Article:
Fang, X, Pyle, JA, Chipperfield, MP orcid.org/0000-0002-6803-4149 et al. (3 more authors) (2019) Challenges for the recovery of the ozone layer. Nature Geoscience, 12 (8). pp. 592-596. ISSN 1752-0894

https://doi.org/10.1038/s41561-019-0422-7

Journal: Nature Geoscience

Content type: Perspective

Title (proposed): Challenges for the recovery of the ozone layer

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Challenges for the recovery of the ozone layer

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Abstract

[From the Editor---FIRST PARAGRAPH: We have already edited your first paragraph for clarity and to match our style. The revised first paragraph is included at the end of this email. You can adjust as you see fit, but please keep the first paragraph to the same length (or shorter) and include the revised first paragraph in your revised manuscript]

[< 200 words]

The recovery of stratospheric ozone from past depletion is underway, due to the 1987 Montreal Protocol and its subsequent amendments, which have been effective in phasing out the production and consumption of the major ozone-depleting substances (ODSs). However, the rate at which this recovery will continue faces a number of uncertainties. Here, we present our insights on anthropogenic challenges for future ozone recovery, based on recent findings and updated observational data on atmospheric ODSs. These challenges partly relate to controlled ODSs, e.g., unexpected emissions of CFC-11 (CCl_3F) and slower-than-expected declines in atmospheric CCl_4. Further challenges include emissions of uncontrolled short-lived ODSs (e.g., CH_2Cl_2 and $CHCl_3$), which observations show have been increasing in the atmosphere through 2017, potential emission increases in natural ODSs (e.g., CH_3Cl and CH_3Br) induced by climate change, changes in atmospheric concentrations of greenhouse gases N_2O and CH_4, and stratospheric geoengineering. We discuss the implications of these challenges for future policy and science, and suggest how they can be addressed to ensure effective monitoring of the success of the Protocol, e.g., expanding geographic coverage of atmospheric observations on ODSs, enhancing the ability of ODS source attribution modeling, and improving understanding of the interactions between climate change and ozone recovery.

Main

[~500 words]

The stratospheric ozone layer (approximately 15 to 35 kilometers above Earth's surface) protects life on Earth by preventing harmful incoming solar ultraviolet radiation that can cause skin cancers, damage to ecosystems, and other harmful effects, from reaching the surface. The Montreal Protocol was signed in 1987, and subsequently strengthened through amendments and adjustments (see Figure 1a), to minimize the depletion of the ozone layer by phasing out the anthropogenic production and consumption of ozone-depleting substances (ODSs), such as chlorofluorocarbons (CFCs), bromochlorofluorocarbons (halons), and hydrochlorofluorocarbons (HCFCs)[1, 2]. The total global emissions of ODSs have been declining since the late 1980s (Figure 1b), and the observed atmospheric abundances of most ODSs are declining after peaking in the 1990s and 2000s[3, 4]. The emergence of ozone recovery following the phase-out of ODSs under the Montreal Protocol has been demonstrated, particularly in the Antarctic and in the upper stratosphere, after accounting for atmospheric circulation, temperature, and volcanic factors[5, 6, 7]. Outside of the tropics, it is projected that total column ozone will return to 1980 historical levels in the coming decades, e.g., about 2060 for Antarctic spring[8].

While the long-term ozone layer recovery from the ODS phase-out is well underway, challenges are posed for the exact timing and extent of recovery in the coming decades. Figure 2 is a schematic illustration of ozone recovery, and the return date of ozone to 1980 levels. Unexpected emission increases in several ODSs (e.g., CFC-11 (CCl_3F)[9], CFC-13 ($CClF_3$)[10], CFC-113a (CF_3CCl_3)[11], CFC-114[a,10], CFC-115 (CF_3CClF_2)[10], HCFC-133a (CF_3CH_2Cl)[11], CH_2Cl_2[12], and $CHCl_3$[13]) have been uncovered by recent studies and could represent an important

[a]CFC-114 represents the combination of CFC-114 ($CClF_2CClF_2$) and its isomer CFC-114a (CCl_2FCF_3).

challenge for future ozone layer recovery. For example, a delay of nearly 30 years has been projected if the atmospheric abundance of a CH_2Cl_2 follows a "continued growth" scenario[12], demonstrating the possible damage to the ozone layer of continued emission of chlorinated ODSs (for more discussion see below). Other important challenges include the increases in ODS emissions from natural sources induced by climate change or future potential applications of geoengineering[8, 14]. Future ozone increases might also be challenged in the short term by sporadic volcanic eruptions, which can cause transient ozone depletion over periods of 3-5 years. Such eruptions are part of natural variability and would not alter long-term ozone recovery[14].

