PHILOSOPHICAL
TRANSACTIONS
OF
THE ROYAL
SOCIETY B

Phil. Trans. R. Soc. B (2012) **367**, 1256–1264
doi:10.1098/rstb.2011.0377

Research

Stratospheric ozone depletion due to nitrous oxide: influences of other gases

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The effects of anthropogenic emissions of nitrous oxide (N_2O), carbon dioxide (CO_2), methane (CH_4) and the halocarbons on stratospheric ozone (O_3) over the twentieth and twenty-first centuries are isolated using a chemical model of the stratosphere. The future evolution of ozone will depend on each of these gases, with N_2O and CO_2 probably playing the dominant roles as halocarbons return towards pre-industrial levels. There are nonlinear interactions between these gases that preclude unambiguously separating their effect on ozone. For example, the CH_4 increase during the twentieth century reduced the ozone losses owing to halocarbon increases, and the N_2O chemical destruction of O_3 is buffered by CO_2 thermal effects in the middle stratosphere (by approx. 20% for the IPCC A1B/WMO A1 scenario over the time period 1900–2100). Nonetheless, N_2O is expected to continue to be the largest anthropogenic emission of an O_3-destroying compound in the foreseeable future. Reductions in anthropogenic N_2O emissions provide a larger opportunity for reduction in future O_3 depletion than any of the remaining uncontrolled halocarbon emissions. It is also shown that 1980 levels of O_3 were affected by halocarbons, N_2O, CO_2 and CH_4, and thus may not be a good choice of a benchmark of O_3 recovery.

Keywords: nitrous oxide; stratospheric ozone; carbon dioxide; methane; halocarbon; ozone depletion potential

1. INTRODUCTION

There has been concern about anthropogenic chemical perturbations to the ozone layer for the past four decades. The early literature in the 1970s first focused on perturbations by nitrogen oxide radicals from supersonic aircraft flying in the stratosphere [1,2] and later chlorine radicals from rocket exhaust and chlorofluorocarbons (CFCs) [3,4]. As concern about supersonic aircraft and rocket exhaust impacts on stratospheric ozone died down owing to economic and air transportation issues, and the production of chlorinated compounds was rapidly increasing during the 1970s and 1980s, chlorine-induced ozone depletion received the majority of attention in the literature. The discovery of the ozone hole [5] further focused attention on effects of chlorine (and bromine) on stratospheric ozone. It became clear that ozone layer depletion was not a future but a current occurrence given the high impact of chlorine in the ozone hole observed in 1984 (approx. 40% column ozone loss, increasing to 70% column ozone loss in the 1990s). Thus, this focus was appropriate. Recent calculations show that continuous increased production of halocarbons at a high rate since the 1980s would have eventually caused the complete collapse of the ozone layer [6] and substantial climate warming [7]. Halocarbon production has been greatly reduced owing to the success of the Montreal Protocol (and subsequent amendments), and atmospheric chlorine levels have been measured to be slowly decreasing (first shown in the study of Montzka *et al.* [8]; see [9] for updates). Signs of the slowdown in the decline of ozone have been reported in the upper stratosphere [10] and extensive research is being carried out to find more evidence of recovery [9].

The effects of other source gases that can affect ozone (e.g. nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2)) received less attention during the 1980s and 1990s, in part because their effects over short (e.g. decadal) time periods are relatively small. Interest in the long-term recovery of the ozone layer has re-focused attention on the effects of these gases [11–13]. Much of this research built on the knowledge gained during the previous decades and added long scenario calculations into the future, and found that the effects on stratospheric ozone could be large. This paper will further explore this theme and, in particular, explore the interactions between these gases and stratospheric ozone. The paper is partially a review of basic chemical effects on stratospheric ozone and highlights recent research on the effects of the elimination of N_2O and controlled halocarbons. In addition, new material on the interaction between the various greenhouse gases (GHGs) is presented, emphasizing the role of N_2O. The effects of dynamic changes on ozone owing to GHG increases [9] and the potential effect of water vapour changes on ozone [14] will not be discussed. We focus on global mean total ozone as a metric for the effect of chemical

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One contribution of 12 to a Theo Murphy Meeting Issue 'Nitrous oxide: the forgotten greenhouse gas'.

perturbations on ozone. This is owing to the fact that global ozone depletion is what is generally used in determining ozone depletion potentials (ODPs) and that global mean changes approximately characterize ozone changes at mid-latitudes.

2. PHOTOCHEMISTRY OF NITROUS OXIDE

N_2O is produced at the surface and is relatively inert in the troposphere. Microbial activity in the soil is thought to be the largest source, but there are many smaller contributions (see [15] and the other papers in this issue for discussion). It is transported to the stratosphere and broken down in the middle stratosphere and above via photolysis

