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Nitrous Oxide (N_2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century

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By comparing the ozone depletion potential–weighted anthropogenic emissions of N_2O with those of other ozone-depleting substances, we show that N_2O emission currently is the single most important ozone-depleting emission and is expected to remain the largest throughout the 21st century. N_2O is unregulated by the Montreal Protocol. Limiting future N_2O emissions would enhance the recovery of the ozone layer from its depleted state and would also reduce the anthropogenic forcing of the climate system, representing a win-win for both ozone and climate.

The depletion of the stratospheric ozone layer by human-made chemicals, referred to as ozone-depleting substances (ODSs), was one of the major environmental issues of the 20th century. The Montreal Protocol on Substances That Deplete the Ozone Layer (*1*), MP, emerged from the Vienna Convention for the Protection of the Ozone Layer (*2*). The MP has been highly successful in reducing the emissions, growth rates, and concentrations of chlorine- and bromine-containing halocarbons, the historically dominant ODSs (*3*), and has limited ozone depletion and initiated the recovery of the ozone layer.

The relative contributions of various ODSs to ozone layer depletion are often quantified by the ozone depletion potential (ODP) (*4*). An ODP relates the amount of stratospheric ozone destroyed by the release of a unit mass of a chemical at Earth's surface to the amount destroyed by the release of a unit mass of chlorofluorocarbon 11, CFC-11 ($CFCl_3$). ODPs are widely used for policy formulation because of their simplicity in quantifying the relative ozone-destroying capabilities of compounds.

Through the work of Crutzen (*5*) and Johnston (*6*), nitrogen oxides ($NO_x = NO + NO_2$) are also known to catalytically destroy ozone via

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$O + NO_2 \rightarrow NO + O_2$$
$$\text{net: } O + O_3 \rightarrow 2O_2$$

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The primary source of stratospheric NO_x is surface N_2O emissions [(*7*) and references therein]. N_2O has been thought of as primarily a natural atmospheric constituent, but the influence of its changes on long-term changes in ozone concentrations has also been examined (*8*–*10*).

Nitrous oxide shares many similarities with the CFCs, historically the dominant ODSs. The CFCs and N_2O are very stable in the troposphere, where they are emitted, and are transported to the stratosphere where they release active chemicals that destroy stratospheric ozone through chlorine- or nitrogen oxide–catalyzed processes. They both have substantial anthropogenic sources. Unlike CFCs, N_2O also has natural sources, akin to methyl bromide, which is another important ODS. Assigning an ODP for N_2O and separating out the natural and anthropogenic emissions are therefore no more conceptually difficult than they are for methyl bromide.

In spite of these similarities between N_2O and previously recognized ODSs and in spite of the recognition of the impact of N_2O on stratospheric ozone, N_2O has not been considered to be an ODS in the same sense as chlorine- and bromine-containing source gases. The signatories to the Vienna Convention (*2*) have agreed in Article 2 (General Obligations) to "Adopt appropriate legislative or administrative measures … to control, limit, reduce or prevent human activities under their jurisdiction or control should it be found that these activities have or are likely to have adverse effects resulting from modification or likely modification of the ozone layer." Yet N_2O remains unregulated by the MP (*1*).

Here, we present the ODP of N_2O to be positive and nonzero and show that N_2O is an ozone-depleting substance on the basis of the extent of ozone depletion it causes. Indeed, current anthropogenic ODP-weighted N_2O emissions are the largest of all the ODSs and are projected to remain the largest for the rest of the 21st century.

We have calculated the ODP of N_2O by using the Garcia and Solomon two-dimensional (2D) model [(*11*) and references therein], which is similar to models used previously for such calculations (*12*, *13*). The ODP of N_2O under current atmospheric conditions is computed to be 0.017. This value is comparable to the ODPs of many hydrochlorofluorocarbons (HCFCs) (*3*) such as HCFC-123 (0.02), -124 (0.022), -225ca (0.025), and -225cb (0.033) that are currently being phased out under the MP. We conclude that the value of the ODP of N_2O is robust because (i) our similarly calculated ODPs for CFC-12 (1.03) and HCFC-22 (0.06) agree with the accepted values (*3*); (ii) ozone depletion by NO_x from N_2O dominates the chemical control of ozone in the mid-stratosphere (*13*), a region well represented with 2D models; and (iii) ozone reductions by enhanced N_2O have been reported in other studies (*8*, *10*, *14*), although no published study, to the best of our knowledge, has previously presented an ODP for N_2O.