Here, we present our insights on anthropogenic challenges for future ozone recovery (Figure 3), based on recent findings and updated observational data on atmospheric ODSs. An often used metric of ozone recovery is the date when the atmospheric ozone abundance 'returns' to some previous value, usually the abundance in 1980 (see Figure 2). Such a crude model metric does not make allowance for atmospheric variability, which is usually removed by smoothing and averaging results from multiple simulations[15]. Furthermore, if recovery is approached slowly, the difference between the recovery value and the actual ozone value may be very small, with the values not statistically different from each other, but recovery as defined will be deemed not to have occurred. We use recovery dates below, but these caveats should be borne in mind.

Unexpected emissions in controlled ODSs

[Subheadings – no more than 58 characters]

[~600 words]

CFC-11, a potent ODS, was widely used primarily as a foam-blowing agent, as a refrigerant and in a range of other smaller uses. Global production and consumption of CFC-11 was supposed to

be fully phased out by 2010 as required by the Montreal Protocol[2]. However, atmospheric mole fractions of CFC-11 show that the rate of decline in 2014-2016 was only two-thirds as fast as in 2002-2012[9]. Subsequent modeling shows that there has been an unexpected global CFC-11 emission increase (13 ± 5 kilotonnes per year (25 ± 13%)) over 2014-2016 relative to 2002-2012, indicating that new production had occurred, which had not been reported to the United Nations Environment Programme (UNEP)[9]. Although the country or countries involved were not pinpointed, it was suggested that new production of CFC-11 in East Asia contributed[9]. A recent study using atmospheric measurements and inverse modeling has traced the significant CFC-11 emission increase to eastern China, explaining a substantial fraction (approximately 40–60% or more) of the global emission rise[16]. Emissions of some other controlled ODSs, with much lower atmospheric abundances, have also increased. For example, compared to 2008–2012, for the period 2012–2016, atmospheric mole fractions of CFC-13 continued to increase, CFC-114 and CFC-114a declined more slowly, and CFC-115 reversed from near-zero change to positive growth, which is not expected given their phase-out for emissive uses under the Montreal Protocol[4, 10]. CFC-113a mole fractions and emissions also increased much more rapidly from 2010 to mid-2012 than 1980-2010[11]. However, the primary causes of these CFC emission increases are not clear.

These unexpected emissions in controlled ODSs pose a potential challenge for timely future ozone layer recovery, depending on their magnitude and, in turn, on what mitigating action is taken. Assuming global CFC-11 emissions continue at their average level of 67 kilotonnes yr^{-1} in 2002–2016, the return of mid-latitude and polar equivalent effective stratospheric chlorine (EESC, a measure of stratospheric chlorine and bromine levels which determine ozone layer recovery) to its 1980 values could be delayed by about 7 and 20 years, respectively, compared to

the return date expected when no unreported production is considered[17]. Moreover, unregulated emissions of other ODSs might also occur in the coming decades. For example, HCFCs were widely used as replacements for CFCs in the 1990s and 2000s, but are now being phased out gradually (e.g., production and consumption frozen in 2013 and complete phase-out by 2040 in developing countries)[2]. Beginning in the middle of the 2020s in developing countries (e.g., 2024 for China and 2028 for India) and in 2019 and 2020 in developed countries, production and consumption of hydrofluorocarbons (HFCs), which are being widely used to replace HCFCs, will be controlled and gradually phased out by the Montreal Protocol. This phase-out period is a time when increased scientific vigilance is warranted to ensure production of HCFCs and CFCs remain in compliance with the Montreal Protocol and does not increase in response to the HFC controls.

Carbon tetrachloride (CCl_4) is another important ODS[4], whose production for emissive uses was banned from 2010 onwards[2]. Atmospheric observations show that CCl_4 mole fractions have been declining at a lower rate than expected and that inferred emissions (~ 35 kilotonnes yr^{-1}) are much greater than those derived from feedstock uses (< 4 kilotonnes yr^{-1} in 2012) as reported to UNEP[18]. Some of the discrepancies (total ~ 25 kilotonnes yr^{-1}) have been identified as by-product emissions from chloromethane and perchloroethylene plants and fugitive emissions from the chlor-alkali process[19]. A recent inverse modeling study found that CCl_4 emissions were concentrated in eastern China and did not decline between 2009 and 2016, in contrast to the bottom-up estimates showing significant decreases[20]. If future global CCl_4 emissions do not decline but remain at the current level, the return of mid-latitude EESC to 1980 levels would be delayed by almost two years[17].