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \tag{2.1}$$

and reaction with $O(^1D)$

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \tag{2.2}$$

and

$$N_2O + O(^1D) \rightarrow 2NO. \tag{2.3}$$

The global lifetime of N_2O is approximately 114 years [15], which is determined by the above loss processes in conjunction with the strength of the stratospheric overturning circulation (a 20% uncertainty in the sink is reported in the study of IPCC [15]). The NO produced in reaction (2.3) is the primary source of reactive nitrogen (i.e. NO_x, defined below) in the lower and middle stratosphere (transport of mesospheric NO_x can be significant in the upper stratosphere). Approximately 10 per cent of the N_2O is converted to NO_x in the stratosphere. Figure 1*a* shows the distribution of N_2O produced in the National Oceanic and Atmospheric Administration/National Center for Atmospheric Research (NOCAR) two-dimensional model ([16] and references within). The shape of the contours is a reflection of the stratospheric circulation, upward in the tropics and downward in the extra-tropics. Figure 1*b* shows the production rate of NO_x owing to reaction (2.3) (the blue contours). This occurs at a somewhat lower altitude than the bulk of the N_2O destruction owing to reaction (2.1) (which does not produce NO_x). Reactive nitrogen can be destroyed chemically via

$$N + NO \rightarrow N_2 + O, \tag{2.4}$$

which is shown via the red contours on figure 1*b*. This is the major chemical loss process for total oxidized nitrogen (NO_y, defined below) and accounts for approximately 30 per cent loss of NO_y. The remainder of the NO_y is lost via transport the troposphere (approx. 70%).

3. BASIC OZONE PHOTOCHEMISTRY

The photochemistry of ozone was first described by Chapman [17]. Ozone is produced by the photolysis of O_2

$$O_2 + h\nu \rightarrow O + O \tag{3.1}$$

followed by the reaction of O and O_2

$$O + O_2 + M \rightarrow O_3 + M. \tag{3.2}$$

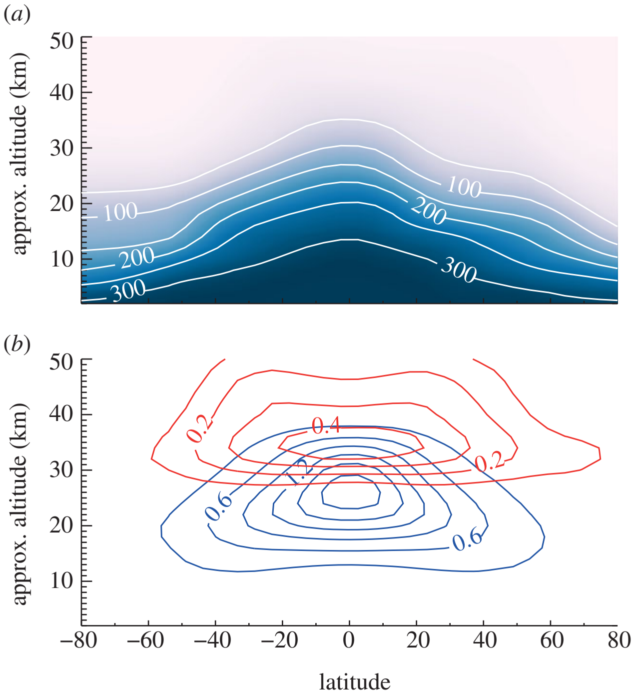

Figure 1. (*a*) The N_2O field (in ppbv) produced by the NOCAR two-dimensional model in year 2000. (*b*) Production of NO_x from N_2O (reaction (2.3), blue contours) and chemical loss rates of NO_x (reaction (2.4), red contours) in year 2000 (in ppbv d^{-1}).

O and O_3 are quickly cycled between each other via

$$O_3 + h\nu \rightarrow O_2 + O \tag{3.3}$$

followed by reaction (3.2). Thus, it is useful to define the $O_x = O + O_3$ family. The loss of O_x (and thus ozone) in the Chapman chemistry occurs via

$$O + O_3 \rightarrow O_2 + O_2 \tag{3.4}$$

with minor contribution by

$$O + O + M \rightarrow O_2 + M. \tag{3.5}$$

Since reactions (3.4) and (3.5) are much slower than reactions (3.2) and (3.3), O_x is much longer lived than either O or O_3 in the stratosphere making the use of the O_x family a conceptual simplification. The photolysis of ozone ($\lambda < 320$ nm) is also the primary source of $O(^1D)$ in the atmosphere, which plays an important role in N_2O chemistry (reactions (2.2) and (2.3)) and many other species.

Between 1930 and the 1970s, it became evident that other loss processes were necessary to explain the abundance of ozone in the ozone layer. It was realized that nitrogen oxide [1,2], hydrogen oxide [18] and chlorine radicals [3,4] also destroyed O_x (i.e. ozone) via catalytic cycles of the form

$$X + O_3 \rightarrow XO + O_2 \tag{3.6}$$

$$XO + O \rightarrow X + O_2 \tag{3.7}$$

and

$$\text{net}: O_3 + O \rightarrow 2O_2, \tag{3.8}$$

with $X = \{NO, HO, Cl\}$. The recycling of the X molecule allows one X to destroy many (typically

