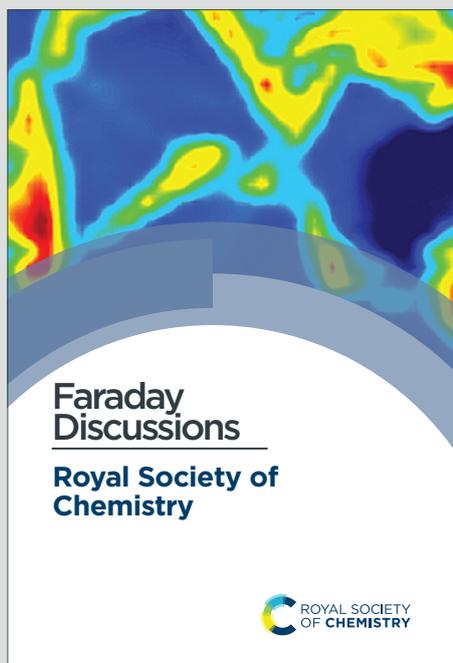


Faraday Discussions

Accepted Manuscript



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: M. P. Chipperfield, S. Heddell, S. Dhomse, W. Feng, S. Chang, G. Mann, X. Zhou and H. Pumphrey, *Faraday Discuss.*, 2024, DOI: 10.1039/D4FD00163J.

1 Ongoing large ozone depletion in the polar lower stratospheres: The role of increased 2 water vapour

View Article Online
DOI: 10.1039/D4FD00163J

3
4 Martyn P. Chipperfield^{1,2}, Saffron Heddell¹, Sandip S. Dhomse^{1,2}, Wuhu Feng^{1,3},
5 Shujie Chang¹, Graham Mann¹, Xin Zhou⁴, and Hugh Pumphrey⁵

- 6
7 1. School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK
8 2. National Centre for Earth Observation, University of Leeds, UK
9 3. National Centre for Atmospheric Science, University of Leeds, UK
10 4. School of Atmospheric Sciences, Chengdu University of Information Technology,
11 Chengdu, China
12 5. School of Geosciences, University of Edinburgh, UK

13
14 *For submission to Royal Society of Chemistry Faraday Discussion meeting on Atmospheric
15 Chemistry in Cold Environments, Feb 17-19th 2025.*

17 Abstract

18 The very low temperatures of the polar lower stratosphere lead to the efficient seasonal
19 depletion of ozone following the formation of polar stratospheric clouds (PSCs) and
20 heterogeneous chlorine-activating reactions on their surface. The Montreal Protocol has
21 controlled the production of major chlorine- (and bromine-) containing Ozone Depleting
22 Substances (ODSs) and the stratospheric Cl and Br loadings have been slowly decreasing for
23 over two decades. However, we are still experiencing very large (by some measures record)
24 ozone depletion in the Antarctic and cold Arctic springs. There are a variety of factors
25 involved but here we focus on the possible role of increased stratospheric water vapour, for
26 example as occurred due to the eruption of the underwater volcano Hunga Tonga-Hunga
27 Ha'apai in January 2022. We perform idealised TOMCAT three-dimensional chemical
28 transport model experiments to investigate the impacts if a Hunga-like eruption had been
29 followed by conditions such as the very cold Arctic winter of 2019/2020, and contrast the
30 impact in the cold Antarctic spring of 2020 with the previous warmer, more disturbed year of
31 2019. In the Antarctic, efficient dehydration by sedimenting ice PSCs limits the impact of a 1
32 ppmv increase in H₂O to a maximum additional depletion of 16 Dobson Units (DU) in 2020
33 and 11 DU in 2019 at the vortex edge in late September. A 1 ppmv H₂O increase in the cold
34 Arctic vortex of 2019/2020 causes a maximum of 16 DU additional depletion at the vortex
35 edge in mid March. The direct chemical impact of water vapour from Hunga-like eruption on
36 polar ozone is therefore modest in any given year, given natural variability. However, regular
37 increased H₂O injection or production from increased CH₄ oxidation could represent an
38 important factor in gradual long-terms trends.



39 1. Introduction

40 The polar lower stratosphere is one of the coldest environments in the atmosphere. In the
41 Antarctic winter and spring, temperatures are regularly below 195 K, the typical formation
42 threshold of polar stratospheric clouds (PSCs), composed of water vapour and nitric acid
43 (nitric acid trihydrate (NAT), Solomon 1999). Temperatures usually also fall below 188 K, at
44 which point ice PSCs can form and grow large enough to sediment to lower altitudes (e.g.
45 Tritscher et al., 2021). The formation of PSCs allows heterogeneous reactions to activate
46 chlorine, i.e. convert reservoir species such as HCl and ClONO₂ to photochemically active
47 species such as Cl₂ and HOCl (Solomon et al., 1986). These species then photolyse to release
48 Cl atoms which can lead to rapid springtime ozone loss through catalytic cycles involving
49 ClO and BrO. At present large ozone depletion regularly occurs every Antarctic spring due to
50 the widespread occurrence of low temperatures and PSCs. Temperatures in the Arctic
51 wintertime lower stratosphere are warmer and more variable than the Antarctic, but
52 occasional years (e.g. 2019/2020) are cold enough for widespread NAT PSC formation and
53 therefore large springtime ozone loss (Manney et al., 2020; Feng et al., 2021).

54 The discovery of the Antarctic ozone hole (Farman et al., 1985), and its subsequent
55 explanation by Cl/Br chemistry, helped to precipitate and strengthen the Montreal Protocol.
56 This international agreement aims to control the production of the long-lived source gases
57 which deliver the chlorine and bromine to the stratosphere, causing a trend of decreasing
58 ozone in the Antarctic, and to smaller extent the Arctic and mid-latitudes. Examples of these
59 so-called ozone-depleting substances (ODSs) are chlorofluorocarbons (CFCs) and bromine-
60 containing halons. Following successful implementation of the Montreal Protocol,
61 stratospheric chlorine and then bromine peaked in 1990s (see WMO, 2022). This decrease in
62 stratospheric halogen loading has led to the detection of ozone recovery (i.e. decreased
63 depletion by halogens) in the upper stratosphere (Newchurch et al., 2003) and the Antarctic
64 lower stratosphere (Solomon et al., 2016). Evidence for a clear trend in ozone recovery has
65 not yet been detected in other regions due to the slow decay rate of stratospheric chlorine and
66 bromine and the confounding effects of natural variability (e.g. Chipperfield et al., 2017).

67 Despite action taken under the Montreal Protocol, and the expected long-term recovery of the
68 ozone layer, we continue to experience years with large (even record) ozone depletion in both
69 polar regions. For example, the calendar year 2020 saw extremely large depletion at both
70 poles (Chapter 4 WMO, 2022). There is likely a range of factors in causing continued low
71 polar ozone, some of which are linked to recent extreme phenomena. The large Australian
72 fires around new year 2019/2020 injected smoke particles high into the stratosphere, causing
73 transient perturbations to chemistry and ozone depletion (e.g. Santee et al., 2022; Solomon et
74 al., 2023). The eruption of the underwater Hunga Tonga-Hunga Ha'apai (hereafter Hunga)
75 volcano in January 2022 injected an enormous quantity (150 Tg) of water vapour into the
76 stratosphere (increasing the existing global stratospheric burden by 10%). Note that Hunga
77 only injected a very small amount (0.5 Tg) of SO₂. The additional water vapour is expected to
78 persist in the stratosphere for many years and will impact the ozone layer directly through
79 gas-phase (increased HOx) and heterogeneous chemistry (increased occurrence of PSCs and

View Article Online
DOI: 10.1039/D4FD00163J



80 changed aerosol activity) chemistry (Santee et al., 2023). Water vapour is also a radiatively
81 active gas. The excess H₂O caused a strong cooling in the SH mid-latitude stratosphere
82 shortly after the eruption (Schoeberl et al., 2022; Vomel et al., 2022), which in turn
83 strengthened the mid-latitude jet and slowed down the Brewer-Dobson Circulation (BDC)
84 (Coy et al., 2022).

85 Prior to the eruption of Hunga, there had been concern over the impact of future, long-term
86 hydration of the stratosphere, e.g. due to increased methane oxidation or changing tropopause
87 temperatures, on climate, chemistry and polar ozone. von de Gaathen et al. (2021) argued that
88 Arctic ozone depletion in future cold winters through 2100 may increase despite large
89 reductions in chlorine and bromine due to increases in stratospheric water vapour and
90 increased PSC occurrence. In some ways the current Hunga-hydrated stratosphere is a test
91 case for such future conditions.

92 This paper discusses the impact of a Hunga-like volcanic eruption on polar ozone loss under
93 meteorological conditions experienced in the past 7 years. We use idealised ‘counter factual’
94 simulations to explore how ozone would respond under conditions that are optimal for the
95 extensive occurrence of PSCs, for example Arctic winter 2019/2020. In reality, the Hunga
96 water vapour from the January 2022 eruption began to affect Antarctic ozone in 2023 and
97 Arctic ozone in 2023 and 2024. In the case of the Arctic, both of these years were warm and
98 disturbed so the potential for additional PSC occurrence at the critical time for ozone loss
99 (January-March) was limited. For the Antarctic in 2023 efficient dehydration by sedimenting
100 ice clouds appeared to limit the effect on ozone in the vortex core (Wohlmann et al., 2024;
101 Zhou et al., 2024) and may even be a primary route for the removal of this excess water
102 vapour from the stratosphere. Dehydration does not occur to any large extent in the warmer
103 Arctic stratosphere, so this may potentially allow a larger effect from enhanced water vapour.

104 The layout of the paper is as follows. Section 2 describes the TOMCAT off-line 3-D
105 chemical transport model (CTM) and set-up of the model simulations. Section 3 presents our
106 results for long-term ozone changes and the potential impact of a Hunga-like eruption on
107 different Arctic and Antarctic winters. Section 4 summarises our conclusions.