Emission increases in uncontrolled ODSs

[~450 words]

Important uncertainties in the timing of ozone layer recovery also arise from the uncertain impact of very short-lived substances (VSLSs) with atmospheric lifetimes of typically <6 months. Historically, VSLSs were thought to have minimal impact on ozone layer depletion because they largely degrade in the troposphere, but observations show VSLSs do reach the stratosphere[21]. For many of these gases, anthropogenic emissions (e.g., industrial processes) dominate over natural sources (e.g., ocean and soil)[4]. However, VSLSs, such as dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$), are currently not regulated under the Montreal Protocol[2].

Atmospheric measurements show increases in both atmospheric CH_2Cl_2 mole fractions (e.g., from ~30 ppt in 2004 to ~60 ppt in 2015 in the Northern Hemisphere; ppt refers to parts per trillion as a dry air mole fraction) and in derived global emissions over 2004-2015[12, 21]. Global 3-D model simulations show that return of Antarctic ozone to 1980 values could be substantially delayed by 17-31 years under the assumption of "continued growth" through 2050, or by even 5 years if it is assumed they remain at 2015 levels[12]. It should be noted that the "continued growth" scenario is strictly hypothetical and is not based on a market analysis or future demand. New observational data from the Advanced Global Atmospheric Gases Experiment (AGAGE) network[3] show that CH_2Cl_2 continued to rise up to 2018, at a rate of 1.8 ppt yr^{-1} over 2015-2017 (3.0 ppt yr^{-1} over 2016-2017) compared to the growth rate of 1.4 ppt yr^{-1} over 2004-2014 (see Figure 4).

Another recent study found that atmospheric $CHCl_3$ mole fractions were relatively stable or decreasing during 1990-2010, but were followed by a rapid increase through 2015[13]. Using high frequency measurement data from two AGAGE stations in East Asia, combined with regional inverse modelling, hot spots of $CHCl_3$ emissions have been found in eastern China and the total

annual emissions derived for eastern China grew by 49 (41–59) kilotonnes between 2010 and 2015, which could explain the entire global emission increases[13]. By comparison with the results for CH_2Cl_2 described above, if atmospheric $CHCl_3$ growth continued at the average rate observed during 2010-2015, the ozone layer recovery delay could be 4–8 years; alternatively, the delay could be 0.4 years if no further growth in atmospheric $CHCl_3$ mole fractions exists beyond 2015[13]. More recent observational data from the AGAGE network[3] show that $CHCl_3$ mole fractions continued to grow at a rate of 0.35 ppt yr^{-1} over 2015-2017 (0.89 ppt yr^{-1} over 2016-2017), compared to the growth rate of 0.33 ppt yr^{-1} over 2010-2014 (see Figure 4).

Thus, CH_2Cl_2 and $CHCl_3$ are potential threats for future ozone layer recovery if their atmospheric abundances continue to grow. It is important to ensure continuous measurements of CH_2Cl_2 and $CHCl_3$ to understand their emission sources and to develop models to simulate better the impacts of these gases on stratospheric ozone loss. Elimination of CH_2Cl_2 and $CHCl_3$ emissions in the future would rapidly limit their impacts on stratospheric ozone, since these short-lived gases would be cleansed from the atmosphere within a few years.

Climate change and ODS emissions from natural sources

[350 words]

Ozone layer recovery during this century will be controlled not only by the decline in ODSs but also, to a large and increasing extent, by the increase in greenhouse gases (GHGs) and the associated future climate change. There is a strong coupling between climate change and stratospheric ozone change in both directions. For example, the influence of the Antarctic ozone hole has led to a range of significant summertime surface climate changes in the Southern Hemisphere[22]. Studies have also shown that GHG-induced climate change can cause ozone changes in different regions[8, 14, 23, 24], e.g., an increase in ozone in the upper stratosphere at all

latitudes and a decrease the lower stratospheric ozone in the tropics[8, 23]. This is because GHG-induced climate change impacts both chemical reactions (e.g., upper stratospheric cooling reduces gas-phase catalytic ozone loss rates and can lead to "super-recovery" of ozone) and atmospheric circulation (e.g., likely increase in mid-latitude lower stratospheric ozone because the Brewer-Dobson circulation transporting ozone from the tropics to the extratropics may be speeding up[8, 25]). The wide range of possible future levels of CO_2, CH_4, and N_2O limits accurate projections of the ozone layer recovery[8].