We examine here a few important factors that influence the ODP of N_2O. At mid-latitudes, chlorine-catalyzed ozone destruction contributes most to depletion in the lowest and upper stratospheres, that is, below and above the ozone maximum. Nitrogen oxides contribute most to ozone depletion just above where ozone concentrations are the largest. This leads to efficient ozone destruction from NO_x (*13*). The ODP of N_2O is lower than that of CFCs primarily because only ~10% of N_2O is converted to NO_x, whereas the CFCs potentially contribute all their chlorine.

There are important interconnections between the roles of nitrogen oxides with chlorine such that the N_2O ODP may be different from the calculated value in the past and future. It is well known that nitrogen oxides dampen the effect of chlorine-catalyzed ozone destruction via the formation of $ClONO_2$, which ties up some of the chlorine in a benign form. However, as shown by Kinnison *et al.* (*9*), other reactions, such as the conversion of ClO to Cl by NO, can offset the damping.

We quantify the dependence of the ODP of N_2O on atmospheric concentrations of chorine by calculating it for 1959 concentrations of strato-

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spheric Cl_y (essentially preindustrial). We find the ODP for 1959 to be 0.026, showing that Cl_y concentrations have a moderate effect on the efficiency of N_2O-caused ozone destruction. These results for the 1959 and 2000 Cl_y concentrations bracket the range expected for the rest of the 21st century; it shows that the N_2O's ozone destructiveness per emitted unit mass should increase by about 50% when the stratospheric chlorine loading returns to preindustrial concentrations.

Nitrogen oxide chemistry is also dependent on odd hydrogen, bromine, and methane levels, but the dependence of N_2O's ODP on these factors is expected to be much smaller than the effect of chlorine (*13*).

Whereas enhanced stratospheric sulfate aerosols after volcanic injections increase the effectiveness of chlorine to destroy ozone, they will decrease the effectiveness of NO_x emissions by sequestering the catalytically active NO_x in HNO_3. Such an influence has been observed after the Mount Pinatubo eruption (*15*). Therefore, we anticipate that the ODP of N_2O will be reduced when the sulfate loading is enhanced. However, high volcanic sulfate loadings are unpredictable and sporadic, and their effects are short-lived, lasting only a few years. We assess the extent of their influence by calculating ODPs at peak sulfate loadings observed after the eruption of Mount Pinatubo (*13*, *16*).

For the remaining discussion, we will use an ODP of 0.017 as though it were independent of atmospheric conditions, atmospheric composition, and time. This value is a conservative choice for the reasons discussed above.

It is important to note that the ODP alone cannot fully quantify the impact of a chemical that is released into the atmosphere. The entire emission history, and even the potential future emission projections, must be considered by using an extensive quantity like ODP-weighted emission as a metric rather than an intensive quantity such as ODP, which only considers the ozone depletion per unit mass. Figure 1 compares the anthropogenic N_2O emissions with those from the major ODSs (now controlled under the MP) for 1987 and 2008. It is clear that ODP-weighted anthropogenic emissions of N_2O were a substantial fraction of the ODP-weighted emissions of CFC-11, CFC-12, and CFC-113 even in 1987, just before the adoption of the MP. They were likely larger than the sum of the ODP-weighted emission of halons and were much larger than that of methyl bromide.

Even though N_2O's ODP is only 0.017, roughly one-sixtieth of CFC-11s, the large anthropogenic emissions of N_2O more than make up for its small ODP, making anthropogenic N_2O emissions the single most important of the anthropogenic ODS emissions today (Fig. 1). For example, the global anthropogenic emission of N_2O now (produced mainly as a byproduct of fertilization, fossil fuel combustion and industrial processes, biomass and biofuel burning, and a few other processes) is roughly 10 million metric tons per year compared with slightly more than a million metric tons from all CFCs at the peak of their emissions.

Figure 2 compares estimated ODP-weighted emissions of various ODSs controlled by the MP during the late 20th and all of the 21st centuries [see (*13*) for details of the calculation]. Recent estimates of expected future N_2O emissions under various greenhouse gas mitigation requirements continue to show that N_2O emissions are unlikely to be lower than they are today, even under the most stringent reduction requirements (*17*). From the top graph of Fig. 2, it is clear that N_2O is the largest ODS emission today and indeed is expected to remain the largest throughout the rest of this century for all of these emission scenarios. If anthropogenic N_2O emissions were to continue unabated, by 2050 they could represent an ODP-weighted emission in excess of 30% of the peak CFC ODP-weighted emissions of 1987. These fundamental conclusions on the influences of anthropogenic N_2O are not particularly sensitive to the uncertainties in the total anthropogenic emission rate or to the uncertainties in specific sectoral emissions (*13*).

