp-18-8409-2018, 2018.

Dobson, G.M.B., and D.H. Harrison, Measurements of the amount of ozone in the Earth's atmosphere and its relation to other geophysical conditions, Proc. R. Soc. Lond. A, 110, 662-693, doi:10.1098/rspa.1926.0040, 1926.

Fang, X., Park, S., Saito, T. et al. Rapid increase in ozone-depleting chloroform emissions from China. Nature Geosci 12, 89–93, https://doi.org/10.1038/s41561-018-0278-2, 2019.

Farman, J. C., Gardiner, B. G. & Shanklin, J. D.: Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction, Nature, 315, 207–210, doi:10.1038/315207a0, 1985.

Feng, W., Dhomse, S. S., Arosio, C., Weber, M., Burrows, J. P., Santee, M. L., & Chipperfield, M. P., Arctic ozone depletion in 2019/20: Roles of chemistry, dynamics and the Montreal Protocol. Geophys. Res. Lett., 48, e2020GL091911. doi:10.1029/2020GL091911, 2021.

Feng, W., Plane, J. M. C., Chipperfield, M. P., Saiz-Lopez, A., and Booth, J.-P., Potential stratospheric ozone depletion due to iodine injection from small satellites. Geophys. Res. Lett., 50, e2022GL102300. doi:10.1029/2022GL102300, 2023.

Froidevaux, L., Anderson, J., Wang, H.-J., Fuller, R. A., Schwartz, M. J., Santee, M. L., Livesey, N. J., Pumphrey, H. C., Bernath, P. F., Russell III, J. M., and McCormick, M. P.: Global OZone Chemistry And Related trace gas Data records for the Stratosphere (GOZCARDS): methodology and sample results with a focus on HCl, H_2O, and O_3, Atmos. Chem. Phys., 15, 10471–10507, doi:10.5194/acp-15-10471-2015, 2015.

Hofmann, D.J., and Solomon, S.: Ozone destruction through heterogeneous chemistry following the eruption of El Chichon. J. Geophys. Res. Atmos., 94, 5029–5041, https://doi.org/10.1029/JD094iD04p05029, 1989.

Hossaini, R., M.P. Chipperfield, S.A. Montzka, A.A. Leeson, S.S. Dhomse and J.A. Pyle, The increasing threat to stratospheric ozone from dichloromethane, Nature Communications, 8, 15962, doi:10.1038/ncomms15962, 2017.

Hossaini, R., Chipperfield, M.P., Montzka, S., Rap, A., Dhomse, S. and Feng, W., Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone, *Nature Geoscience*, doi:10.1038/ngeo2363, 2015.

Jenkins, S, Smith, C., Allen, M., and Grainger, R., Tonga eruption increases chance of temporary surface temperature anomaly above 1.5 °C, Nature Climate Change, 13. pp. 127-129, https://doi.org/10.1038/s41558-022-01568-2, 2023.

Johnston, H.: Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust, Science, 173, 517–522, doi:10.1126/science.173.3996.517, 1971.

Jones, C. E., Hornsby, K. E., Sommariva, R., Dunk, R. M., von Glasow, R., McFiggans, G., & Carpenter, L. J.: Quantifying the contribution of marine organic gases to atmospheric iodine. Geophysical Research Letters, 37(18), L18804. https://doi.org/10.1029/2010GL043990, 2010.

Karagodin-Dovennel, A., Rozanov, E., Sukhodolov, T., Egorova, T., Saiz-Lopez, A., Cuevas, C.A., Fernandez, R.P., Sherwen, T., Volkamer, R., Koenig, T.K., Giroud, T., and Peter, T., Iodine chemistry in the chemistry-climate model SOCOL-AVERv2-I, Geosci. Model Dev., 14, 6623-6645, https://doi.org/10.5194/gmd-14-6623-2021, 2021.

Khaykin, S., Legras, B., Bucci, S., Sellitto, P., Isaksen, L., Tencé, L., Bekki, S., Bourassa, A., Rieger, L., Zawada, D., Jumelet, J., and Godin-Beekmann, S.: The 2019/20 Australian wildfires generated a persistent smoke-charged vortex rising up to 35km altitude, Nat. Commun. Earth Environ., 1, 22, doi:10.1038/s43247-020-00022-5, 2020.