One future challenge for ozone recovery is that human-induced climate change may increase natural emissions of halogenated ODSs (CH_3Cl, CH_3Br, $CHBr_3$, etc.) from ocean and land. Past studies suggest that atmospheric levels of CH_3Cl from the ocean may rise due to future GHG-driven warming, with a response of about 90 ppt CH_3Cl/°C[26], from current levels of ~550 ppt in 2015[4]. Production and emissions of CH_3Br from the ocean will be enhanced in a warming climate[27]. Emissions of $CHBr_3$ from the ocean are projected to increase by 31% during 2010-2100 under a scenario of high greenhouse gas emissions[28]. Models project that Antarctic ozone recovery will be delayed by ~20 years if atmospheric concentrations of natural ODSs increase at ~0.2%/yr in a future climate warming[29]. Mitigating climate warming would mitigate the risk of increases in ODS emissions from natural sources.

N_2O and CH_4 included in climate agreements

[~400 words]

N_2O is a powerful greenhouse gas included in climate agreements, e.g., the 2015 Paris Agreement, which aims to keep global temperature rise this century to less than 2°C above pre-industrial levels. Anthropogenic sources, which include agriculture, stationary and mobile combustion, nitric and adipic acid production, biomass burning, and wastewater treatment,

207 contribute approximately one-third of total N_2O emissions, while natural sources (mainly
208 microbial activity in the oceans and natural soils) comprise the rest[30]. Atmospheric N_2O mole
209 fractions have been growing continuously from 319 ppb (parts per billion) in 2005 to 330 ppb in
210 2017 as observed in the AGAGE network[3] (Figure 4). N_2O is also an important ODS, and
211 increases in its atmospheric abundance lead to ozone depletion. Currently, N_2O provides the
212 largest contribution among all individual ODS emissions to stratospheric ozone loss[31]. There are
213 multiple options for mitigating N_2O in anthropogenic sectors[32]. N_2O is not included in the
214 Montreal Protocol although it has been proposed to regulate N_2O under the ozone regime as
215 well[32]. The return of globally averaged total column ozone to 1980 levels will be more than 5
216 years later compared with the scenario in which no anthropogenic N_2O emissions occur after
217 2020[17]. Therefore, atmospheric N_2O levels will exert an important influence on future ozone
218 layer recovery.

219 CH_4, with atmospheric mole fractions of ~1840 ppb in 2016[4], is also a powerful greenhouse
220 gas and is included in climate agreements. Its future growth rate is uncertain and, in consequence,
221 so is its potential future impact on climate, which could be very large. Anthropogenic methane is
222 emitted from industry, agriculture, and waste management activities. CH_4 also impacts ozone by:
223 (1) increasing atmospheric odd hydrogen species and H_2O, which decrease ozone; (2) cooling of
224 the stratosphere which decreases ozone loss; (3) deactivating chlorine which decreases ozone
225 loss; and (4) increasing the NO_x-ozone production in the troposphere. Studies show that the
226 return of global average total ozone relative to 1980 level would be accelerated by ~15 years if
227 CH_4 follows the high-emission scenario of Representative Concentration Pathways (RCPs; RCP-
228 8.5[33]; 3750 ppb in 2100)[17]. However, the return of global average total ozone relative to 1980
229 level would be delayed by ~35 years if CH_4 follows the low-emission RCP scenario (RCP-2.6[33];

230 1254 ppb in 2100)[17]. Thus, the impact of CH_4 on future ozone layer recovery depends
231 significantly on the rather uncertain future CH_4 emission trajectory.

232 **Stratospheric geoengineering**

233 [~150 words]

234 To tackle climate change, geoengineering projects like injecting sulfate aerosol into the
235 stratosphere for solar-radiation management have been proposed[e.g., 34]. Such injections might
236 have some appeal because they are the only known way at present to reduce temperatures
237 quickly and effectively, but they would also entail new risks, including likely depletion of
238 stratospheric ozone. Thus, stratospheric geoengineering may become another challenge for future
239 ozone recovery. Specifically, modeling studies show that an injection of sulfate aerosol large
240 enough to compensate for surface warming caused by the doubling of atmospheric CO_2 would
241 cause the Antarctic ozone hole to persist into the next century[35]. It has been proposed that the
242 injection of alkaline calcite ($CaCO_3$) aerosol particles rather than acidic sulfate aerosol would
243 enable stratospheric geoengineering while reducing or even reversing ozone depletion[36].
244 However, more studies are needed to investigate further the effects of using calcite aerosols and
245 other alternatives.