It should be noted that the largest uncertainty in ODP-weighted emission comparisons comes from the uncertainties in the emission estimates of N_2O, rather than in the calculated ODP. The magnitudes of the sectoral emissions of N_2O, mostly from agricultural practices and industrial sources, are highly uncertain, but the total human-caused emissions are constrained by observed increases in N_2O concentrations and N_2O's lifetime. The Intergovernmental Panel on Climate Change (IPCC)'s fourth assessment report estimates (*18*) a total annual emission during the 1990s of 17.7 TgN, of which 6.7 TgN (10.5 million metric tons of N_2O) were anthropogenic in origin.

Nitrous oxide is a greenhouse gas and is controlled under the Kyoto Protocol; it may be controlled via future climate negotiations. Therefore, it is also interesting to compare the contribution of N_2O to climate forcing with the contributions of other major greenhouse gases. The bottom graph of Fig. 2 shows the CO_2 equivalent [100-year global warming potential (GWP) weighted] emissions of various non-CO_2 greenhouse gases. Among these gases, N_2O's contribution to climate forcing is second only to methane and is already much larger than that of all currently recognized ODSs. These projections of ODP- and GWP-weighted N_2O emissions show that N_2O is an important gas for both the future ozone layer and climate. They also support, and now quantify, previous suggestions that reductions in N_2O emissions would benefit both the ozone layer and climate (*10*). Numerous N_2O mitigation options are currently available. Examples include more efficient use of fertilizer on cropland (*19*) and the capture and destruction of byproduct N_2O emissions in chemical processes (e.g., manufacturing adipic and nitric acids) (*20*). It may be more desirable to reduce nonindustrial N_2O emissions when its ozone layer depletion impact is considered in addition to its impact on climate.

The World Metereological Organization/United Nations Environment Programme (WMO/UNEP) 2007 assessment (*3*) states that the largest single option available to hasten ozone layer recovery is the recapture and destruction of ODSs (mostly CFCs and halons) that are already produced but not yet emitted to the atmosphere, that is, the so-called banks. However, much of the banked halocarbons reside in applications that are generally not cost-effective to recover

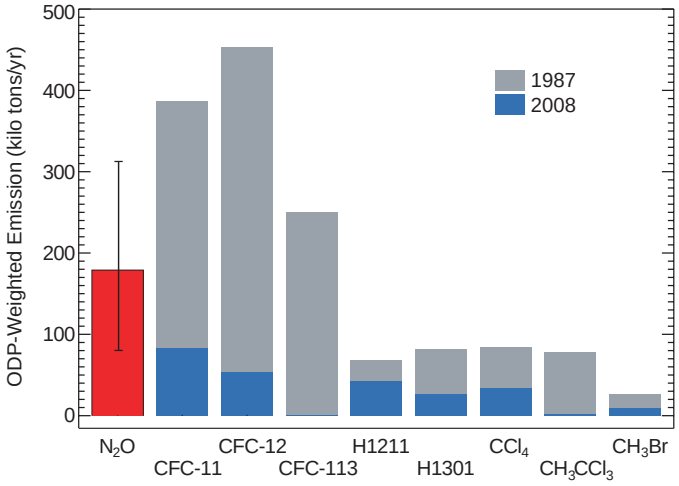

Fig. 1. Comparison of annual N_2O ODP-weighted emissions from the 1990s [IPCC, 2007 (*18*, *23*)] with emissions of other ozone-depleting substances in 1987, when the emissions of chlorine- and bromine-containing ODSs were near their highest amount, and for 2008. Emissions during 2008 were inferred from observations taken by the Global Monitoring Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration for CFC-11, CFC-12, Halon 1211 (H1211), Halon 1301 (H1301), and CH_3Br; all other emissions are taken from WMO (*3*). ODPs for all, except N_2O, are assumed to be the semi-empirical ODPs from WMO (*3*). Even at the height of ODS emissions in the 1980s, annual anthropogenic N_2O emissions were the fourth most important. Currently, anthropogenic N_2O emissions represent the largest contribution to ozone-depleting gas emissions. HCFC-22, the most important CFC replacement, would fall below the 1987 amount of CH_3Br for both time periods if included in the figure. The N_2O error bar represents a bottom-up uncertainty range. The lower end of the range is calculated by summing the lowest emissions estimates, and the higher end by summing the highest estimates, of the various individual sources provided by the IPCC (*18*).

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(e.g., foams in buildings) or in applications with continued demand and unavailability of suitable replacements (e.g., halons for fire fighting and CFCs for medical uses). Based on our value of the ODP and the IPCC fourth assessment report emission estimates for N_2O, the total 2005 banks (*3*) of ODSs are equivalent to roughly 20 years of continued anthropogenic emissions of N_2O at today's rate. Thus, although policy decisions regarding banks of halons and CFCs do represent the largest option for ozone protection today, the effect of N_2O can be expected to dominate in the future as the banks of these ODSs are either released to the atmosphere or are captured and destroyed. Furthermore, the destruction of the existing ODS bank represents a one-time benefit, whereas reductions in N_2O emissions have the ability to continue providing benefits into the future.