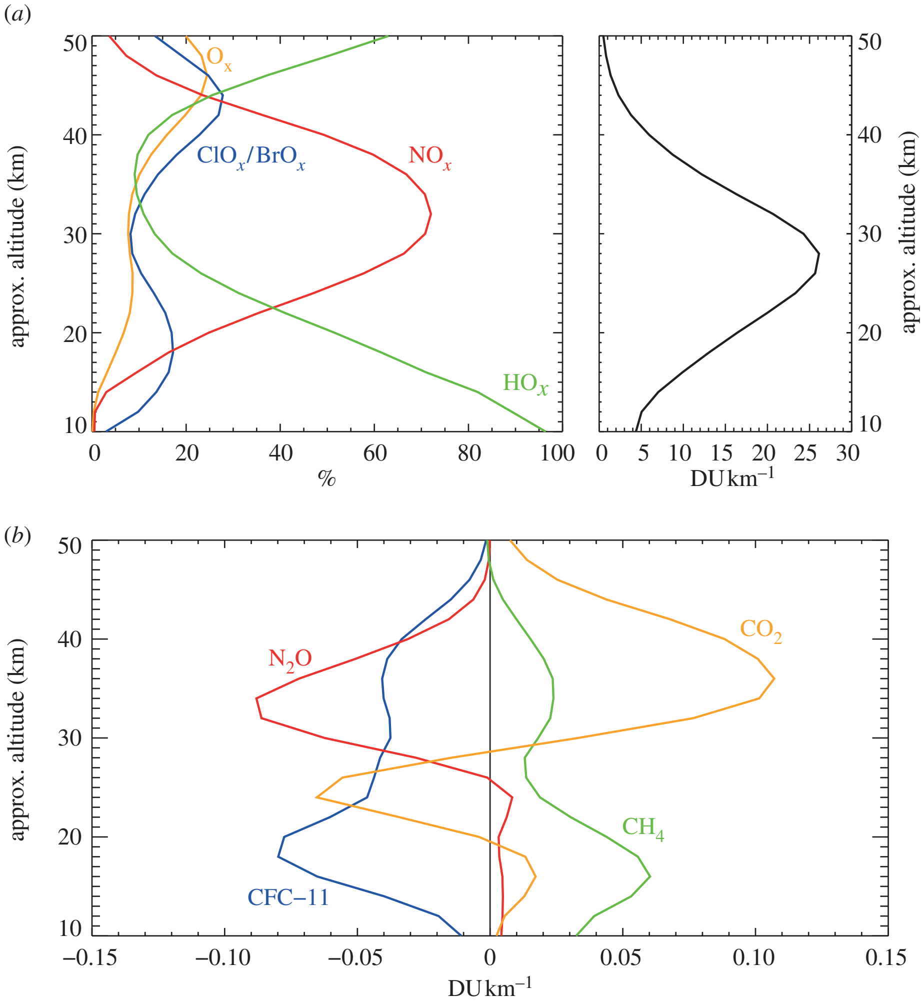

Figure 2. (*a*) The left panel shows the relative global mean ozone loss rates by chemical family computed for 2000 levels of source gases by the NOCAR two-dimensional model. The right panel shows the global mean ozone profile, which highlights the ozone layer maximum in the middle stratosphere. (*b*) The ozone changes by surface boundary condition perturbation for the following perturbation levels: 20 ppbv N_2O, 100 pptv CFC-11, 250 ppbv CH_4 and 50 ppmv CO_2. The background atmosphere is defined to be at 2000 levels for the non-perturbed gases according to the combined IPCC A1B/WMO A1 scenario. Note that Dobson Units (DU) are a measure of ozone column amount ($1\ \mathrm{DU} = 2.69 \times 10^{16}\ \mathrm{mol\ cm^{-2}}$) and DU km^{-1} is a density unit ($1\ \mathrm{DU\ km^{-1}} = 2.69 \times 10^{11}\ \mathrm{mol\ cm^{-3}}$).

10^3–10^5 [19]) ozone molecules before it is converted to a less-reactive molecule. This cycle is representative of the many forms of catalytic cycles that have been found to be important [20]. Bromine is interesting as its most important catalytic cycle is a combined ClO/BrO cycle, and thus increases in chlorine make bromine more potent as an ozone-destroying agent.

The individual radicals are short-lived and are also usefully modelled as part of long-lived families (e.g. $NO_x = N + NO + NO_2 + NO_3 + N_2O_5$; $NO_y = NO_x + HNO_3 + HNO_4 + ClONO_2 + BrONO_2$), where NO_x represents the sum of the short-lived nitrogen species and NO_y the sum of the short- and long-lived nitrogen species. In this framework, reaction (2.3) is the source of NO_y (and thus NO_x) and reaction (2.4) its chemical loss. Analogous definitions are obtained for ClO_x, Cl_y, BrO_x, Br_y and HO_x. The global annual mean ozone loss rates by the chemical families are shown in figure 2*a* as computed in the NOCAR two-dimensional model for the year 2000. It is evident that the NO_x cycle is dominant in the middle stratosphere, HO_x in the upper and lower stratosphere, and ClO_x/BrO_x in the upper and lower stratosphere. The global mean ozone profile is also shown in the figure, which shows the ozone maximum in the middle stratosphere. The NO_x-induced ozone loss is largest near the ozone maximum, which is one reason for its importance.

The relative abundance of the short-lived species (e.g. NO_x) compared with the long-lived species (e.g. HNO_3) plays an important role in determining the amount of ozone loss by a family. The long-lived species sequester reactive atoms in non-reactive (to ozone) forms and are called reservoirs. These reservoir species are slowly converted back to more reactive forms, typically by photolysis or reaction with OH. For example, the NO_x family's effect on ozone decreases from the middle to lower stratosphere largely because the HNO_3 reservoir becomes substantially more stable in the lower stratosphere. Similarly, in the ClO_x family, HCl and $ClONO_2$ are important reservoirs that control the effectiveness of ClO_x-induced ozone losses.