Khaykin, S., Podglajen, A., Ploeger, F., Grooß, J.-U., Tence, F., Bekki, S., et al.: Global perturbation of stratospheric water and aerosol burden by Hunga eruption, Nat. Commun. Earth Environ., 3(1), 1–15, doi:10.1038/s43247-022-00652-x, 2022.

https://doi.org/10.5194/egusphere-2023-1409
Preprint. Discussion started: 30 June 2023

Klekociuk, A.R., M.B. Tully, P.B. Krummel, S.I. Henderson, D. Smale, R. Querel, S. Nichol, S.P. Alexander, P.J. Fraser, and G. Nedoluha, The Antarctic ozone hole during 2018 and 2019, J. South. Hemisphere Earth Syst. Sci., 71, 66–91, doi:10.1071/ES20010, 2021.

Koenig, T.K., Baidar, S., Campuzano-Jost, P. Cuevas, C.A., Dix, B., Fernandez, R.P., Guo, H., amuel, R.H., Kinnison, D., Nault, B.A., Ullmann, K., Jimenez, J.L., Saiz-Lopez, A., and Volkamer, R., Quantitative detection of iodine in the stratosphere, Proc. Natl. Acad. Sci., 117, 1860-1866, doi:101.073/pnas.1916828117, 2020.

Kutterolf, S., Hansteen, T., Appel, K., Freundt, A., Kruger, K., Pérez, W., and Wehrmann, H.: Combined bromine and chlorine release from large explosive volcanic eruptions: A threat to stratospheric ozone?, Geology, 41, 707–710, https://doi.org/10.1130/G34044.1, 2013.

Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of atmospheric brown carbon, *Chem. Rev*., 115, 4335–4382, https://doi.org/10.1021/cr5006167, 2015.

Legras, B., Duchamp, C., Sellitto, P., Podglajen, A., Carboni, E., Siddans, R., et al. : The evolution and dynamics of the Hunga Tonga– Hunga Ha'apai sulfate aerosol plume in the stratosphere, Atmos. Chem. Phys., 22(22), 14957–14970. https://doi.org/10.5194/ acp-22-14957-2022, 2022.

Liu, C.-C., Portmann, R. W., Liu, S., Rosenlof, K. H., Peng, Y., & Yu, P.: Significant effective radiative forcing of stratospheric wildfire smoke, Geophys. Res. Lett., 49, e2022GL100175. doi:10.1029/2022GL100175, 2022.

McCormick, M.P., L.W Thomason and C.R. Trepte, Atmospheric effects of the Mt Pinatubo eruption, Nature, 373, 399-404, doi:10.1038/373399a0, 1995.

Millan, L., Santee, M.L., Lambert A., Livesey N.J., Werner F., Schwartz, MJ, Pumphrey, H, Manney, GL, Wang, Y, Su, H, Wu, L, Read, WG & Froidevaux, L., 'Hunga Tonga-Hunga Ha'apai Hydration of the Stratosphere', Geophys. Res. Lett., vol. 49, no. 13, e2022GL099381. https://doi.org/10.1029/2022GL099381, 2022.

Mills, M. J., Richter, J. H., Tilmes, S., Kravitz, B., MacMartin, D. G., Glanville, A. A., Tribbia, J. J., Lamarque, J.-F., Vitt, F., Schmidt, A., Gettelman, A., Hannay, C., Bacmeister, J. T., and Kinnison, D. E.: Radiative and chemical response to interactive stratospheric sulfate aerosols in fully coupled CESM1(WACCM), J. Geophys. Res., 122, 13061-13078, doi:10.1002/2017JD027006, 2017.

Molina, M. J. and Rowland, F. S.: Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone, Nature, 249, 810–812, doi:10.1038/249810a0, 1974.

Montzka, S., G. Dutton, P. Yu, E. Ray, R. Portmann, J. Daniel, L. Kuijpers, B. Hall, D. Mondeel, C. Siso, J. Nance, M. Rigby, A. Manning, L. Hu, F. Moore, B. Miller, and J. Elkins, An unexpected and persistent increase in global emissions of ozone-depleting CFC-11, Nature, 557, 413–417, doi:10.1038/s41586-018-0106-2, 2018.

Montzka, S.A., G.S. Dutton, R.W. Portmann, M.P. Chipperfield, S. Davis, W. Feng, A.J. Manning, E. Ray, M. Rigby, B.D. Hall, C. Siso, J.D. Nance, P.B. Krummel, J. Mühle, D. Young, S. O'Doherty, P.K. Salameh, C.M. Harth, R.G. Prinn, R.F. Weiss, J.W. Elkins, H. Walter-Terrinoni, and C. Theodoridi, A decline in global CFC-11 emissions during 2018–2019, Nature, 590, 428–432, doi:10.1038/s41586-021-03260-5, 2021.