246 **Implications for future policy and science**

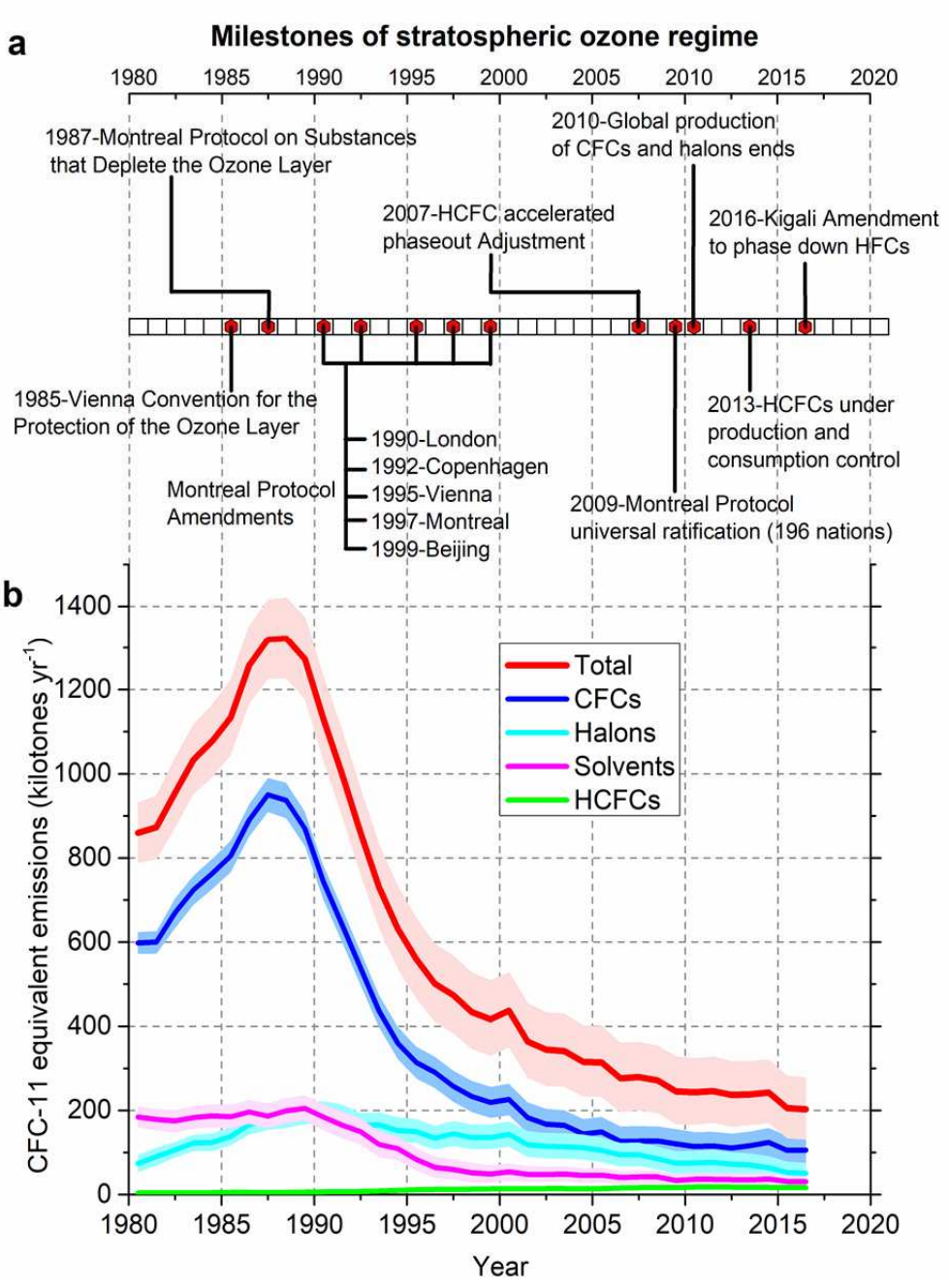
247 [~300 words]

248 To mitigate the threats to future ozone recovery, it is first crucial to ensure that the 32-year-old
249 Montreal Protocol and its amendments are implemented effectively in firmly controlling ODSs.
250 Effective implementation requires that the current issue of unexpected emissions of CFC-11, and
251 other minor CFCs be promptly addressed. Going forward, since other ODSs in addition to those

addressed here may show unexpected emission increases, careful monitoring of the phase-out activities of all ODSs is essential. Given the recent increases in atmospheric CH_2Cl_2 and $CHCl_3$ concentrations, emissions and their potential threat to future ozone recovery, it is important to understand their sources prior to any discussion about mitigation. Threats from N_2O to ozone recovery, and to climate, could be minimized if anthropogenic N_2O becomes controlled effectively. Efforts to mitigate future climate warming may also help avoid any significant increases in natural emissions of some ODSs. The research community must be vigilant in highlighting any geoengineering options which could represent a potential threat to the ozone layer.