108

109 2. Model Simulations

110 We have performed a series of experiments with the TOMCAT/SLIMCAT (hereafter
111 TOMCAT) off-line 3-D CTM (Chipperfield, 2006). The model contains a detailed
112 description of stratospheric chemistry, including heterogeneous reactions on sulfate aerosols
113 and PSCs. The model was forced using European Centre for Medium-Range Weather
114 Forecasts (ECMWF) ERA5 winds and temperatures (Hersbach et al., 2020) and run with a
115 resolution of 2.8° × 2.8° with 32 levels from the surface to ~60 km following Dhomse et al.
116 (2019). The surface mixing ratios of long-lived source gases (e.g., CFCs, hydrofluorocarbons,
117 CH₄, N₂O) were taken from WMO (2022) scenario A1. The solar cycle was included using
118 time-varying solar spectral irradiance (SSI) data (1995–2023) from the Naval Research
119 Laboratory (NRL) solar variability model, referred to as NRLSSI2 (update of Coddington et



120 al., 2016, 2019). Solar fluxes from December 2023 are used to extend the simulation until
121 August 2024. Stratospheric sulfate aerosol surface density (SAD) data until June 2017 were
122 obtained from CMIP6 database ftp://iacftp.ethz.ch/pub_read/luo/CMIP6/ (Arfeuille et al.,
123 2013). From July 2017, we use SAGE-III-based SAD values from Knepp et al. (2024). The
124 implementation of SAD and SSI variability is described in Dhomse et al. (2015) and Dhomse
125 et al. (2016), respectively. The model also has a passive ozone tracer for diagnosing polar
126 chemical ozone loss which is initialised from the chemical ozone tracer every December 1
127 and June 1 (e.g., Feng et al., 2007).

128 We performed a total of four model simulations. The control run (CNTL) was spun up from
129 1977 and integrated until August 2024 including all of the processes described above.
130 Sensitivity run **HT** was initialized from CNTL in January 2022 and integrated until June
131 2024 with a simulation of injection of 150 Tg of H₂O into the stratosphere to mimic Hunga
132 (see Zhou et al., 2024). Run **HT2017** was similar to HT but the Hunga eruption was assumed
133 to occur 5 years earlier in January 2017. This allows us to investigate the impact on a Hunga-
134 like eruption on ozone loss in the cold Arctic winter of 2019/2020. Finally, sensitivity run
135 **EXH2O** was initialised on November 1st 2019 from CNTL but has the instantaneous
136 injection on that date of an additional 1 ppmv water vapour globally, again ahead of the cold
137 Arctic winter of 2019/2020. Run EXH2O allows us to investigate the impact of a uniform
138 additional amount of water vapour in a series of polar winters in a way that is independent of
139 model transport timescales to disperse a localised eruption plume.

140 We also diagnose the direct chemical impact of the increased H₂O on stratospheric ozone
141 through gas-phase and heterogeneous chemistry. The impacts are simulated with specified
142 realistic meteorology, which is important for temperature-dependent processes such as PSC
143 formation but hence do not account explicitly for dynamical feedbacks. Note that the
144 injection of SO₂ from Hunga is treated as part of the monthly total SAD fields that are read
145 into the model. This is the same for all runs and so in this study we do not diagnose explicitly
146 the impact of this additional SO₂ injection.

147

148 3. Results

149 3.1 Variability of Polar Column Ozone

150 Ozone levels in the polar winter/spring are maintained by a balance of dynamical and
151 chemical processes. In the Antarctic chemical depletion generally dominates while in the
152 Arctic both processes make large and variable contributions to the column amount in any
153 year. **Figure 1a** shows the mean September Antarctic (60°S-90°S) column ozone from 2004
154 to 2023 from the Ozone Monitoring Instrument/Ozone Mapping and Profiler Suite
155 (OMI/OMPS) observations and the model runs. From 2004 to 2018 the observed mean
156 column ranges from around 200 DU to 250 DU with some interannual variability and
157 indications of an increasing trend. As discussed by Solomon et al. (2016) this September
158 increase is consistent with a decreasing rate of chlorine- and bromine-catalysed chemical
159 ozone depletion, i.e. ozone recovery due to the actions of the Montreal Protocol. The year



160 2019 is notable for a large mean September column due to a disturbed polar vortex and
161 increase dynamical replenishment of ozone (see below). Since then, we have experienced a
162 series of four winters (2020-2023) with comparatively low mean column ozone and little
163 interannual variability. This appears to challenge the notion that Antarctic ozone is
164 recovering, but these years do encompass a range of exceptional atmospheric perturbations
165 which likely contributed to lower ozone through either increased chemical depletion or
166 modified transport. Some studies suggest non-negligible chemical depletion of polar ozone
167 caused by the Australian New Year smoke aerosol, with the contribution to ozone loss
168 comparable to that of the sulfate aerosol from the Calbuco eruption in 2015 (Yu et al., 2021;
169 Rieger et al., 2021). The eruption of Hunga in January 2022 is not believed to have impacted
170 Antarctic ozone in 2022 (see discussion of H₂O transport in Section 3.2). For 2023, Zhou et
171 al. (2024) estimated a modest increase in chemical ozone depletion of around 10 DU at the
172 vortex edge due to the increased Hunga water vapour. Interestingly, the impact of the water
173 vapour was limited by dehydration in the vortex core. Regardless of the initial amount of
174 water vapour in the model vortex, formation and sedimentation of ice PSCs removes all of
175 the gas-phase H₂O except for a residual amount determined by the equilibrium vapour
176 pressure.

177 **Figure 2a** shows mean March Arctic (60°N-90°N) column ozone from observations and our
178 model simulations from 2004 to 2024. The OMI/OMPS observations clearly show 2020 (330
179 DU) and 2011 (335 DU) as the 2 years with extremely low column ozone with, by this
180 metric, slightly lower values in 2020. The low ozone in these cold years was caused by
181 increased PSC activity and related chemical ozone loss, coupled with smaller dynamical
182 replenishment (see e.g. Wohltmann et al., 2020; Feng et al., 2021). In recent years the mean
183 Arctic column was relatively small in 2021 and 2022, larger in 2023 and then exceptionally
184 large in 2024 (Newman et al., 2024).

185 The chemical ozone tracer from model run CNTL captures the overall interannual variability
186 in both polar regions very well (**Figures 1a** and **2a**). Results from the model run can be used
187 to separate the contributions of dynamics and transport, for example by comparing the
188 passive ozone tracer between the start of winter (July in Antarctic, December in Arctic) with
189 late spring. These differences show that much of the interannual variability in springtime
190 column ozone, averaged over these wide latitude bands, is determined by transport (e.g. 2019
191 in the Antarctic, 2010/2011 and 2019/2020 in the Arctic).

192

193 3.2 Transport of Hunga water vapour

194 **Figure 3** shows the zonal mean monthly mean H₂O anomalies after the Hunga injection in
195 model run HT compared with Microwave Limb Sounder (MLS) measurements (Millan et al.,
196 2024) for selected months until April 2024 (updated from Zhou et al., 2021). The model
197 successfully captures many aspects of the transport of the Hunga H₂O over this time period.
198 While the injected total mass in the model is consistent with MLS, the simulation has slightly
199 larger peak anomalies and smaller horizontal extent after injection. The simulated plume



200 spread is in very good agreement with the SH observations through 2024, in particular
201 regarding the characteristics and behaviour of the excess H₂O at the mixing barriers in the
202 stratosphere, including the Antarctic vortex edge and the subtropics. Around 4-6 months after
203 the eruption, the excess H₂O moves into the Southern Hemisphere (SH) mid-latitudes within
204 the shallow branch of the BDC. However, it does not intrude into the 2022 Antarctic polar
205 vortex due to the strong polar night jet at the vortex edge. Only after the breakdown of the
206 Antarctic polar vortex in November 2022 did the H₂O reach the pole (Manney et al., 2023).
207 The subtropical transport barrier in 2022 summer, favoured by weak wave forcing in the
208 easterly phase of the Quasi-Biennial Oscillation, confines the excess H₂O to the SH, until the
209 transition to westerlies at the end of 2022. This also explains the improvement of the model
210 in 2023 compared with 2022 in representing the H₂O transport across the equator. H₂O enters
211 the deep branch of the BDC in 2023, ascending from the tropics and descending into the high
212 latitudes in the SH. The model reproduces well the timing of the Hunga-injected H₂O
213 penetrating the polar vortex, and the altitudes of the H₂O plume. This indicates that the model
214 has a good representation of both the poleward horizontal H₂O transport by the shallow
215 branch of the BDC and the ascent of the water-enriched air to high levels by the deep branch
216 of the BDC.

217 In contrast, the arrival of the Hunga H₂O in the Northern Hemisphere (NH) is not simulated
218 as well as the SH. Comparison of the highlighted 1 ppmv contour (**Figure 3**) shows that this
219 level of water vapour reaches the Arctic lower stratosphere in mid-2023 in the MLS data; in
220 the model the additional H₂O in this region is still less than this value in spring 2024. To
221 overcome this issue we also performed simulation EXH₂O which imposes a uniform 1 ppmv
222 increase in H₂O.

223

224 3.3 Impact of Increased Water Vapour on Polar Ozone

225 As discussed in Section 1, increased stratospheric water vapour is expected to lead to
226 additional polar ozone loss through increased occurrence of PSCs. **Figure 4** quantifies this
227 chemical effect for the model run with the realistic timing of the Hunga eruption (HT) and the
228 run with the eruption assumed to occur in January 2017 (HT2017). For both runs the column
229 ozone depletion starts in the southern mid-latitudes and reaches the Antarctic polar vortex
230 around 18 months after eruption (i.e. 2023 for run HT) and the Arctic around two years after
231 eruption. The modelled mean impact in the Antarctic maximises at around 10 DU at the
232 vortex edge (65°S) and decreases as H₂O is removed from the model stratosphere with an e-
233 folding time of around 4 years (Zhou et al., 2024) (**Figure 1b**). In the Arctic the largest
234 impact occurs in run HT2017 in early 2020, i.e. as expected in the very cold Arctic vortex of
235 that year (see **Figure 2b**).