Anthropogenic influence on ozone occurs via changes in the emission of source gases. These source gas changes can affect all of the chemical families both chemically (e.g. N_2O produces NO_x but also has a large effect on ClO_x via $ClONO_2$) and radiatively. Radiative changes can affect stratospheric temperatures and so dynamically alter the stratosphere. Changes in stratospheric temperature can also affect the chemistry via reaction rates and dynamic changes can affect the distribution of long-lived species (and thus the chemistry) and the ozone field itself. Figure 2*b* shows the effect of perturbations owing to the source gases N_2O, CH_4, CO_2 and CFC-11 for year 2000 levels of source gases on ozone. The primary effect of these source gas changes is as follows: N_2O causes more NO_x and NO_x-induced ozone loss; CFC-11 causes more ClO_x and ClO_x-induced ozone loss; CH_4 causes ozone increases via photochemical production chemistry that occurs not only in the troposphere but also in the lower stratosphere (the CH_4 effect in the upper stratosphere is described below); CO_2 has a radiative effect that cools the stratosphere and thus causes a reduction in the ozone loss via the strongly temperature-dependent reaction (3.4) (CO_2 increase also induces the strengthening of the Brewer–Dobson circulation in climate models which decreases/increases ozone in the tropical/extratropical lower stratosphere). These effects are discussed in more detail below.

4. TIME SERIES

Figure 2*b* shows the effect of particular steady-state perturbations of the source gases for non-varying year 2000 conditions. However, these long-lived source gases have been altered continuously by mankind during the twentieth century and are expected to continue to be in the future. In this paper, we use the Intergovernmental Panel on Climate Change (IPCC) A1B scenario for the GHGs and the World Meteorological Organization (WMO) A1 scenario for the halocarbons (this will be labelled A1B/A1). The A1B scenario has rapid increases in GHGs until the mid-twenty-first century and slower growth after that, with CO_2 and N_2O rising to 703 ppmv and 372 ppbv, respectively, by 2100 [21]. The WMO A1 scenario includes time series of 16 chlorine- and bromine-containing source gases (CFCs, hydrochlorofluorocarbons (HCFCs), methyl bromine, carbon tetrachloride, and so on) based on their measured (and estimated) rise and projected fall during the mid-twentieth century to 2100 [9]. It is widely recognized that the large halocarbon increases during the 1970s to the mid-1990s caused a large drop in the ozone during this time frame and that CO_2 and N_2O change in the twenty-first century will probably strongly perturb ozone into the future [9]. Figure 3 shows the modelled time series of ozone in the twentieth and twenty-first centuries using the A1B/A1 scenario along with ozone observations from satellites [22]. The halocarbon-induced ozone depletion in the period 1970–2000 is clearly evident. The year when the Montreal Protocol, which reduced emissions of halocarbons, entered into force is labelled on the figure. The recovery of ozone is evident in the model output during the twenty-first century. Using this scenario, ozone returns to values larger than were present in 1900. This is often called ‘super-recovery’ and is primarily caused by increase of CO_2 [12,23].

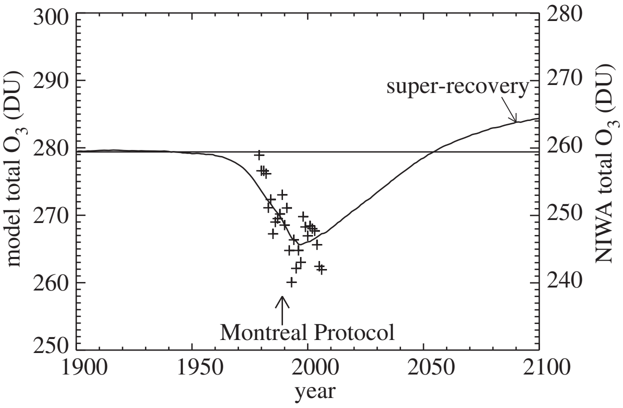

Figure 3. The global mean ozone time series computed with the NOCAR two-dimensional model using the IPCC A1B/WMO A1 scenario. The global mean ozone levels from satellite observations from the NIWA analysis [22] are shown by the crosses. The year when the Montreal Protocol limited halocarbon emissions is indicated. Global mean ozone shows a super-recovery (an evolution to larger values than in the past) in this scenario caused primarily by CO_2-induced changes on stratospheric temperatures. Solid line, model; plus symbols, satellite observations.

We use the global mean total ozone to compare the effects of the different gases, which is a common choice when the overall effect on ozone is desired as the effects of ozone changes at low and mid-latitudes are accounted for. It is also the metric used in comparing the ozone-depletion potentials (ODPs; see §6) of anthropogenic emissions of ozone-depleting substances (ODSs). Global mean ozone does not weight changes in the ozone hole very heavily because of the relatively small area involved and thus is not very sensitive to the effects of source gas changes on the ozone hole. The buildup of halocarbons caused the ozone hole and it is expected to recover when halocarbons return to natural levels. The ozone hole is caused by heterogeneous reactions on aerosol particles that convert chlorine reservoirs to active forms in the cold environment of polar winter in the lower stratosphere [24]. The NO_x and HO_x families do not cause an ozone hole as their reservoirs do not react on aerosol in that environment. In fact, HNO_3, the dominant nitrogen reservoir, is produced in many of the heterogeneous reactions. However, N_2O and CH_4 do somewhat alter the effect of ClO_x/BrO_x in the ozone hole while halocarbon levels remain high (and CO_2 can affect it through temperature and dynamic changes). Thus, the relative magnitudes of effects of the source gases discussed in this paper would be different if, for example, ozone at high latitudes were compared instead of global mean ozone.