With all these potential future challenges for ozone recovery, it is imperative that accurate monitoring of atmospheric ozone, ODSs, GHGs, and climate change continue throughout the coming decades. A substantial proportion of the world, e.g., western China, South and Southeast Asia, and South America, is currently not covered by existing atmospheric ODS measurement networks[3, 4], so that ODS-relevant information (e.g., emission strengths and spatial distributions) for those regions is severely lacking. Thus, enhancing the spatial coverage of the monitoring networks is crucial at global and regional scales. Methods need to be improved for pinpointing emission locations by inverse modeling, attributing emissions among anthropogenic and natural sources, and understanding the interplay between climate change and ozone layer recovery. In the future, alarms informed by regional inverse modeling studies could precede a global alarm, since regional atmospheric measurements respond much faster to unexpected emission increases than remote global measurements. Finally, our ability to model the future interactions between climate change and ozone recovery in coupled Earth system models needs to be improved through coordinated model development and evaluation.

Figures



276

277 **Figure 1. (a) Milestones of the stratospheric ozone control regime and (b) CFC-11**
278 **equivalent emissions during 1980-2016.** Emissions are derived from the WMO 2018 report[4]
279 using atmospheric measurement data, converted to CFC-11-equivalents using their Ozone
280 Depletion Potential (ODP) values[8]. Species are grouped into CFCs, halons, solvents (CCl_4 and
281 CH_3CCl_3), and HCFCs. Shading indicates the 1-sigma uncertainty.