236

237 3.3.1 Antarctic winter/springs of 2019 and 2020



238 The impact of the increased water vapour in model runs HT2017 and EXH2O on NAT and
239 ice PSC occurrence in Antarctic winters 2019 and 2020 is shown in **Figures 5a and b**.
240 Clearly, as NAT forms at a higher temperature than ice (195 K versus 188 K), it has an earlier
241 onset and more extensive coverage. The additional PSC occurrence compared to control run
242 CNTL is small but most pronounced in early winter. As noted by Zhou et al. (2024), efficient
243 dehydration the model vortex core after the onset of ice PSCs in June removes most of the
244 additional water vapour. This is confirmed by the modelled time series of water vapour for
245 the two years (**Figures 6e and 7e**). The excess mean water vapour in May is removed so that
246 by September the model runs CNTL, HT2017 and EXH2O all have similar mean mixing
247 ratios. This difference in early PSC occurrence has only a small effect of chlorine processing
248 (**Figures 6a-d and 7a-d**). Again, the largest differences in the areal mean occur in early
249 winter. By late winter and spring, the main period for ozone loss, the extent of activation is
250 similar in the three simulations.

251 **Figures 8 and 9** show the impact on column ozone of the additional H₂O on two example
252 days in late September 2019 and 2020. The largest additional depletion occurs at the edge of
253 the polar vortex where the PSC occurrence is not saturated, and dehydration is not extensive.
254 In the warmer, more disturbed vortex of 2019 the approximately 1 ppmv additional H₂O
255 (**Figure 6e**) in run HT2017 causes a maximum additional O₃ depletion of 11 DU (**Figure 8d**).
256 In 2020 the additional H₂O in run HT2017 is reduced to 0.4 ppmv (**Figure 7e**) and the
257 column impact is only 8 DU. In contrast, the additional 1 ppmv H₂O in run EXH2O causes a
258 depletion of an additional 16 DU (**Figure 9e**). For polar-cap-mean ozone these impacts
259 translate to September-mean depletion in run HT2017 of 11 DU in 2018 (not discussed
260 above), 7 DU in 2019 and 3 DU in 2020. Run EXH2O produces additional depletion of 8 DU
261 in 2020 (**Figure 1b**).

262

263 3.3.2 Arctic Ozone

264 **Figure 2a** summarised the observed mean March column ozone in recent years and indicates
265 how Arctic ozone levels depend on the occurrence of low temperatures. Both the 2022/2023
266 and 2023/2024 Arctic ozone loss seasons showed comparatively warm conditions in the polar
267 vortex in spring relative to the long-term climatology. These conditions are unfavourable for
268 ozone loss initiated by heterogeneous reactions, preventing a significant effect from the
269 Hunga eruption on ozone depletion in these years. While the 2022/2023 Arctic winter started
270 with temperatures below the long-term average in January 2023, a major sudden stratospheric
271 warming (SSW) on February 16th, 2023 caused the vortex to break up by the end of February,
272 before chlorine-catalysed ozone loss could have a major effect (Druckenmiller et al., 2024).
273 Although the 2023/2024 Arctic winter was initially unusually cold, it was characterised by an
274 early major SSW on 16 January, from which the vortex recovered, and a second major SSW
275 on March 4th that caused an early breakup of the vortex (see Newman et al., 2024).

276 Given the nature of the Arctic winters since the Hunga eruption here we look at the potential
277 for a larger impact during a cold Arctic winter. We therefore use TOMCAT to simulate the



278 impact that Hunga could have had on the cold Arctic winter of 2019/2020 through simulation
279 HT2017. In order to allow the modelled H₂O injection to reach the Arctic (given the slower
280 than observed interhemispheric transport shown in **Figure 3**) we inject the H₂O in 2017, 3
281 years ahead of the target winter. To circumvent uncertainty in the timing of H₂O transport, in
282 run EXH2O we simply increase model H₂O globally by 1 ppmv in November 2019.

283 In contrast to the Antarctic, the occurrence of ice PSCs in the Arctic is rare. The additional
284 water vapour in runs HT2017 and EXH2O at the start of winter is maintained through to
285 spring (**Figure 10e**). There appear to be two small signals of dehydration around early
286 December in all 3 runs and in late January, especially in run EXH2O. This January event is
287 reflected in the larger scale occurrence of ice PSCs across the polar region (**Figure 5c**) This
288 lack of dehydration could potentially allow the additional H₂O to have a larger impact in a
289 cold Arctic winter than in the dehydrated Antarctic. However, the impact of NAT occurrence
290 in run EXH2O compared to run CNTL is small. The corresponding impact on chlorine
291 activation and polar cap ozone is also small.

292 The largest column ozone depletion modelled on March 21st 2020 is 3 DU at the vortex edge
293 in run HT2017 and 16 DU in run EXH2O with the large H₂O perturbation (**Figure 11**). The
294 polar cap March mean ozone impacts for 2020 are around 2 DU and 9 DU, respectively
295 (**Figure 2b**), with a decreasing impact in later warmer years with less additional H₂O.

297 4. Conclusions

298 We have performed a series of three-dimensional model experiments to investigate the
299 impacts of a large injection of water vapour into the stratosphere on polar ozone depletion.
300 These simulations mimic some details of a Hunga-like underwater volcanic eruption. In
301 particular, we investigated the potential impact of increased water vapour in cold Antarctic
302 and Arctic winters, through increased PSC occurrence.

303 As noted by previous studies (e.g. Wohltmann et al., 2023; Zhou et al., 2024) efficient
304 Antarctic dehydration by sedimenting ice PSCs limits the impact of an example additional 1
305 ppmv H₂O to a maximum additional depletion of 16 DU in 2020 and 11 DU in 2019 at the
306 vortex edge in late September. Similar dehydration does not occur in the warmer Arctic, even
307 in the extreme cold conditions of 2019/2020. Under these conditions an additional 1 ppmv
308 H₂O causes a maximum of 16 DU additional depletion at the vortex edge in mid March. Note
309 that our simulations only diagnose the direct chemical impact of the increased water vapour.
310 As an important climate gas, changes in stratospheric water vapour will lead to changes in
311 temperature and circulation which can also have an impact on column ozone in different
312 regions.

313 Our model results shows that direct chemical impact of water vapour from a large Hunga-like
314 eruption (which would produce increases of less than 1 ppmv after large-scale spreading of
315 the plume) would be small compared to observed interannual variability in springtime
316 column ozone (Fleming et al., 2024), especially in the Arctic. However, should increases in



317 stratospheric water vapour be sustained this additional depletion could be important for long-
318 term trends. Such hydration could occur, for example, through warmer tropical tropopause
319 temperatures or through increasing levels of stratospheric methane, which produces H₂O on
320 oxidation.

321 Finally, is worth noting, that around 40 years after the discovery of the ozone hole, and after
322 over 20 years since stratospheric chlorine and bromine started to decline, we are still
323 experiencing very large ozone depletion at both poles. These low levels are related, at least in
324 part, to a series of exceptional events such as wildfire smoke and volcanic eruptions.
325 Nevertheless, these events and state of the ozone layer emphasise the need for continued
326 observations, laboratory studies and chemistry-climate modelling of the stratosphere (see
327 Chipperfield and Bekki, 2024).

328

329 **Conflict of Interest:** The authors declare no conflicts of interest.

330

331 **Acknowledgements:** MPC and SSD were supported by the NCEO TerraFIRMA, NERC
332 LSO3 (NE/V011863/1) and ESA OREGANO (4000137112/22/I-AG) projects. WF was
333 supported by the NCAS Long-Term Science programme (NE/ R015244/1). XZ was
334 supported by the National Natural Science Foundation of China (42275059, 12411530093).

335

336 **Author Contributions:** Conceptualization: MPC. Methodology: MPC. Formal analysis: SF,
337 SSD, WF, XZ, MPC. Writing – original draft: MPC. Writing – review and editing: all
338 coauthors.

339

340 **Data availability:** The OMI/OMPS data is available from
341 <https://ozonewatch.gsfc.nasa.gov/meteorology/figures/ozone>
342 The MLS data is available from <https://mls.jpl.nasa.gov/>

343

344 References

345 Arfeuille, F., Luo, B. P., Heckendorn, P., Weisenstein, D., Sheng, J. X., Rozanov, E., et al., Modeling
346 the stratospheric warming following the Mt. Pinatubo eruption: uncertainties in aerosol extinctions.
347 *Atmos. Chem. Phys.*, **13**, 11221–11234. <https://doi.org/10.5194/acp-13-11221-2013>, 2013.

348 Chipperfield, M., New version of the TOMCAT/SLIMCAT off-line chemical transport model:
349 Intercomparison of stratospheric tracer experiments. *The Quarterly Journal of the Royal*
350 *Meteorological Society*, **132**, 1179–1203. <https://doi.org/10.1256/qj.05.51>, 2006.

351 Chipperfield, M. P., Bekki, S., Dhomse, S., Harris, N. R. P., Hassler, B., Hossaini, R., et al., Detecting
352 recovery of the stratospheric ozone layer. *Nature*, **549**, 211–218. <https://doi.org/10.1038/nature23681>,
353 2017.