Morgenstern, O., M.I. Hegglin, E. Rozanov, F.M. O'Connor, N.L. Abraham, H. Akiyoshi, A.T. Archibald, S. Bekki, N. Butchart, M.P. Chipperfield, M. Deushi, S.S. Dhomse, R.R. Garcia, S.C. Hardiman, L.W. Horowitz, P. Jöckel, B. Josse, D. Kinnison, M. Lin, E. Mancini, M.E. Manyin, M. Marchand, V. Marécal, M. Michou, L.D. Oman, G. Pitari, D.A. Plummer, L.E. Revell, D. Saint-Martin, R. Schofield, A. Stenke, K. Stone, K. Sudo, T.Y. Tanaka, S. Tilmes, Y. Yamashita, K. Yoshida, and G. Zeng, Review of the global models used within phase 1 of the Chemistry–Climate Model Initiative (CCMI), Geosci. Model Dev., 10, 639–671, doi:10.5194/gmd-10-639-2017, 2017.

Müller, R.: Paul Jozef Crutzen, Biogr. Mems. Fell. R. Soc., 73, 127-156, doi:10.1098/rsbm.2022.0011, 2022.

https://doi.org/10.5194/egusphere-2023-1409
Preprint. Discussion started: 30 June 2023

Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., et al., Bromine and iodine chemistry in a global chemistry-climate model: Description and evaluation of very short-lived oceanic sources. Atmos. Chem. Phys., 12(3), 1423–1447. https://doi.org/10.5194/acp-12-1423-2012, 2012.

Newchurch, M. J., Yang, E.-S., Cunnold, D. M., Rein-sel, G. C., Zawodny, J. M., and Russell, J. M.: Evidence for slowdown in stratospheric ozone loss: First stage of ozone recovery, J. Geophys. Res., 108, 4507, https://doi.org/10.1029/2003JD003471, 2003.

Park, S., Li, S., Mühle, J., O'Doherty, S., Weiss, R. F., Fang, X., Reimann, S., and Prinn, R. G.: Toward resolving the budget discrepancy of ozone-depleting carbon tetrachloride (CCl4): an analysis of top-down emissions from China, Atmos. Chem. Phys., 18, 11729–11738, https://doi.org/10.5194/acp-18-11729-2018, 2018.

Park, S., Western, L.M., Saito, T. et al. A decline in emissions of CFC-11 and related chemicals from eastern China. Nature 590, 433–437, doi:10.1038/s41586-021-03277-w, 2021.

Pazmino, A., Goutail, F., Godin-Beekmann, S., Hauchecorne, A., Pommereau, J.-P., Chipperfield, M. P., Feng, W., Lefèvre, F., Lecouffe, A., Van Roozendael, M., Jepsen, N., Hansen, G., Kivi, R., Strong, K., Walker, K. A., and Colwell, S.: Trends in polar ozone loss since 1989: First signs of recovery in Arctic ozone column, EGUsphere [preprint], https://doi.org/10.5194/egusphere-2023-788, 2023.

Peterson, D., Fromm, M., McRae, R. H. D., Campbelle, J. R., Hyer, E. J., Taha, G., et al.: Australia's black summer pyrocumulonimbus super outbreak reveals potential for increasingly extreme stratospheric smoke events, Npj Clim. Atmospheric Sci., 4(38), 2235–2255, https://doi.org/10.1038/s41612-021-00192-9, 2021.

Peterson, D. A., J. R. Campbell, E. J. Hyer , M. D. Fromm , G. P. Kablick , J. H. Cossuth , and M. T. DeLand: Wildfire-driven thunderstorms cause a volcano-like stratospheric injection of smoke, Npj Clim. Atmospheric Sci., 1, 30, doi:10.1038/s41612-018-0039-3, 2018.

Pitari, G., Aquila, V., Kravitz, B., Robock, A., Watanabe, S., Cionni, I., Luca, N. D., Genova, G. D., Mancini, E., and Tilmes, S.: Stratospheric ozone response to sulfate geoengineering: Results from the Geoengineering Model Intercomparis on Project (GeoMIP), J. Geophys. Res., 119, 2629–2653, https://doi.org/10.1002/2013JD020566, 2014.

Proud, S.R., Prata, A., and Schmauss, S.: The January 2022 eruption of Hunga Tonga-Hunga Ha'apai volcano reached the mesosphere, Science, 378:554–7, doi:10.1126/science.abo4076, 2022.

Pyle, D. and Mather, T.: Halogens in igneous processes and their fluxes to the atmosphere and oceans from volcanic activity: A review, Chem. Geol., 263, 110–121, https://doi.org/10.1016/j.chemgeo.2008.11.013, 2009.

Pyle, J.A., J. Keeble, N.L. Abraham, M.P. Chipperfield and P.T. Griffiths, Integrated ozone depletion as a metric for ozone recovery, Nature, 608, 719-723, doi:10.1038/s41586-022-04968-8, 2022.