5. NONLINEAR INTERACTIONS

The emission of a gas can induce a straightforward change in the chemistry of its chemical family (e.g. N_2O emission causing more NO_x production and more NO_x-induced ozone loss). However, the emission of a gas can also induce changes in other chemical families, which can arise owing to either chemical interactions or radiative effects on

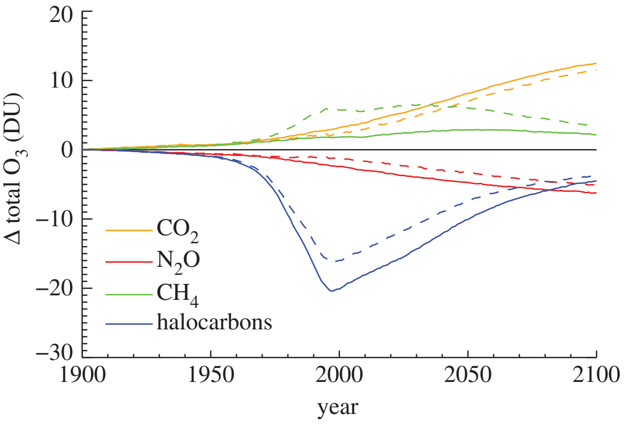

Figure 4. The individual source gas changes are isolated using different atmospheric base states (constant 1900 source gas levels and the combined IPCC A1B/WMO A1 scenario). In all cases, the size of the perturbation is obtained from the A1B/A1 scenario (dashed lines) minus constant 1900 source gas levels (solid lines). The degree to which the solid and dashed lines are different (for each gas) indicates the level of nonlinear interactions between the gases. These limit our ability to unambiguously separate the effect of these gases on ozone.

the temperature and dynamics. The magnitude of these effects is dependent on the levels of the other source gases that control the chemical families. These interactions make the impact on ozone levels of one gas to not be unambiguously separable from another. Thus, the impact of a perturbation of a source gas is nonlinear (i.e. it depends on the state of the system). One way to probe the magnitude of the nonlinearities is to compute the effect of individual perturbations of the gases but with different background concentrations of the other gases. In order to quantify the size of the nonlinear interactions, we compute the effect of the perturbations with two background conditions: constant 1900 source gas levels and the full A1B/A1 scenario. Figure 4 shows the result of this calculation on global mean ozone. The graph shows the effect of individual perturbations of each gas from 1900 source gas levels to the A1B/A1 scenario levels on ozone. The solid and dashed lines signify the different atmospheres to which the perturbations are added. The solid lines all use constant 1900 source gas levels for the non-perturbed gases while the dashed lines use the A1B/A1 scenario. The degree to which the dashed and solid lines (for each gas) differ gives an estimate of the size of the nonlinear interaction. The ozone changes (relative to 1900 levels) obtained in this calculation are also shown in table 1 for 1980, 2000 and 2100. The total of the individual perturbations is compared with their combined effect (i.e. the ozone changes for the actual scenario) in this table as well, quantifying the nonlinear contributions.

The largest nonlinear effects are evident between the halogens and methane. To first order they are caused by the reaction

$$Cl + CH_4 \rightarrow HCl + CH_3, \tag{5.1}$$

which couples methane with chlorine by converting active chlorine (Cl) to a chlorine reservoir (HCl), a reservoir species that does not directly destroy ozone. The increase in methane converts active chlorine to the benign HCl reservoir, such that the fraction of active chlorine is smaller for larger methane levels given a fixed amount of chlorine. This shows that the global ozone loss from halocarbons would have been considerably more severe if the buildup of methane had not occurred. In this model, the difference is approximately 4 DU, which can be compared with a total loss of approximately 16 DU for the A1B/A1 scenario and approximately 20 DU for the constant 1900 base state. In other words, the concomitant increase in CH_4 with that of the halocarbons suppressed the extent of ozone depletion by roughly 20 per cent. Of course, without a choice of which gas change we consider primary and which is secondary, there is no way to unambiguously separate the effects of gases with nonlinear interactions. In the upper stratosphere, CH_4 increases cause HO_x increases and thus more ozone losses from HO_x catalytic cycles. This is relatively more important at low halocarbon levels as the coupling with HCl is decreased.

The effect of N_2O changes is also dependent on the background state, and by 2100 there is an approximately 1 DU difference from the N_2O perturbation because of the background state, out of a total depletion of approximately 5 DU for the A1B/A1 scenario base state. This is primarily caused by the CO_2 increases [25]. In contrast to the chemical influence of CH_4 on halocarbon-induced ozone depletion, the influence of CO_2 occurs via thermal changes to the stratosphere, which then alter the chemistry. The loss of NO_x from the stratosphere is partly controlled by reaction (2.4) (N+NO), but the concentration of N atoms is controlled by

$$N + O_2 \rightarrow NO + O. \tag{5.2}$$

While the N+NO reaction is nearly insensitive to temperature, the N+O_2 reaction has a large activation energy (29.8 kJ mol^{-1}). Therefore, a temperature decrease caused primarily by the radiative effect of CO_2 (but also by O_3 changes and thus anything that affects ozone) will cause an increase in N atoms (relative to NO) and thus an increase in the loss rate of NO_y via reaction (2.4). In 2100, the effect of the CO_2 increase causes the ozone destruction owing to N_2O (relative to 1900 ozone levels) to be approximately 17 per cent less than it would be without the CO_2 increase.