- 354 Chipperfield, M.P., and S. Bekki, Opinion: Stratospheric ozone – Depletion, recovery and new
355 challenges, *Atmos. Chem. Phys.*, **24**, 2783–2802, [doi:10.5194/acp-24-2783-2024](https://doi.org/10.5194/acp-24-2783-2024), 2024. View Article Online
DOI: 10.1039/D4FD00163J
- 356 Coddington, O., Lean, J., Pilewskie, P., Snow, M., & Lindholm, D., A solar irradiance climate data
357 record. *Bulletin of the American Meteorological Society*, **97**, 1265–1282.
358 <https://doi.org/10.1175/BAMS-D-14-00265.1>, 2016.
- 359 Coddington, O., Lean, J., Pilewskie, P., Snow, M., Richard, E., Kopp, G., et al. Solar Irradiance
360 variability: comparisons of models and measurements. *Earth and Space Science*, **6**, 2525–2555.
361 <https://doi.org/10.1029/2019EA000693>, 2019.
- 362 Coy, L., Newman, P. A., Wargan, K., Partyka, G., Strahan, S. E., & Pawson, S., Stratospheric
363 circulation changes associated with the Hunga Tonga - Hunga Ha'apai eruption. *Geophys. Res. Lett.*,
364 **49**, e2022GL100982. <https://doi.org/10.1029/2022GL100982>, 2022.
- 365 Dhomse, S., Chipperfield, M. P., Damadeo, R. P., Zawodny, J. M., Ball, W. T., Feng, W., et al., On
366 the ambiguous nature of the 11-year solar cycle signal in upper stratospheric ozone. *Geophys. Res.*
367 *Lett.*, **43**, 7241–7249. <https://doi.org/10.1002/2015GL069958>, 2016.
- 368 Dhomse, S., Chipperfield, M. P., Feng, W., Hossaini, R., Mann, G. W., & Santee, M. L., Revisiting
369 the hemispheric asymmetry in mid-latitude ozone changes following the Mount Pinatubo eruption: A
370 3-D model study. *Geophys. Res. Lett.*, **42**, 3038–3047. <https://doi.org/10.1002/2015GL063052>, 2015.
- 371 Dhomse, S. S., Feng, W., Montzka, S. A., Hossaini, R., Keeble, J., McQuaid, J., et al., Delay in
372 recovery of the Antarctic ozone hole from unexpected CFC-11 emissions. *Nature Communications*,
373 **10**, 5781. <https://doi.org/10.1038/s41467-019-13717-x>, 2019.
- 374 Druckenmiller, M.L., R.L. Thoman, and T.A. Moon, Eds., The Arctic [in “State of the Climate in
375 2023”]. *Bulletin of the American Meteorological Society*, **105**, S277–S330, doi: 10.1175/BAMS-D-
376 24-0101.1, 2024.
- 377 Farman, J. C., Gardiner, B. G. & Shanklin, J. D.: Large losses of total ozone in Antarctica reveal
378 seasonal ClOx/NOx interaction, *Nature*, **315**, 207–210, doi:10.1038/315207a0, 1985.
- 379 Feng, W., Chipperfield, M. P., Davies, S., von der Gathen, P., Kyrö, E., Volk, C. M., et al. Large
380 chemical ozone loss in 2004/2005 Arctic winter/spring. *Geophys. Res. Lett.*, **34**, L09803.
381 <https://doi.org/10.1029/2006GL029098>, 2007.
- 382 Feng, W., S.S. Dhomse, C. Arosio, M. Weber, J.P. Burrows, M.L. Santee and M.P. Chipperfield,
383 Arctic ozone depletion in 2019/20: Roles of chemistry, dynamics and the Montreal Protocol,
384 *Geophys. Res. Lett.*, **48**, e2020GL091911, [doi:10.1029/2020GL091911](https://doi.org/10.1029/2020GL091911), 2021.
- 385 Fleming, E.L., P.A. Newman, Q. Liang, and L.D. Oman, Stratospheric temperature and ozone impacts
386 of the Hunga Tonga-Hunga Ha'apai water vapor injection. *J. Geophys. Res.*, **129**, e2023JD039298,
387 doi: 10.1029/2023JD039298, 2024.
- 388 Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., H, A., M, J., et al., The ERA5 global reanalysis.
389 *The Quarterly Journal of the Royal Meteorological Society*, **146**, 1999–2049.
390 <https://doi.org/10.1002/qj.3803>, 2020.
- 391 Knepp, T. N., Kovilakam, M., Thomason, L., and Miller, S. J.: Characterization of stratospheric
392 particle size distribution uncertainties using SAGE II and SAGE III/ISS extinction spectra, *Atmos.*
393 *Meas. Tech.*, **17**, 2025–2054, <https://doi.org/10.5194/amt-17-2025-2024>, 2024.



- 394 Manney, G. L., Livesey, N. J., Santee, M. L., Froidevaux, L., Lambert, A., Lawrence, Z. D., et al.,
 395 Record-low Arctic stratospheric ozone in 2020: MLS observations of chemical processes and View Article Online
 396 comparisons with previous extreme winters. *Geophys. Res. Lett.*, **47**, e2020GL089063. DOI: 10.1039/D4FD00163J
 397 <https://doi.org/10.1029/2020GL089063>, 2020.
- 398 Manney, G.L., M.L. Santee, A. Lambert, L.F. Millán, K. Minschwaner, F. Werner, Z.D. Lawrence,
 399 W.G. Read, N.J. Livesey, and T. Wang, Siege in the southern stratosphere: Hunga Tonga-Hunga
 400 Ha'apai water vapor excluded from the 2022 Antarctic polar vortex. *Geophys. Res. Lett.*, **50**,
 401 e2023GL103855, doi: 10.1029/2023GL103855, 2023.
- 402 Millán, L., W.G. Read, M.L. Santee, A. Lambert, G.L. Manney, J.L. Neu, M.C. Pitts, F. Werner, N.J.
 403 Livesey, and M.J. Schwartz, The evolution of the Hunga hydration in a moistening stratosphere.
 404 *Geophys. Res. Lett.*, **51**, e2024GL110841, doi: 10.1029/2024GL110841, 2024.
- 405 Newchurch, M. J., Yang, E.-S., Cunnold, D. M., Reinsel, G. C., Zawodny, J. M., & Russell, J. M.,
 406 Evidence for slowdown in stratospheric ozone loss: First stage of ozone recovery. *J. Geophys. Res.*,
 407 **108**, 4507. <https://doi.org/10.1029/2003JD003471>, 2003.
- 408 Newman, P. A., Lait, L. R., Kramarova, N.A., Coy, L., Frith, S. M., Oman, L. D., & Dhomse, S. S.
 409 Record high march 2024 Arctic total column ozone. *Geophys. Res. Lett.*, **51**, e2024GL110924.
 410 <https://doi.org/10.1029/2024GL110924>, 2024.
- 411 Rieger, L.A., W.J. Randel, A.E. Bourassa, and S. Solomon, Stratospheric temperature and ozone
 412 anomalies associated with the 2020 Australian New Year fires, *Geophys. Res. Lett.*, **48**,
 413 e2021GL095898, doi:10.1029/2021GL095898, 2021.
- 414 Santee, M. L., Lambert, A., Manney, G. L., Livesey, N. J., Froidevaux, L., Neu, J. L., et al.:
 415 Prolonged and pervasive perturbations in the composition of the Southern Hemisphere midlatitude
 416 lower stratosphere from the Australian New Year's fires, *Geophys. Res. Lett.*, **49**, e2021GL096270.
 417 <https://doi.org/10.1029/2021GL096270>, 2022.
- 418 Santee, M.L., A. Lambert, L. Froidevaux, G.L. Manney, M.J. Schwartz, L.F. Millán, N.J. Livesey,
 419 W.G. Read, F. Werner, and R.A. Fuller, Strong evidence of heterogeneous processing on stratospheric
 420 sulfate aerosol in the extrapolar Southern Hemisphere following the 2022 Hunga Tonga-Hunga
 421 Ha'apai eruption. *J. Geophys. Res.*, **128**, e2023JD039169, doi: 10.1029/2023JD039169, 2023.
- 422 Schoeberl, M. R., Wang, Y., Ueyama, R., Taha, G., Jensen, E., & Yu, W., Analysis and impact of the
 423 Hunga Tonga - Hunga Ha'apai stratospheric water vapor plume. *Geophys. Res. Lett.*, **49**,
 424 e2022GL100248. <https://doi.org/10.1029/2022GL100248>, 2022.
- 425 Solomon, S.: Stratospheric ozone depletion: a review of concepts and history, *Rev. Geophys.*, **37**,
 426 275–316, doi:10.1029/1999RG900008, 1999.
- 427 Solomon, S., Garcia, R. R., Rowland, F. S. & Wuebbles, D. J.: On the depletion of Antarctic ozone,
 428 *Nature*, **321**, 755–758, doi:10.1038/321755a0, 1986.
- 429 Solomon, S., Ivy, D. J., Kinnison, D., Mills, M. J., Neely, R. R., & Schmidt, A., Emergence of healing
 430 in the Antarctic ozone layer. *Science*, **353**, 269–274. <https://doi.org/10.1126/science.aae0061>, 2016.
- 431 Solomon, S., Stone, K., Yu, P., Murphy, D.M., Kinnison, D., Ravishankara, A.R., and Wang, P.:
 432 Chlorine activation and enhanced ozone depletion induced by wildfire aerosol, *Nature*, **615**,
 433 10.1038/s41586-022-05683-0, 2023.