We also point out that increases in anthropogenic N_2O emissions or decreases due to abatement strategies would affect a number of issues of importance to stratospheric ozone: (i) it would affect the date for the recovery of the ozone layer; (ii) it would imply that the use of a single parameter such as equivalent effective stratospheric chlorine (EESC) to estimate the recovery of the ozone layer should be reevaluated; (iii) it would have implications for the recovery of the polar ozone hole that might differ from that of global ozone; (iv) N_2O could be an unintended by-product of enhanced crop growth for biofuel production (*21*) or iron fertilization to mitigate CO_2 emissions (*22*). Such an enhancement would lead to the unintended "indirect" consequence of ozone layer depletion and increased climate forcing by an alternative fuel used to curb global warming, as pointed out by Crutzen *et al.* (*21*).

For historical reasons, it is interesting to compare ozone depletion caused by anthropogenic N_2O emissions with that from the original projections for 500 U.S. supersonic transports (*7*), SSTs. The total increase in stratospheric NO_x by that fleet of SSTs is comparable to that from today's total anthropogenic N_2O emission, indicative of the significance of anthropogenic N_2O.

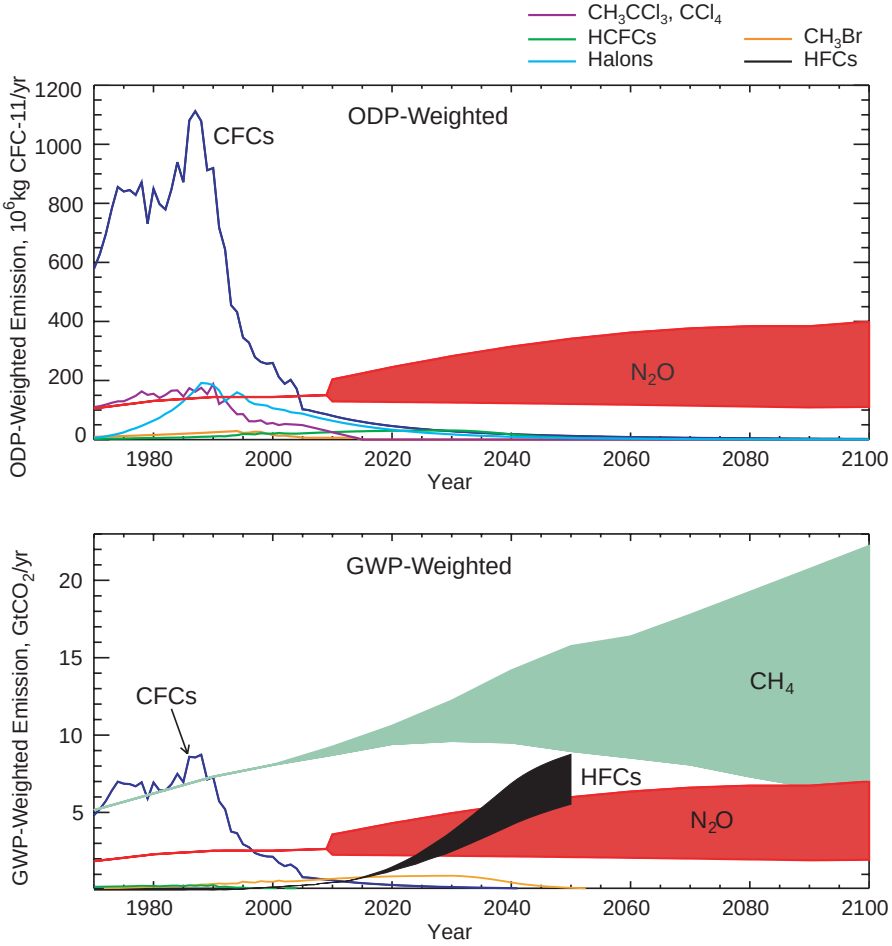

Fig. 2. Historical and projected ODP- and GWP-weighted emissions of the most important ODSs and non-CO_2 greenhouse gases. Non-N_2O ODS emissions are taken from WMO (*3*). Hydrofluorocarbon (HFC) projections are taken from Velders *et al.* (*24*), do not include HFC-23, and are estimated assuming unmitigated growth. The HFC band thus represents a likely upper limit for the contribution of HFCs to GWP-weighted emissions. CH_4 emissions represent the range of the Special Report on Emissions Scenarios (SRES) A1B, A1T, A1FI, A2, and B1 scenarios (*23*). The range of anthropogenic N_2O emissions is inferred from the mixing ratios of these same SRES scenarios [see (*13*) for details of calculation].

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