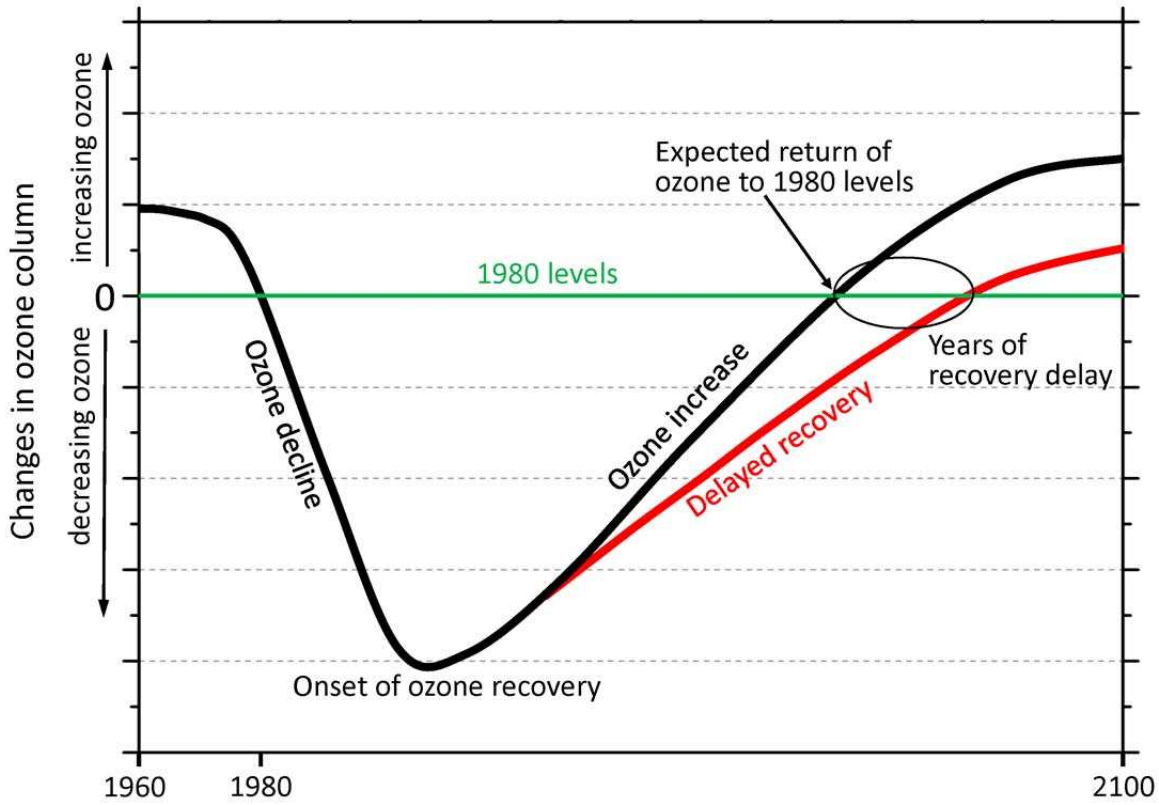
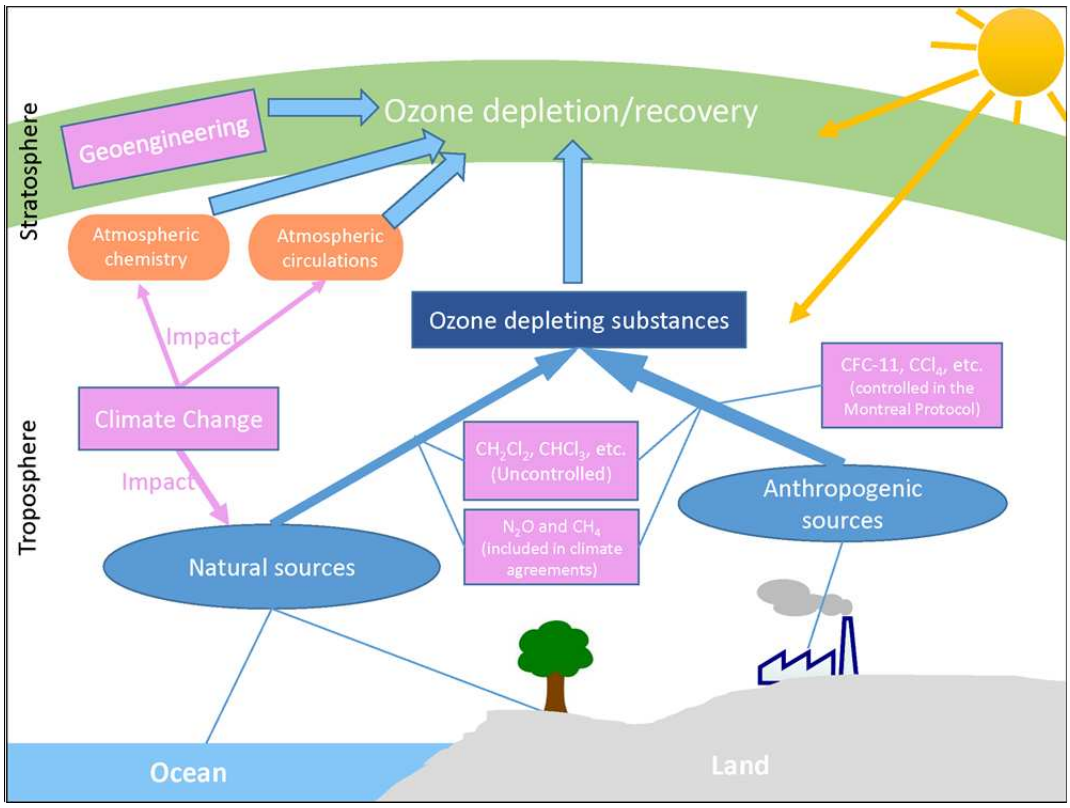
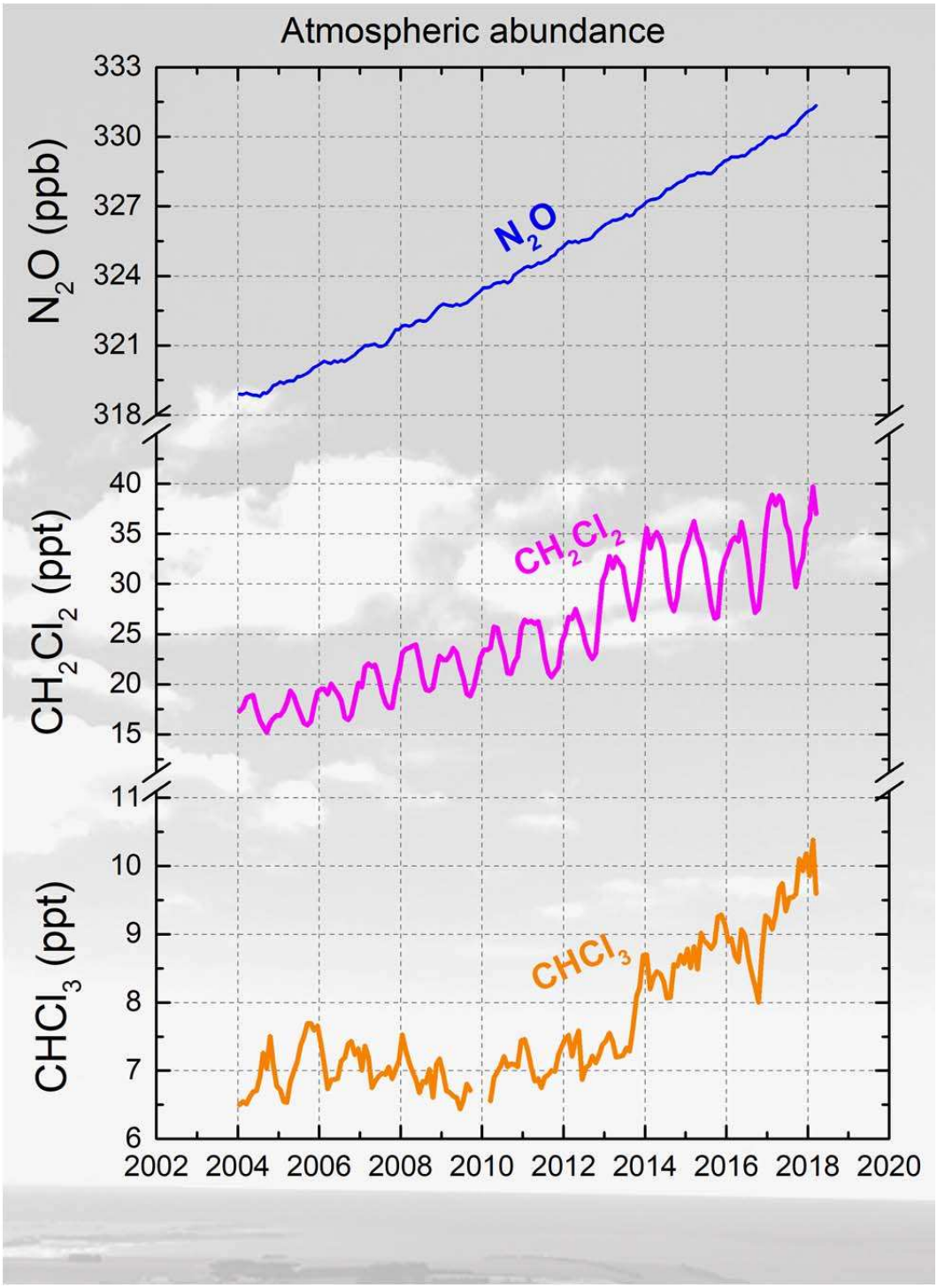