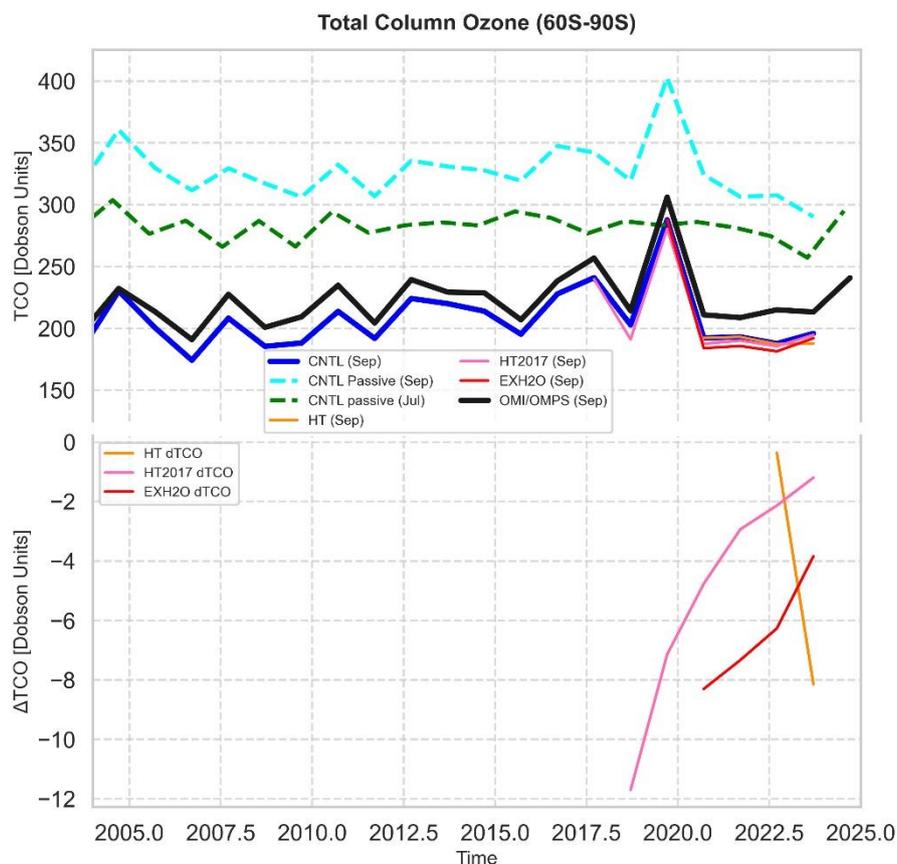


- 434 Tritscher, I., M.C. Pitts, L.R. Poole, S.P. Alexander, F. Cairo, M.P. Chipperfield, J.-U. Grooss, M.
435 Hoepfner, A. Lambert, B.P. Luo, S. Molleker, A. Orr, R. Salawitch, M. Snels, R. Spang, W. Woitode
436 and T. Peter, Polar stratospheric clouds: Satellite observations, processes, and role in ozone depletion,
437 *Rev. Geophys.*, **59**, e2020RG000702, [doi:10.1029/2020RG000702](https://doi.org/10.1029/2020RG000702), 2021.
- 438 Vomel, H., Evan, S., & Tully, M., Water vapor injection into the stratosphere by Hunga Tonga -
439 Hunga Ha'apai. *Science*, 377(6613), 1444-1447. <https://doi.org/10.1126/science.abq2299>, 2022.
- 440 von der Gathen, P., R. Kivi, I. Wohltmann, R.J. Salawitch, and M. Rex, Climate change favours large
441 seasonal loss of Arctic ozone, *Nat. Commun.*, **12**, 3886, doi:10.1038/s41467-021-24089-6, 2021.
- 442 WMO Scientific assessment of ozone depletion: 2022. Global Ozone Research and Monitoring
443 Project – GAW Report no. 278. Geneva, Switzerland: World Meteorological Organization, 2022.
- 444 Wohltmann, I., von der Gathen, P., Lehmann, R., Maturilli, M., Deckelmann, H., Manney, G. L., et al.
445 Near-complete local reduction of Arctic stratospheric ozone by severe chemical loss in spring 2020.
446 *Geophys. Res. Lett.*, **47**, e2020GL089547. <https://doi.org/10.1029/2020GL089547>, 2020.
- 447 Wohltmann, I., M.L. Santee, G.L. Manney, and L.F. Millán, The chemical effect of increased water
448 vapor from the Hunga Tonga-Hunga Ha'apai eruption on the Antarctic ozone hole. *Geophys. Res.*
449 *Lett.*, **51**, e2023GL106980, doi: 10.1029/2023GL106980, 2024.
- 450 Yu, P., S.M. Davis, O.B. Toon, R.W. Portmann, C.G. Bardeen, J.E. Barnes, H. Telg, C. Maloney, and
451 K.H. Rosenlof, Persistent stratospheric warming due to 2019– 2020 Australian wildfire smoke,
452 *Geophys. Res. Lett.*, **48**, e2021GL092609, doi:10.1029/2021GL092609, 2021.
- 453 Zhou, X., S.S. Dhomse, W. Feng, G. Mann, S. Heddell, H. Pumphrey, B.J. Kerridge, B. Latter, R.
454 Siddans, L. Ventress, R. Querel, P. Smale, E. Asher, E.G. Hall, S. Bekki and M.P. Chipperfield,
455 Antarctic vortex dehydration in 2023 as a substantial removal pathway for Hunga Tonga-Hunga
456 Ha'apai water vapour, *Geophys. Res. Lett.*, **51**, e2023GL107630, [doi:10.1029/2023GL107630](https://doi.org/10.1029/2023GL107630), 2024.
- 457



458 **Figures**

459

View Article Online
DOI: 10.1039/D4FD00163J

460

461

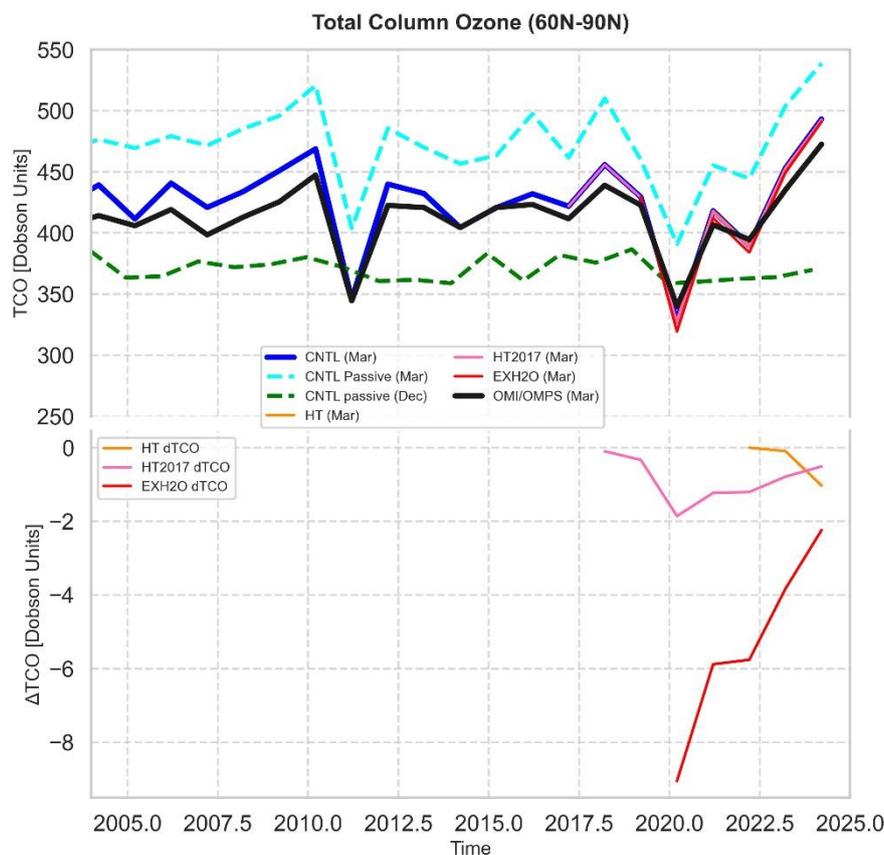
462 **Figure 1.** Antarctic (60° – 90° S, geographical latitude) monthly mean column ozone (DU) from 2004
 463 to 2023. The upper panel (a) shows September OMI/OMPS observations and model simulations
 464 CNTL, HT (2022 on), HT2017 (2017 on) and EXH2O (2019 on). The dashed lines show the passive
 465 ozone from CNTL for September (blue) and the previous July (green). The lower panel (b) shows the
 466 difference in mean October ozone (DU) between runs CNTL and HT, HT2017 and EXH2O. Updated
 467 and adapted from Feng et al. (2021).

468



469

470

View Article Online
DOI: 10.1039/D4FD00163J

471

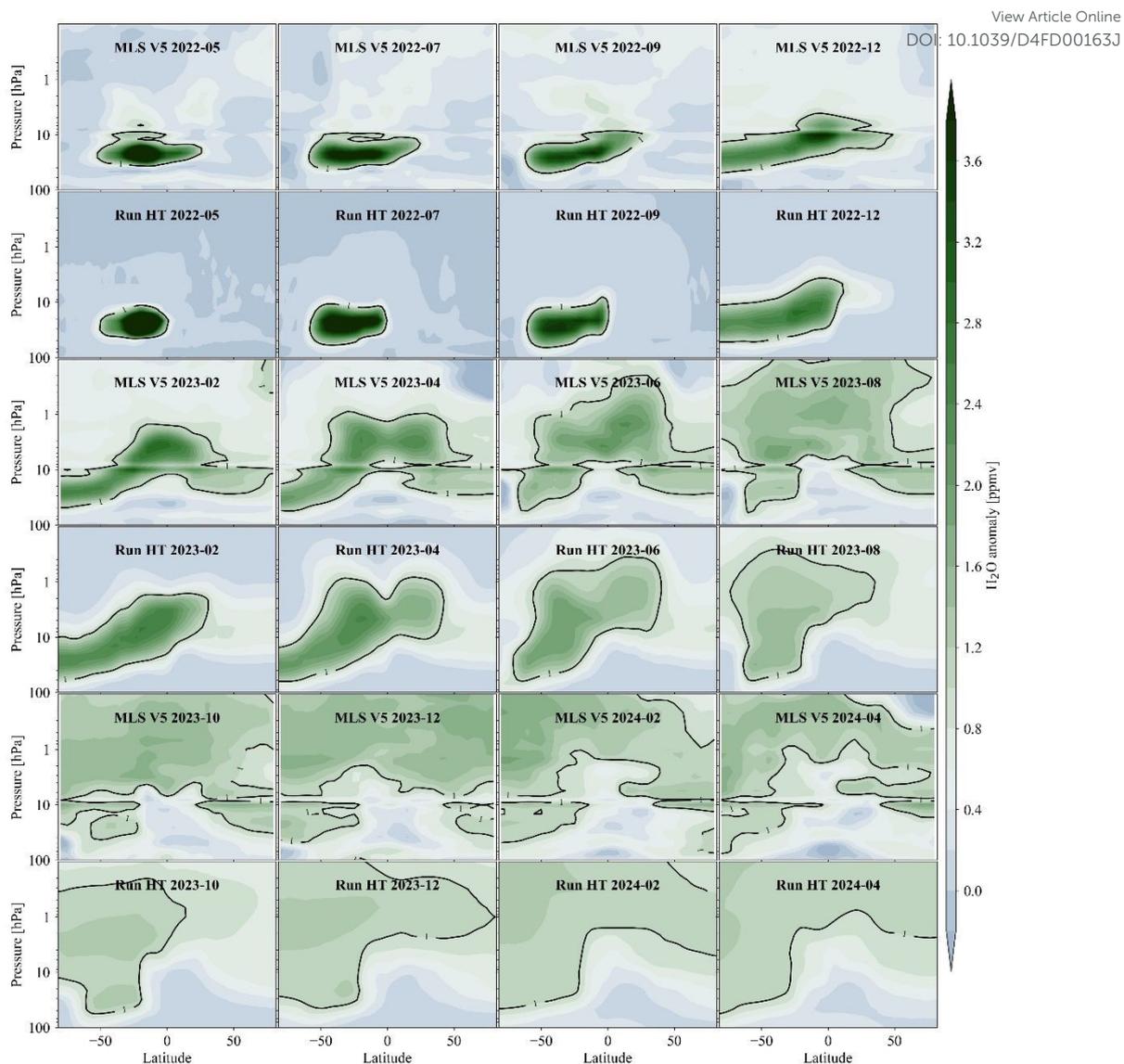
472

473 **Figure 2.** As **Figure 1** but for the Arctic (60° – 90° N, geographical latitude) monthly mean March
 474 column ozone (DU) from 2004 to 2024. The upper panel (a) shows OMI/OMPS observations and
 475 model simulations CNTL, HT, HT2017 and EXH2O. The dashed lines show the passive ozone from
 476 CNTL for March (blue) and the previous December (green). The lower panel (b) shows the difference
 477 in mean March column ozone (DU) between run CNTL and runs HT, HT2017 and EXH2O. Updated
 478 and adapted from Feng et al. (2021).