There are also nonlinear effects between the halocarbons and N_2O (or more precisely the Cl_y and NO_y families). This comes about primarily because of the coupling between NO_x and ClO_x via chlorine nitrate ($ClONO_2$), which acts as a reservoir species for both families. The dominant effect is that $ClONO_2$ increases as NO_y increases (owing to N_2O) or as ClO_x increases (owing to halocarbons), and this tends to reduce the ozone loss owing to both families. This effect is dominant in the lower stratosphere and largely disappears as halocarbons return to pre-industrial levels, increasing the potency of N_2O [26].

In addition to the effect of thermal changes on the NO_y loss rate discussed above, thermal changes in the stratosphere have many other effects that can influence ozone [9]. These changes are particularly important while halocarbons are elevated and occur owing to temperature dependencies in both gas phase

Table 1. Global mean ozone changes between 1900 and the year listed for each of the perturbations using scenario IPCC A1B/WMO A1. The base state defines the levels of the non-perturbed gases and the ozone level about which the changes are computed. The base states are either defined at constant 1900 source gas levels or levels varying with the A1B/A1 scenario. The total row is the sum of the individual computations, whereas the combined row is the ozone changes with all gases following the A1B/A1 scenario (relative to 1900 ozone levels). The difference between these values for different base states gives one indication of how the nonlinear effects between the gases affect the ozone changes. All values are in Dobson Units (DU).

	1980		2000		2100	
perturbation	base state 1900	base state A1B/A1	base state 1900	base state A1B/A1	base state 1900	base state A1B/A1
halocarbons	−9.42	−7.81	−20.11	−15.97	−4.51	−3.75
CO_2	1.92	1.65	3.21	2.40	12.48	11.57
N_2O	−1.43	−1.17	−2.41	−1.18	−6.24	−5.15
CH_4	1.42	3.03	1.82	5.74	2.17	3.45
total	−7.51	−4.30	−17.50	−9.01	3.91	6.12
combined	−5.82		−13.35		4.97	

and heterogeneous processes. Many of these effects are particularly severe at high latitudes. For example, the stability of the polar vortex could be either enhanced (or weakened) by increases in GHGs, which could increase (or decrease) halocarbon-induced ozone loss in the vortex. There is presently no consensus on the magnitude (or even the sign) of this particular effect on ozone [9].

It is interesting to note that the ozone changes obtained in the model calculation for 1980 (relative to 1900 ozone levels) are not negligible. These values are listed in table 1, separated by source gas and including the combined effect. The modelled global mean ozone depletion owing to halocarbons is found to be between −7.81 and −9.42 DU, which is significant. However, the combined ozone change from all the gases is −5.82 DU, which illustrates the relatively large degree of opposing effects on ozone (the ozone losses from halocarbons and N_2O versus ozone increases owing to CH_4 and CO_2). The importance of CH_4 on the halocarbon effects, as noted above, is evident in 1980. The fact that 1980 ozone levels are already perturbed relative to 1900 is important to consider as many studies have used 1980 levels as a benchmark of ozone recovery. In reality, 1980 ozone levels are already affected by not just the halocarbons but by N_2O, CO_2 and CH_4 as well.

6. OZONE-DEPLETION POTENTIALS

It is useful to have a metric to compare the impact of various source gas emissions on ozone. The most commonly used metric is the ODP, defined as the time-integrated global ozone depletion induced by a perturbation of an equal mass emission of gas X relative to a reference gas (always taken to be CFC-11, labelled F11 below)

$$\mathrm{ODP_X} = \frac{\int_0^\infty [\Delta \mathrm{O_3}]_\mathrm{X}^P \mathrm{d}t}{\int_0^\infty [\Delta \mathrm{O_3}]_\mathrm{F11}^P \mathrm{d}t}, \tag{6.1}$$

where $[\Delta O_3]$ is the global mean total ozone change induced by the perturbation (the P superscript refers to the pulse emission and the subscript is the perturbation compound). It must be kept in mind that the ODP depends on the base state of the atmosphere and makes the assumption that the other sources gases do not change during the time integration. The potential magnitudes of these assumptions on the ODP are estimated by the effect of changes in the background atmosphere on ozone as shown in figure 4. For N_2O, these assumptions can cause the ODP to change by up to approximately 20 per cent for reasonable changes in other gases in the atmosphere. Since these changes are relatively small, ODPs remain a very useful metric for comparing emissions of ozone-destroying compounds.