Figure 2. Schematic illustration of ozone recovery. The solid black line represents ozone depletion from 1960, turnround and then ozone recovery towards 2100. The zero line is drawn at the 1980 ozone value. The red line illustrates a future scenario with larger emissions of ODSs which causes a delay in ozone recovery and later return to the 1980 value. Please refer to Figures 6-4 and 6-5 in WMO (2018)[17] as examples for quantitative historical ozone trajectory and projected trajectories from various scenarios.



289

290 **Figure 3. Schematic illustration of potential challenges for ozone recovery.** Ozone-depleting
291 substances are released from both anthropogenic and natural sources. Some controlled
292 substances (e.g., CFC-11 and CCl_4) are only from anthropogenic sources. Some substances (e.g.,
293 CH_2Cl_2 and N_2O) are from both anthropogenic and natural sources. Climate change impacts
294 atmospheric chemistry, circulation, and emissions of ODSs from natural sources. The purple
295 boxes show the five potential challenges for the recovery of the ozone layer.



296

297 **Figure 4. Continuous growth of global atmospheric abundances of N_2O (ppb), CH_2Cl_2 (ppt),**
298 **and $CHCl_3$ (ppt) from 2004 to 2017 derived from the AGAGE global observation network[3].**
299 The data were accessed on March 11, 2019 via http://agage.mit.edu/data/. The term of 'ppt'
300 refers to parts per trillion; 'ppb' refers to parts per billion.

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Acknowledgements

X.F., and R.G.P., are supported by the National Aeronautics and Space Administration (NASA, USA) grants NAG5-12669, NNX07AE89G, NNX11AF17G and NNX16AC98G to MIT. S.P. is supported by the National Strategic Project-Fine particle of the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIT), the Ministry of Environment (ME), and the Ministry of Health and Welfare (MOHW) (No. NRF-2017M3D8A1092225). We thank the station personnel in AGAGE stations for continuously measuring atmospheric N_2O, CH_2Cl_2, $CHCl_3$, and other referenced species as well, and Ray H. Wang in Georgia Institute of Technology, Atlanta, GA, USA for producing global monthly mean data of these species based on the measurements at individual AGAGE stations. We thank Zhen Dai from Harvard University for useful discussions on stratospheric geoengineering.

Author contributions

X.F. and R.G.P. were responsible for the overall project design. All authors wrote up the paper and improved by many iterations.

Competing financial interests

The authors declare no competing financial interests.

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