479



480



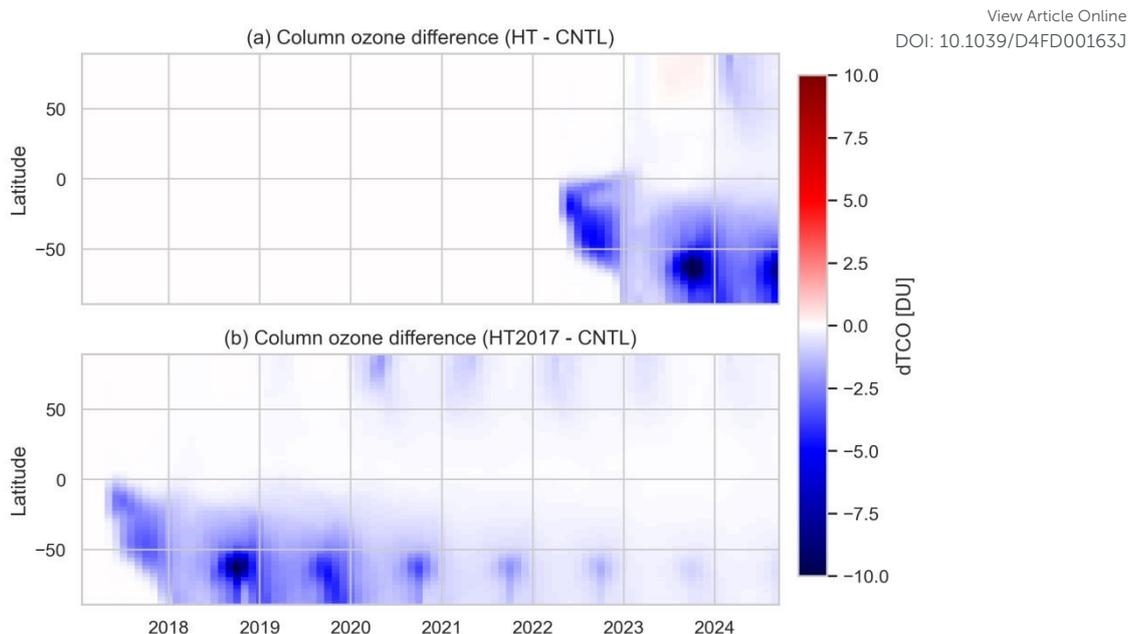
481

482 **Figure 3.** Water vapour (H₂O) evolution after the Hunga eruption. Zonal mean latitude-pressure cross
 483 sections of H₂O anomalies observed by MLS v5 and simulated by model run HT from May 2022 to
 484 April 2024. Updated from Figure 1b of Zhou et al. (2024).

485



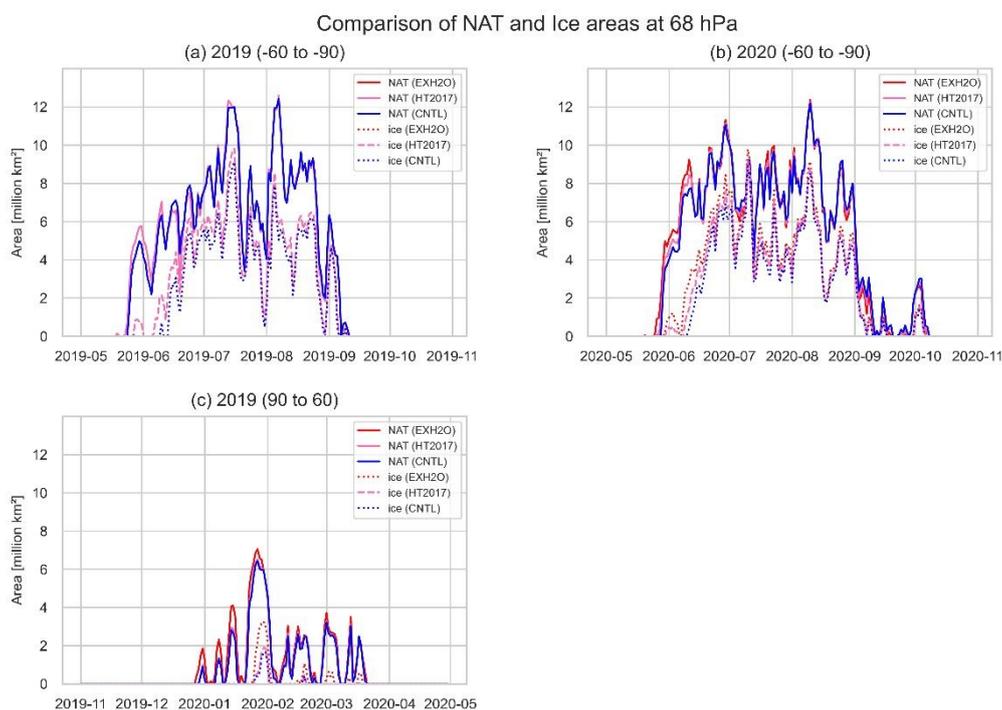
486



487

488 **Figure 4.** Latitude-time series of column ozone (DU) difference for runs (a) HT and (b) run HT2017
489 compared to control run CNTL from 2017 to August 2024.

490



491

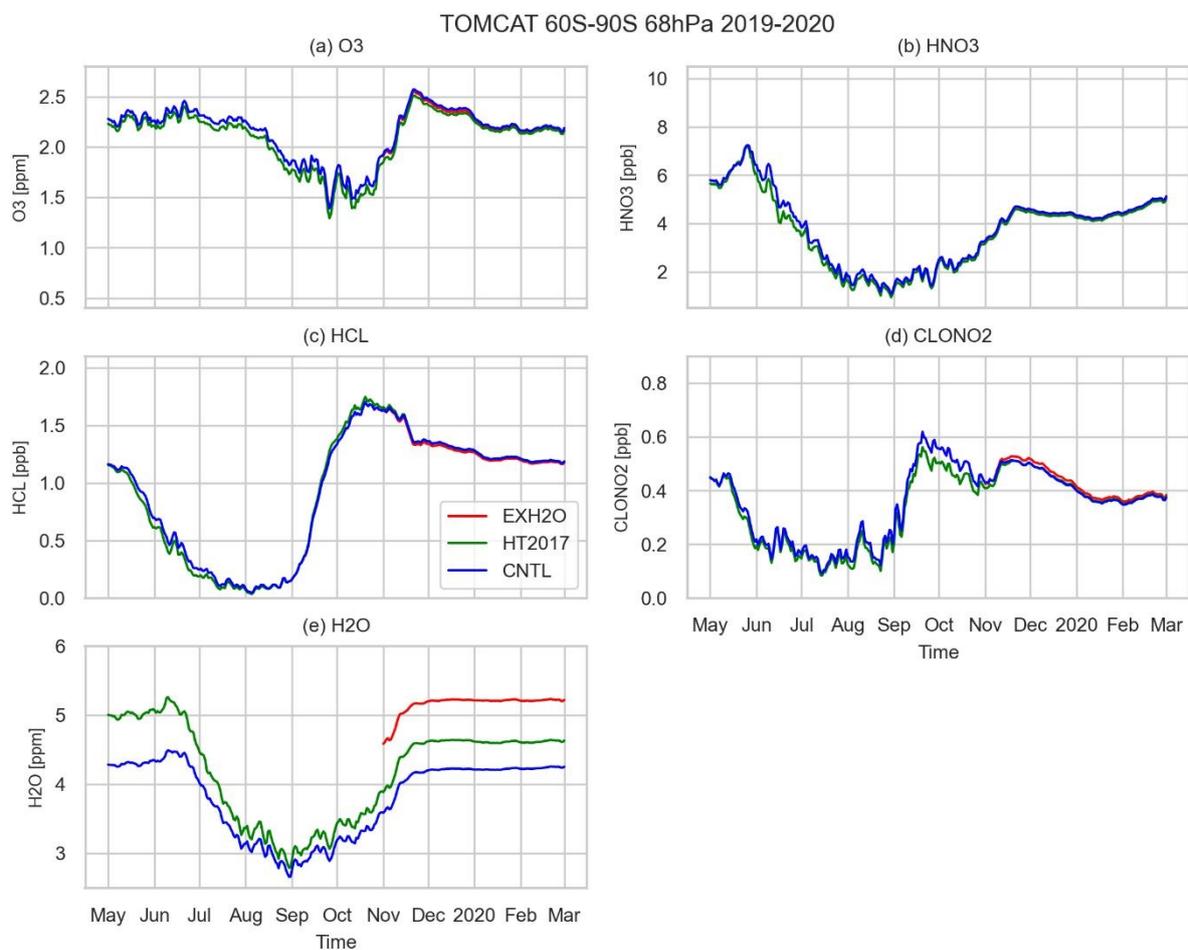
492 **Figure 5.** Extent of polar stratospheric cloud (PSC) area (million km²) for nitric acid trihydrate
493 (NAT) and ice particles at 68 hPa from model runs CNTL, HT2017 and EXH2O for (a) 60°S-
494 90°S in 2019, (b) 60°S-90°S in 2020, and (c) 60°N-90°N in 2019/2020.