Rigby, M., Park, S., Saito, T. et al. Increase in CFC-11 emissions from eastern China based on atmospheric observations. Nature 569, 546–550, /doi:10.1038/s41586-019-1193-4, 2019.

Robock, A.: Volcanic eruptions and climate, Rev. Geophys., 38, 191–219, https://doi.org/10.1029/1998RG000054, 2000.

Saiz-Lopez, A., Plane, J.M.C., Baker, A.R., Carpenter, L.J., von Glasow, R., Gómez Martín, J.C., McFiggans, G., and Saunders, R.W., Atmospheric Chemistry of Iodine, *Chemical Reviews*, 112 (3), 1773-1804, DOI: 10.1021/cr200029u., 2012.

Santee, M. L., Lambert, A., Manney, G. L., Livesey, N. J., Froidevaux, L., Neu, J. L., et al.: Prolonged and pervasive perturbations in the composition of the Southern Hemisphere midlatitude lower stratosphere from the Australian New Year's fires, Geophys. Res. Lett., 49(4), e2021GL096270. https://doi.org/10.1029/2021GL096270, 2022.

Schoeberl, M. R., Wang, Y., Ueyama, R., Taha, G., Jensen, E., and Yu, W.: Analysis and Impact of the Hunga Tonga-Hunga Ha'apai Stratospheric Water Vapor Plume, Geophys. Res. Lett., 49, e2022GL100248, https://doi.org/10.1029/2022GL100248, 2022.

Sellitto, P., Belhadji, R., Kloss, C., & Legras, B.: Radiative impacts of the Australian bushfires 2019–2020—Part 1: Large-scale radiative forcing, Atmos. Chem. Phys., 22(14), 9299–9311, https://doi.org/10.5194/acp-22-9299-2022, 2022a.

https://doi.org/10.5194/egusphere-2023-1409
Preprint. Discussion started: 30 June 2023

Sellitto, P., Podglajen, A., Belhadji, R., Boichu, M., Carboni, E., Cuesta, J., Duchamp, C., Kloss, C., Siddans, R., Bègue, N., Blarel, L., Jegou, F., Khaykin, S., Renard, J.-B., and Legras, B., The unexpected radiative impact of the Hunga Tonga eruption of 15th January 2022, Commun. Earth Environ., 3, 288, https://doi.org/10.1038/s43247-022-00618-z, 2022b.

Sherry, D., A. McCulloch, Q. Liang, S. Reimann and P.A. Newman, Current sources of carbon tetrachloride (CCl_4) in our atmosphere, Env. Res. Lett., 13, 024004, doi:10.1088/1748-9326/aa9c87, 2018.

Sherwen, T., Evans, M. J., Carpenter, L. J., Andrews, S. J., Lidster, R. T., Dix, B., et al. (2016). Iodine's impact on tropospheric oxidants: A global model study in GEOS-chem. Atmos. Chem. Phys., 16(2), 1161–1186. doi:10.5194/acp-16-1161-2016.

Stenchikov, G., Kirchner, I., Robock, A., Graf, H.-F., Antuña, J. C., Grainger, R. G., Lambert, A., and Thomason, L.: Radiative forcing from the 1991 Mount Pinatubo volcanic eruption, J. Geophys. Res., 103, 13837–13857, https://doi.org/10.1029/98JD00693, 1998.

Stocker, M., Ladstädter, F., and Steiner, A.: Observing the climate impact of large wildfires on stratospheric temperature, Nat. Sci. Rep., https://doi.org/10.1038/s41598-021-02335-7, 2021.

Solomon, S., and P. J. Crutzen: Analysis of the August 1972 solar proton event including chlorine chemistry, J. Geophys. Res., 86, 1140-1146, 1981.

Solomon, S., Garcia, R. R., and Ravishankara, A. R., On the role of iodine in ozone depletion, *J Geophys. Res-Atmos.*, 99, 20491-20499, doi:10.1029/94JD02028, 1994.

Solomon, S.: Stratospheric ozone depletion: a review of concepts and history, Rev. Geophys., 37, 275–316, doi:10.1029/1999RG900008, 1999.

Solomon, S.: Paul J. Crutzen (1933–2021), Science 371, 892, doi:10.1126/science.abh0217, 2021a.

Solomon, S. 2021b Risks to the stratospheric ozone shield in the Anthropocene, Ambio, 50, 44–48, doi:10.1007/ s13280-020-01431-8, 2021b.