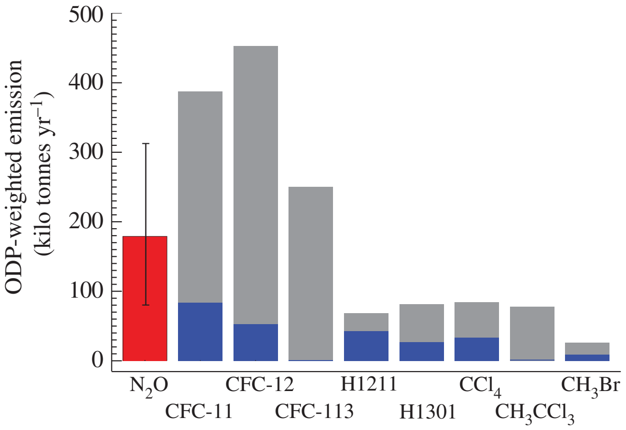

Figure 5. The ODP-weighted emission of anthropogenic N_2O (red) and the listed halocarbons for 1987 (grey) and 2008 (blue) emission levels. The ODP-weighted emission (i.e. the ODP multiplied by the emission level) is proportional to the total future global mean ozone loss from the emission (assuming no intervening changes). The ODP-weighted emission of N_2O was large even in 1987 when anthropogenic halocarbon emissions were near their peak and is larger than the individual halocarbons by 2008. Adapted from fig. 1 of Ravishankara *et al.* [26].

The ODP is rarely calculated using the formula above. Instead, it can be re-written in steady-state form

$$\mathrm{ODP_X} = \frac{m_\mathrm{F11}}{m_\mathrm{X}} \frac{\Delta \mu_\mathrm{F11}}{\Delta \mu_\mathrm{X}} \frac{\tau_\mathrm{X}}{\tau_\mathrm{F11}} \frac{[\Delta \mathrm{O_3}]_\mathrm{X}}{[\Delta \mathrm{O_3}]_\mathrm{F11}}, \tag{6.2}$$

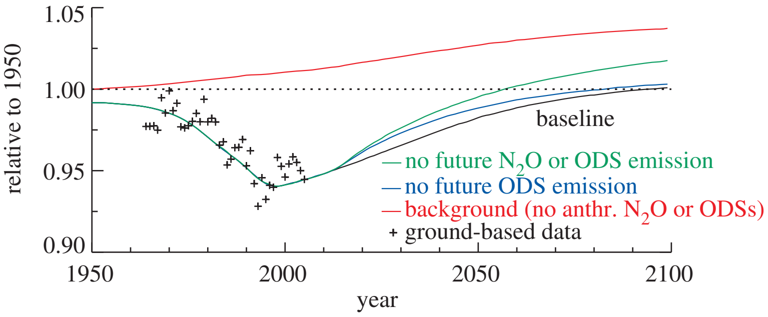

Figure 6. The changes in global mean ozone relative to 1950 computed with the NOCAR two-dimensional model. The full A1B/A1 scenario (labelled baseline) is shown along with scenarios that include removing the remaining unregulated halocarbon (i.e. ODS) emissions after 2010 and eliminating all anthropogenic N_2O emissions after 2010. The effect of eliminating future unregulated halocarbon emissions would increase ozone levels until approximately 2070, while the elimination of anthropogenic N_2O emissions has a larger effect by the end of the twenty-first century. The evolution of ozone without either anthropogenic halocarbon or N_2O emissions is shown by the red line, to which the green curve will slowly converge. Adapted from fig. 2 of Daniel *et al.* [28].

where m is the mass, $\Delta\mu$ the mixing ratio perturbation, τ the lifetime and $[\Delta O_3]$ is the steady-state annual and global mean total ozone change induced by the perturbation. This steady-state formulation is valid for source gases characterized by a first-order decay process. It also assumes that the ozone change is linear over the range of changes of gas X and CFC-11, which is valid for the sizes of perturbations considered here. The ODP of N_2O computed with the NOCAR model for year 2000 conditions is 0.017 [26].

The ODP provides the global mean ozone loss for a gas per unit mass emission relative to CFC-11. In order to estimate the effect of an actual emission amount on ozone, it is useful to compute the ODP-weighted emission (i.e. the ODP multiplied by the emission) as the emissions can vary by large factors (this is particularly true in the case of N_2O compared with the halocarbons). The total future ozone losses induced by emissions are approximately proportional to the ODP-weighted emissions (neglecting the non-linear effects caused by other constituent changes). The ODP-weighted emissions of anthropogenic N_2O are compared with many of the important halocarbons for 2008 and 1987 as shown in figure 5 [26]. Note that the ODP-weighted emission of anthropogenic N_2O was significant when compared with the halocarbons even in 1987, when emissions of halocarbons were large immediately before the enactment of the Montreal Protocol. By 2008, anthropogenic N_2O was the most significant ozone-destroying compound being emitted. Owing to the phase-out of anthropogenic halocarbon emissions, it is likely to become even more dominant in the near future. This would only be expected to change if there were a large reduction in anthropogenic N_2O emissions in the future (this can probably only occur with changes in agricultural practices; see McElroy *et al.* [27] and the papers in this special issue).

Given the nonlinear effects discussed in the previous section, one would expect the ODP of N_2O to change by up to -20 per cent by the end of the twenty-first century because of changes in the other gases. This is primarily owing to the effect of increasing CO_2, which increases the loss of NO_y because of stratospheric cooling (as discussed above). While not negligible, these changes in the N_2O ODP do not alter the conclusions of the study of Ravishankara *et al.* [26] that N_2O will probably remain the dominant ozone-destroying compound emitted by human activities in the twenty-first century.