495



496

497

View Article Online
DOI: 10.1039/D4FD00163J

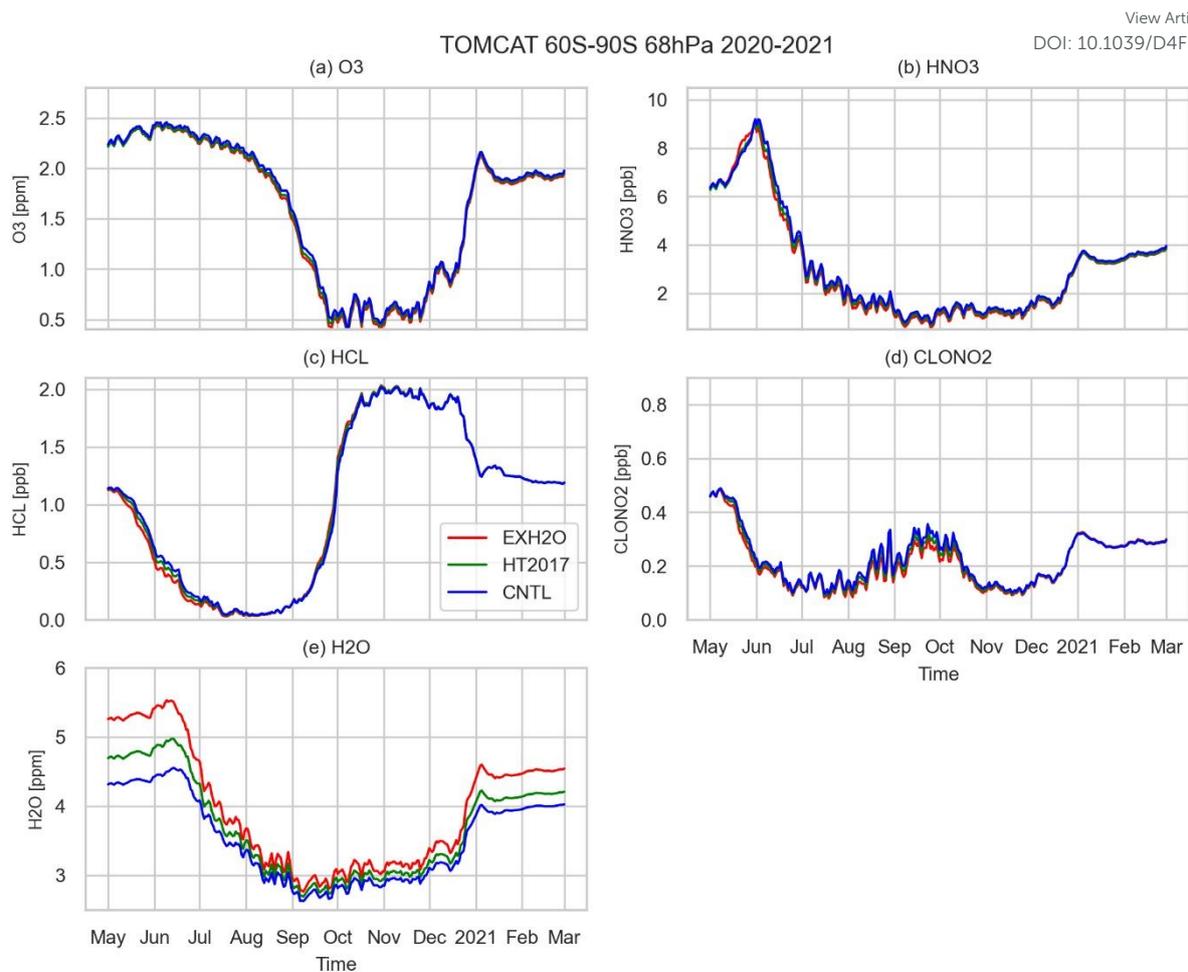
498

499 **Figure 6.** Mean volume mixing ratios for 60°S-90°S for May 2019 to February 2020 at 68 hPa
 500 from model runs CNTL, HT2017 and EXH2O (November 2019 onwards) for (a) O₃, (b)
 501 HNO₃, (c) HCl, (d) ClONO₂ and (e) H₂O.

502



503



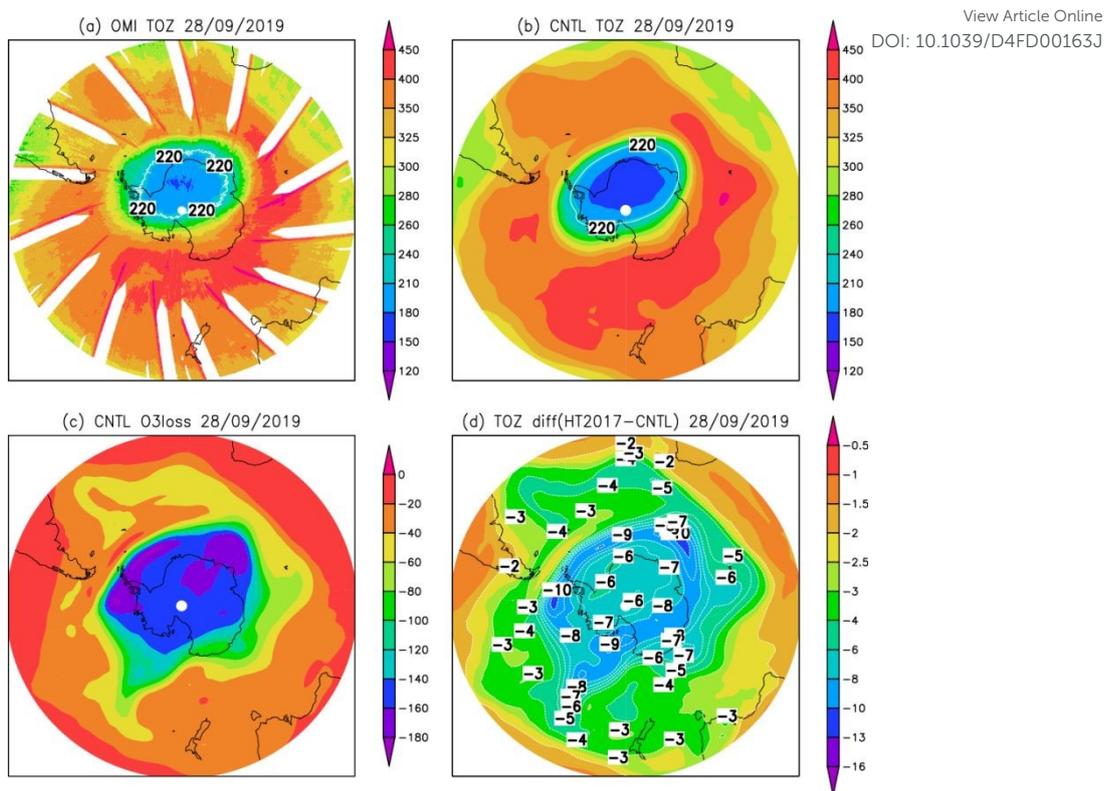
504

505 **Figure 7.** Mean volume mixing ratios for 60°S-90°S for May 2020 to February 2021 at 68 hPa
 506 from model runs CNTL, HT2017 and EXH2O for (a) O₃, (b) HNO₃, (c) HCl, (d) ClONO₂
 507 and (e) H₂O.

508



509



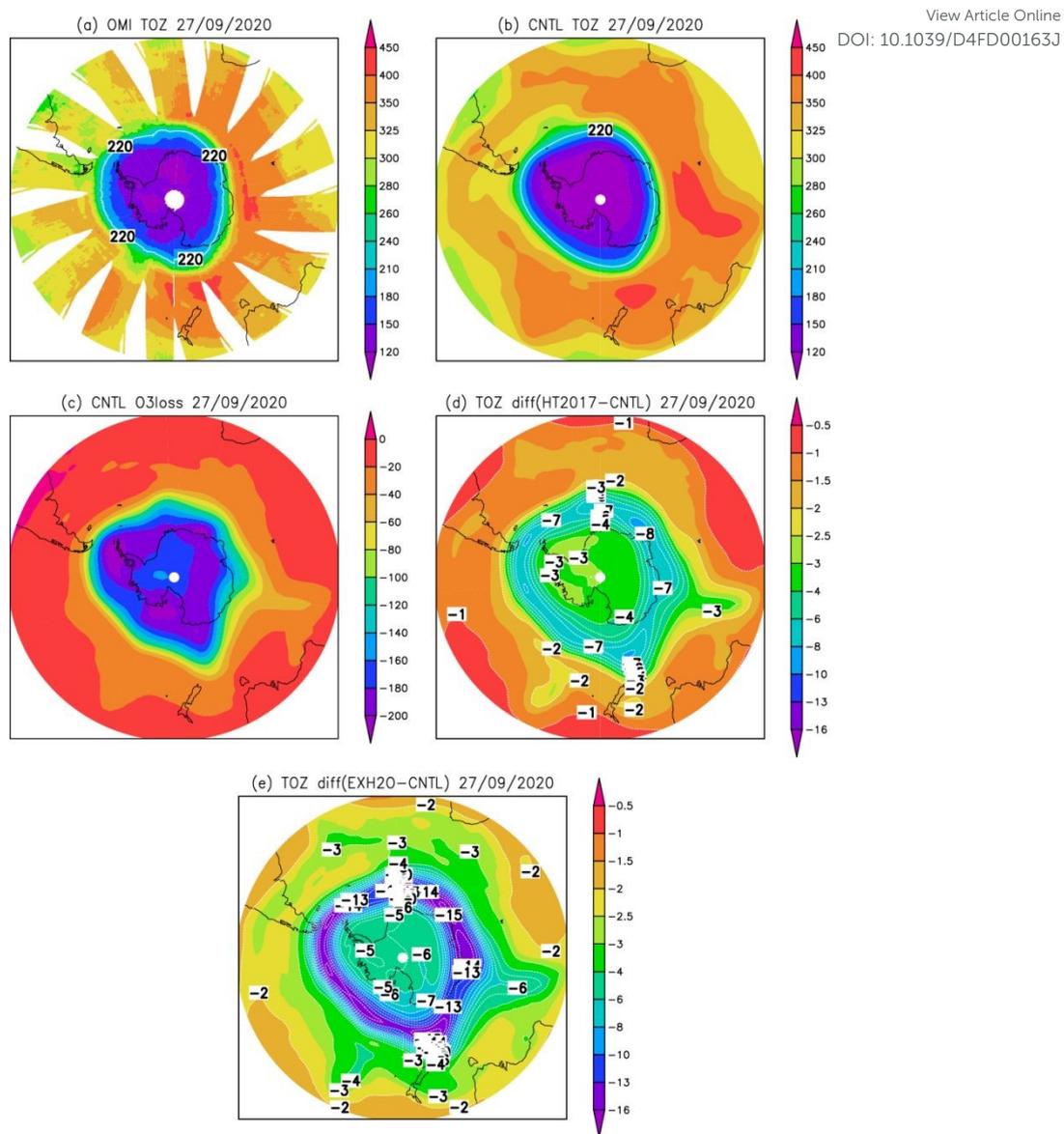
510

511 **Figure 8.** Total column ozone (DU) on September 28, 2019 (a) observed by OMI, (b) from model run
 512 CNTL, (c) chemical ozone loss (DU) from run CNTL (active minus passive) and (d) difference in
 513 column ozone (DU) between runs HT2017 and CNTL. In panels (a) and (b) the 220 DU contour is
 514 indicated in white.