Solomon, S., Garcia, R. R., Rowland, F. S. & Wuebbles, D. J.: On the depletion of Antarctic ozone, Nature, 321, 755–758, doi:10.1038/321755a0, 1986.

Solomon, S., Ivy, D. J., Kinnison, D., Mills, M. J., Neely, R. R. & Schmidt, A.: 2016 Emergence of healing in the Antarctic ozone layer, Science, 353, 269–274, doi:10.1126/science.aae0061, 2016.

Solomon, S., Stone, K., Yu, P., Murphy, D.M., Kinnison, D., Ravishankara, A.R., and Wang, P.: Chlorine activation and enhanced ozone depletion induced by wildfire aerosol, Nature, 615, 10.1038/s41586-022-05683-0, 2023.

Steinbrecht, W., L. Froidevaux, R. Fuller, R. Wang, J. Anderson, C. Roth, A. Bourassa, D. Degenstein, R. Damadeo, J. Zawodny, S. Frith, R. McPeters, P. Bhartia, J. Wild, C. Long, S. Davis, K. Rosenlof, V. Sofieva, K. Walker, N. Rahpoe, A. Rozanov, M. Weber, A. Laeng, T. von Clarmann, G. Stiller, N. Kramarova, S. Godin-Beekmann, T. Leblanc, R. Querel, D. Swart, I. Boyd, K. Hocke, N. Kämpfer, E. Maillard Barras, L. Moreira, G. Nedoluha, C. Vigouroux, T. Blumenstock, M. Schneider, O. García, N. Jones, E. Mahieu, D. Smale, M. Kotkamp, J. Robinson, I. Petropavlovskikh, N. Harris, B. Hassler, D. Hubert, and F. Tummon, An update on ozone profile trends for the period 2000 to 2016, Atmos. Chem. Phys., 17, 10,675–10,690, doi:10.5194/acp-17-10675-2017, 2017.

Stolarski, R. S. and Cicerone, R. J. Stratospheric chlorine: A possible sink for ozone. *Can. J. Chem.* **52**, 1610–1615, 1974.

Velders, G.J.M., S.O. Andersen, J.S. Daniel, D.W. Fahey and M. McFarland, The importance of the Montreal Protocol in protecting climate, PNAS, 104, 4814-4819, doi:10.1073/pnas.0610328104, 2007.

Villamayor, J., Iglesias-Suarez, F., Cuevas, C.A. et al.: Very short-lived halogens amplify ozone depletion trends in the tropical lower stratosphere. Nat. Clim. Chang. 13, 554–560,. doi:10.1038/s41558-023-01671-y, 2023.

Weber, M., W. Steinbrecht, C. Arosio, R. van der A, S.M. Frith, J. Anderson, M. Coldewey-Egbers, S. Davis, D. Degenstein, V.E. Fioletov, L. Froidevaux, D. Hubert, C.S. Long, D. Loyola, A. Rozanov, C. Roth, V. Sofieva, K. Tourpali, R. Wang, and J.D. Wild, Stratospheric ozone, in [State of the Climate in 2019], Bull. Am. Met. Soc., 101 (8), S78–S81, doi:10.1175/BAMS-D-20-0104.1, 2020.

https://doi.org/10.5194/egusphere-2023-1409
Preprint. Discussion started: 30 June 2023

Weber, M., W. Steinbrecht, C. Arosio, R. van der A, S.M. Frith, J. Anderson, L. Castia, M. Coldewey-Egbers, S. Davis, D. Degenstein, V.E. Fioletov, L. Froidevaux, D. Hubert, D. Loyola, C. Roth, A. Rozanov, V. Sofieva, K. Tourpali, R. Wang, and J.D. Wild, Stratospheric ozone, [State of the Climate in 2020], Bull. Am. Met. Soc., 102 (8), S92–S95, doi:10.1175/2021BAMSStateoftheClimate.1, 2021.

WMO Scientific assessment of ozone depletion: 2010. Global Ozone Research and Monitoring Project Report no. 52. Geneva, Switzerland: World Meteorological Organization, 2011.

WMO Scientific assessment of ozone depletion: 2018. Global Ozone Research and Monitoring Project Report no. 58. Geneva, Switzerland: World Meteorological Organization, 2018.

WMO Scientific assessment of ozone depletion: 2022. Global Ozone Research and Monitoring Project – GAW Report no. 278. Geneva, Switzerland: World Meteorological Organization, 2022.

Xu, J., Li, D., Bai, Z., Tao, M., and Bian, J.: Large Amounts of Water Vapor Were Injected into the Stratosphere by the Hunga Tonga–Hunga Ha'apai Volcano Eruption, Atmosphere, 13,912. doi:10.3390/atmos13060912, 2022.