Despite the high level of success of the Montreal Protocol in avoiding deeper ozone depletion [7], additional policy options remain to increase future ozone levels. Future O_3 depletion can be reduced by further tightening halocarbon controls or reducing N_2O emissions. Increasing CO_2 (or to a lesser degree CH_4) could also counter global ozone loss but would induce other large global consequences (e.g. global warming, ocean acidification, sea level rise, and so on). Figure 6 shows the evolution of global ozone changes relative to 1950 owing to the full A1B/A1 scenario and the effect of eliminating halocarbon ODS and anthropogenic N_2O emissions after 2010 [28]. While eliminating halocarbon ODS emissions causes ozone increases in the 2010–2060 time period, their influences are small by 2100 as the halocarbons decay to near natural levels by that time even with only the current controls. In contrast, eliminating the anthropogenic N_2O emission would have a much larger effect by 2100. It should be noted that in all cases considered here, the global ozone levels by 2100 are expected to be above 1900 levels if CO_2 increases are as large as in the A1B/A1 scenario.

A comparison of the effect of eliminating the individual halocarbons (and anthropogenic methyl bromide and carbon tetrachloride) is shown in figure 7 [28]. This highlights the much larger potential for reducing future ozone depletion by anthropogenic N_2O reductions compared with the elimination of emissions of any of the individual halocarbons, including the banks (i.e. produced gases that already reside in devices, e.g. refrigerators, and could be recaptured), HCFC production, and emission of methyl bromide and carbon tetrachloride.

7. CONCLUSION

The changes in ozone over the 1900–2100 time period driven by changes in halocarbon, N_2O, CH_4

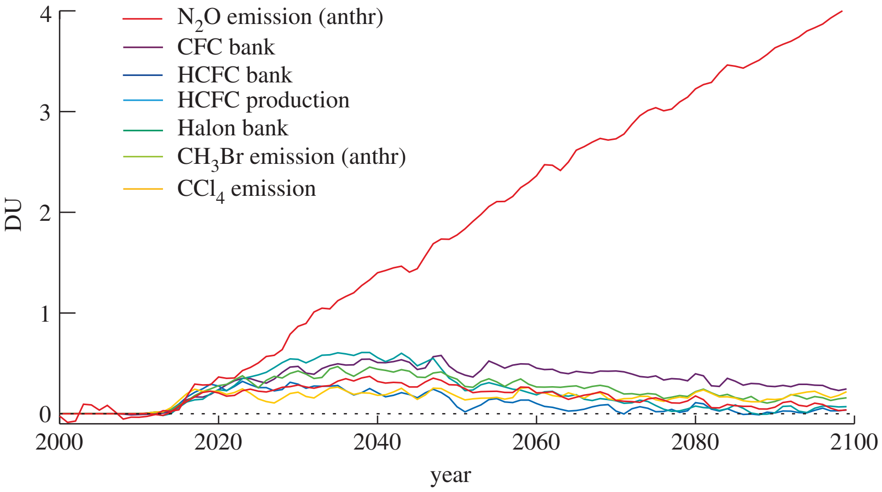

Figure 7. The changes in global mean ozone owing to elimination of anthropogenic N_2O emissions after 2010 when compared with the effect of eliminating the emissions of the CFC banks, HCFC production and banks, the halon banks, anthropogenic methyl bromide and carbon tetrachloride. The elimination of anthropogenic N_2O emission has the largest potential for reducing ozone depletion in the future. Adapted from fig. 4 of Daniel *et al.* [28].

and CO_2 concentrations have been explored with a model of the middle atmosphere. The future evolution of ozone will depend on all of these gases. The large negative effect of the halocarbons evident in ozone between 1950 and the present will decrease in the coming decades of the twenty-first century and non-halocarbon chemicals and climate change will largely control future ozone changes. N_2O is now the largest ozone-destroying gas emitted by human activities based on ODP-weighted emissions [26]. Whether ozone evolves to lower or higher values compared with pre-industrial values depends primarily on the levels of CO_2 relative to the level of N_2O. High emission of CO_2 could cause a so-called ‘super-recovery’ of ozone but would have a large influence on the global climate and oceans.

There is a limit to the extent to which the effect of the source gas emissions can be unambiguously separated owing to nonlinear interactions between the chemical families. The largest of these effects is between CH_4 and the halocarbons. The increase of CH_4 during the twentieth century reduced the effect of halocarbons on global mean ozone by approximately 20 per cent. There are also non-negligible interactions between CO_2 and N_2O on ozone. These effects are of the order of 20 per cent and do not alter the above conclusion of N_2O’s dominant effect on ozone destruction in the future.

By 1980, the decrease in global mean ozone levels was already relatively large when compared with 1900 levels. The changes in ozone were not only due to the halocarbons but also significant changes had already taken place due to N_2O, CO_2 and CH_4. However, there are opposing effects from these gases that make the combined effect smaller than the depletion owing to halocarbons alone. This should be kept in mind by those who use 1980 levels of ozone as a benchmark of recovery.

The elimination of anthropogenic N_2O emissions would have a much larger effect than any of the unregulated halocarbon emissions, singularly or combined [28]. This underscores the opportunity that controlling N_2O emissions provides for reducing future ozone destruction, especially in the twenty-second century and beyond.

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