515



516



517

518 **Figure 9.** Total column ozone (DU) on September 27, 2020 (a) observed by OMI, (b) from model run
 519 CNTL, (c) chemical ozone loss (DU) from run CNTL (active minus passive), (d) difference in column
 520 ozone (DU) between runs HT2017 and CNTL and (e) difference in column ozone (DU) between runs
 521 EXH2O and CNTL. In panels (a) and (b) the 220 DU contour is indicated in white.

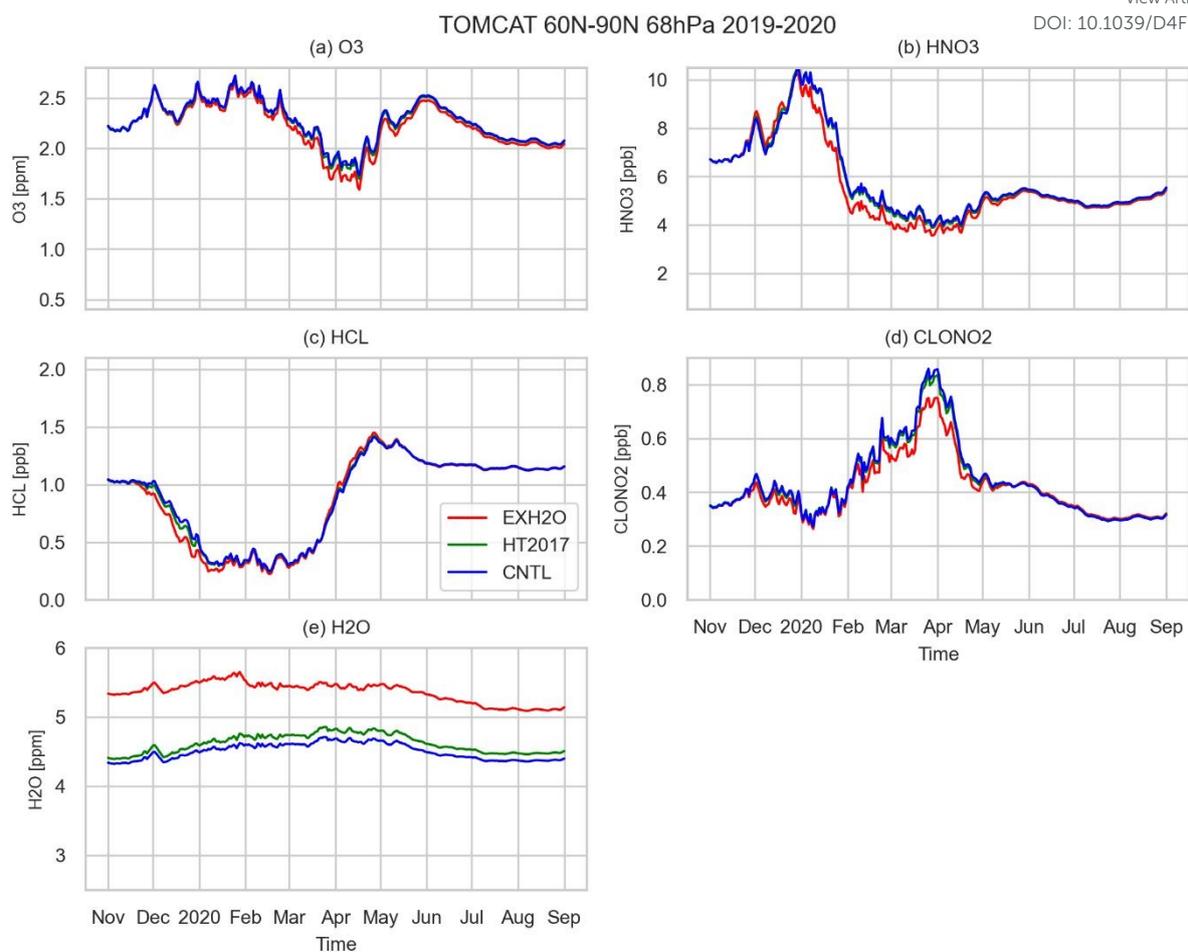
522



523

View Article Online

DOI: 10.1039/D4FD00163J



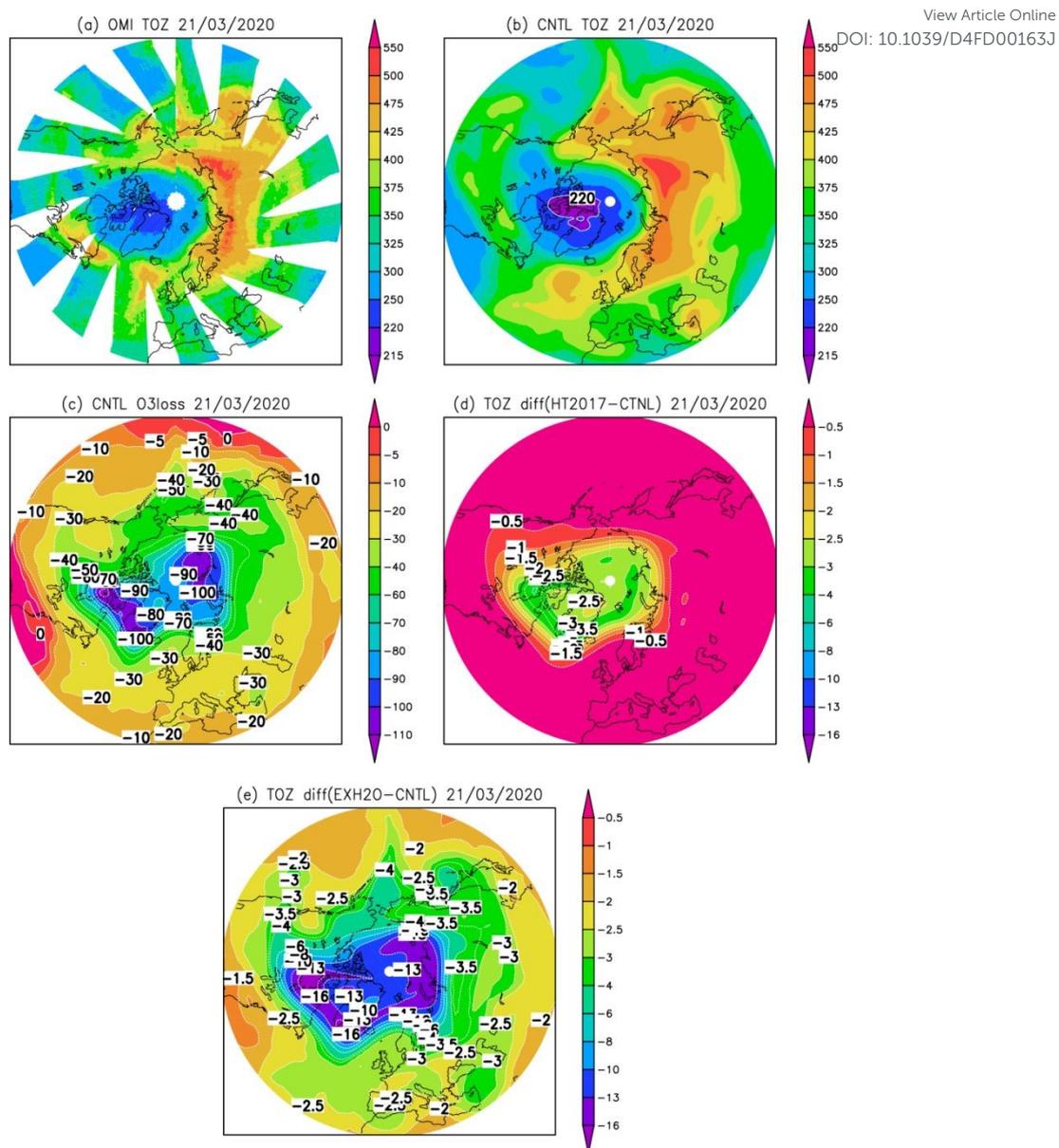
524

525 **Figure 10.** Mean volume mixing ratios (ppmv) for 60°N-90°N for November 2019 to August 2020 at
 526 68 hPa from model runs CNTL, HT2017 and EXH2O for (a) O_3 , (b) HNO_3 , (c) HCl , (d) $ClONO_2$ and
 527 (e) H_2O .

528



529



530

531 **Figure 11.** Total column ozone (DU) on March 21, 2020 (a) observed by OMI, (b) from model run
 532 CNTL, (c) chemical ozone loss (DU) from run CNTL (active minus passive), (d) difference in column
 533 ozone (DU) between run HT2017 and CNTL and (e) difference in column ozone (DU) between runs
 534 EXH2O and CNTL. In panels (a) and (b) the 220 DU contour is indicated in white.



1 **Data Availability**

2

3 Data availability. The OMI/OMPS data is available from
4 <https://ozonewatch.gsfc.nasa.gov/meteorology/figures/ozone>

5 The MLS data is available from <https://mls.jpl.nasa.gov/>

6

View Article Online
DOI: 10.1039/D4FD00163J