Youn, D., Patten, K. O., Wuebbles, D. J., Lee, H., & So, C.-W., Potential impact of iodinated replacement compounds CF3I and CH3I on atmospheric ozone: A three-dimensional modeling study. Atmospheric Chemistry and Physics, 10(20), 10129–10144. https://doi.org/10.5194/acp-10-10129-2010, 2010.

Yu, P., Davis, S. M., Toon, O. B., Portmann, R. W., Bardeen, C.G., Barnes, J. E., et al.: Persistent stratospheric warming due to 2019–2020 Australian wildfire smoke. Geophys. Res. Lett., *48*, e2021GL092609. https://doi.org/10.1029/2021GL092609, 2021.

Zanchettin, D., Khodri, M., Timmreck, C., Toohey, M., Schmidt, A., Gerber, E. P., Hegerl, G., Robock, A., Pausata, F. S. R., Ball, W. T., Bauer, S. E., Bekki, S., Dhomse, S. S., LeGrande, A. N., Mann, G. W., Marshall, L., Mills, M., Marchand, M., Niemeier, U., Poulain, V., Rozanov, E., Rubino, A., Stenke, A., Tsigaridis, K., and Tummon, F.: The Model Intercomparison Project on the climatic response to Volcanic forcing (VolMIP): experimental design and forcing input data for CMIP6, Geosci. Model Dev., 9, 270–2719, https://doi.org/10.5194/gmd-9-2701-2016, 2016.

Zanchettin, D., Timmreck, C., Khodri, M., Schmidt, A., Toohey,M., Abe, M., Bekki, S., Cole, J., Fang, S.-W., Feng, W., Hegerl, G., Johnson, B., Lebas, N., LeGrande, A. N., Mann, G. W.,Marshall, L., Rieger, L., Robock, A., Rubinetti, S., Tsigaridis, K., and Weierbach, H.: Effects of forcing differences and initial conditions on inter-model agreement in the VolMIP volc-pinatubo-full experiment, Geosci. Model Dev., 15, 2265–2292, https://doi.org/10.5194/gmd-15-2265-2022, 2022.

Zhang, J., Wuebbles, D. J., Kinnison, D.E., & Saiz-Lopez, A.: Revising the ozone depletion potentials metric for short-lived chemicals such as CF_3I and CH_3I, J. Geophys. Res., 125, e2020JD032414, https://doi.org/10.1029/2020JD032414, 2020.

Zhu, Y., Bardeen, C. G., Tilmes, S., Mills, M. J., Wang, X., Harvey, V. L., Taha, G., Kinnison, D., Portmann, R. W., Yu, P., Rosenlof, K. H., Avery, M., Kloss, C., Li, C., Glanville, A. S., Millán, L., Deshler, T., Krotkov, N., and Toon, O. B.: Perturbations in stratospheric aerosol evolution due to the water-rich plume of the 2022 Hunga-Tonga eruption, Communications Earth and Environment, 3, 248, https://doi.org/10.1038/s43247-022-00580-w, 2022.

Zuo, M., Zhou, T. J., Man, W. M., Chen, X. L., Liu, J., Liu, F., and Gao, C.: Volcanoes and climate: Sizing up the impact of the recent Hunga Tonga-Hunga Ha'apai volcanic eruption from a historical perspective, Advances in Atmospheric Sciences, 39(12), 1986–1993. https://doi.org/10.1007/s00376-022-2034-1, 2022.

https://doi.org/10.5194/egusphere-2023-1409
Preprint. Discussion started: 30 June 2023

Figures

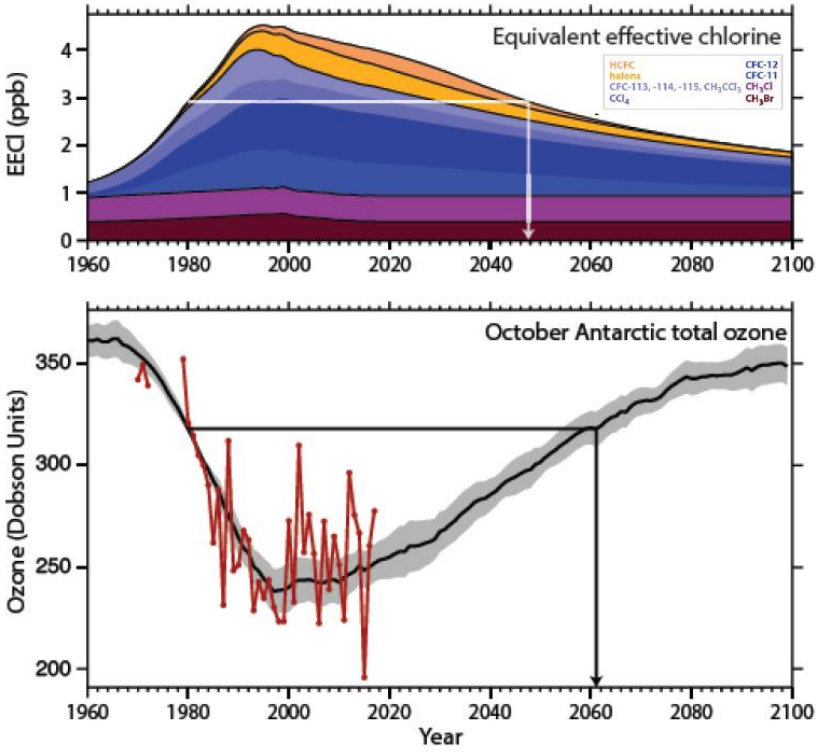

Figure 1: (a) Past observations and projections of the equivalent effective chlorine (EECl; total chlorine + 65 × total bromine at surface, ppb) from different long-lived ODSs between 1960 and 2100. After the signing of the Montreal Protocol and subsequent phase-out of many long-lived ODSs, the EECl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

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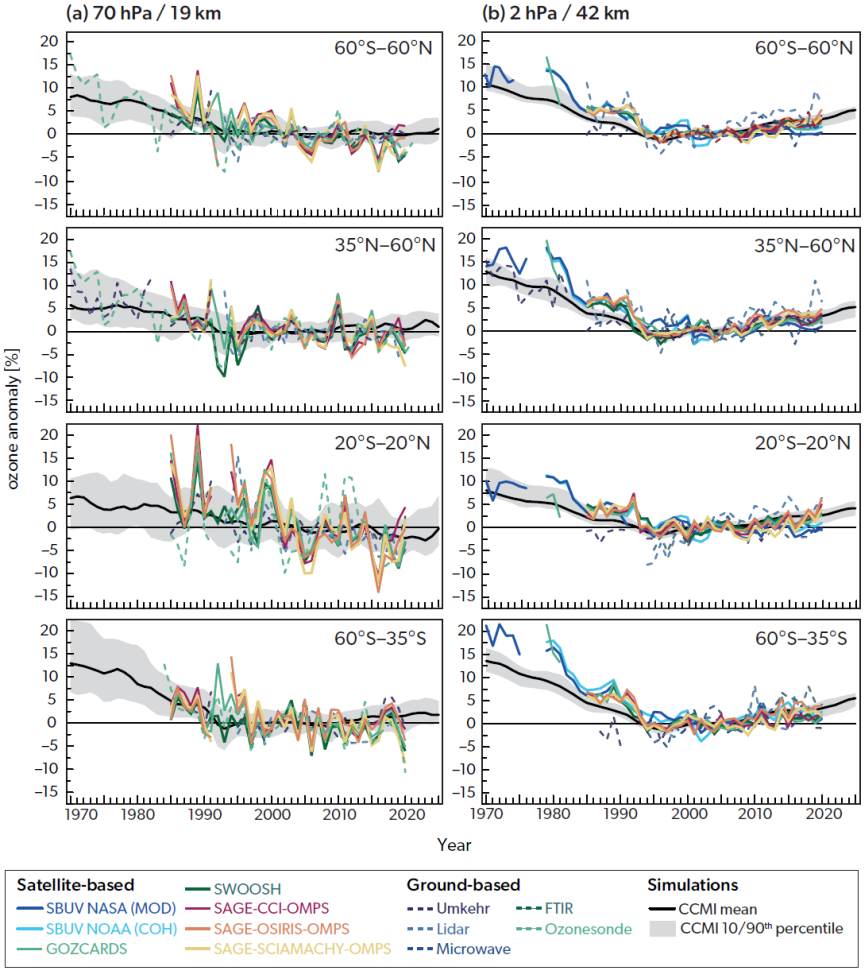

Figure 2. Annual mean anomalies of ozone in (a) the lower stratosphere, near 19 km altitude (70 hPa pressure) and (b) the upper stratosphere, near 42 km (2 hPa), for four latitude bands: 60°S–60°N, 35–60°N, 20°S–20°N (tropics), and 60–35°S. Anomalies are referenced to a 1998–2008 baseline. Coloured lines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

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Preprint. Discussion started: 30 June 2023

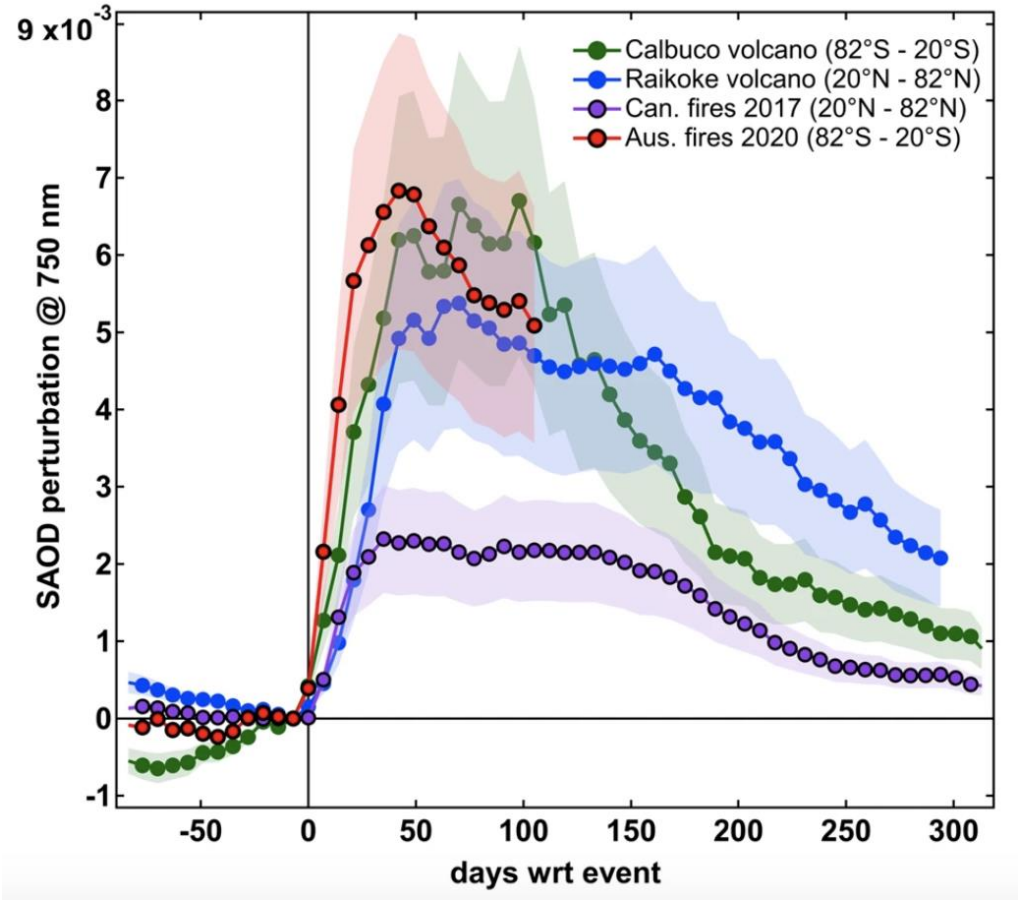

Figure 3. Perturbation of the stratospheric aerosol optical depth (SAOD) due to Australian fires and the strongest events since 1991. The curves represent the SAOD perturbation at 746 nm following the Australian wildfires, the previous record-breaking Canadian wildfires in 2017, and the strongest volcanic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

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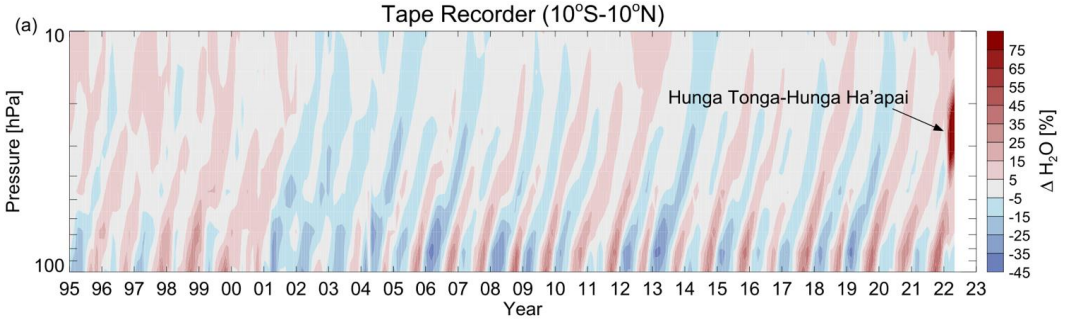

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851 **Figure 4.** Zonal mean H_2O anomalies in the tropics, between 10°S and 10°N (the so-called atmospheric tape recorder). H_2O
852 abundances are based on GOZCARDS (Froidevaux et al., 2015) and Microwave Limb Sounder data. See Millan et al. (2022)
853 for more details.