

## Nitrous Oxide (N<sub>2</sub>O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century

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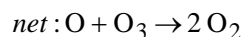
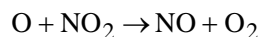
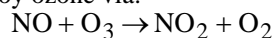
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**By comparing the ozone depletion potential-weighted anthropogenic emissions of N<sub>2</sub>O with those of other ozone depleting substances, ODSs, we show that N<sub>2</sub>O emission currently is the single most important ODS emission and is expected to remain the largest throughout the 21<sup>st</sup> century. N<sub>2</sub>O is unregulated by the Montreal Protocol. Limiting future N<sub>2</sub>O 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 20<sup>th</sup> 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 the 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 (CFC1<sub>3</sub>). ODPs are widely used for policy formulation due to their simplicity in quantifying the relative ozone-destroying capabilities of compounds.

Through the work of Crutzen (5) and Johnston (6), nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) are also known to catalytically destroy ozone via:



The primary source of stratospheric NO<sub>x</sub> is surface N<sub>2</sub>O emissions ((7) and references therein). N<sub>2</sub>O has been thought

of as primarily a natural atmospheric constituent but the influence of its changes on long-term changes in ozone levels has also been examined (8-10).

Nitrous oxide shares many similarities with the CFCs, historically the dominant ODSs. The CFCs and N<sub>2</sub>O are very stable in the troposphere, where they are emitted, and transported to the stratosphere where they release active chemicals that destroy stratospheric ozone through chlorine- or nitrogen oxide-catalyzed processes. They both have significant anthropogenic sources. Unlike CFCs, N<sub>2</sub>O also has natural sources, akin to methyl bromide, which is another important ODS. Assigning an ODP for N<sub>2</sub>O, and separating out the natural and anthropogenic emissions is therefore no more conceptually difficult than it is for methyl bromide.

In spite of these similarities between N<sub>2</sub>O and previously recognized ODSs, and in spite of the recognition of the impact of N<sub>2</sub>O on stratospheric ozone, N<sub>2</sub>O 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<sub>2</sub>O remains presently unregulated by the Montreal Protocol (1).

Here we present the ODP of N<sub>2</sub>O to be positive and non-zero and show that N<sub>2</sub>O is an ozone depleting substance based on the extent of ozone depletion it causes. Indeed, current anthropogenic ODP-weighted N<sub>2</sub>O emissions are the largest of all the ODSs and are projected to remain the largest for the rest of 21<sup>st</sup> century.

We have calculated the ODP of N<sub>2</sub>O using the Garcia and Solomon 2D model ((11) and references therein), which is similar to models used previously for such calculations (12) (see Supporting online material, SOM). The ODP of N<sub>2</sub>O under current atmospheric conditions is computed to be 0.017. This value is comparable to the ODPs of many 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<sub>2</sub>O is robust because: (1) our similarly calculated ODPs for CFC-12 (1.03) and HCFC-22 (0.06) agree with the accepted values (3), (2) ozone depletion by NO<sub>x</sub> from N<sub>2</sub>O dominates the chemical control of ozone in the mid-stratosphere (see SOM), a region well represented with 2D models, and (3) ozone reductions by enhanced N<sub>2</sub>O have been reported in other studies (8, 10, 13), even though no published study, to the best of our knowledge, has previously presented an ODP for N<sub>2</sub>O.

We examine here a few important factors that influence the ODP of N<sub>2</sub>O. At mid-latitudes chlorine-catalyzed ozone destruction contributes most to depletion in the lowest and upper stratospheres, i.e., below and above the ozone maximum. Nitrogen oxides contribute most to ozone depletion just above where ozone levels are the largest. This leads to efficient ozone destruction from NO<sub>x</sub> (see SOM). The ODP of N<sub>2</sub>O being lower than that of CFCs primarily because only ~10% of N<sub>2</sub>O is converted to NO<sub>x</sub>, while the CFCs potentially contribute all their chlorine.

There are important interconnections between the roles of nitrogen oxides with chlorine such that the N<sub>2</sub>O 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<sub>2</sub>, 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<sub>2</sub>O on atmospheric levels of chlorine by calculating it for 1959 levels of stratospheric Cl<sub>y</sub> (essentially pre-industrial). We find the ODP for 1959 to be 0.026, showing that Cl<sub>y</sub> levels have a moderate effect on the efficiency of N<sub>2</sub>O-caused ozone destruction. These results for the 1959 and 2000 Cl<sub>y</sub> levels bracket the range expected for the rest of the 21<sup>st</sup> century; it shows that the N<sub>2</sub>O's ozone destructiveness per emitted unit mass should increase by about 50% when the stratospheric chlorine loading returns to preindustrial levels.

Nitrogen oxide chemistry is also dependent on odd hydrogen, bromine, and methane levels, but the dependence of N<sub>2</sub>O's ODP on these factors is expected to be much smaller than the effect of chlorine (See SOM).

While enhanced stratospheric sulfate aerosols following volcanic injections increase the effectiveness of chlorine to destroy ozone they will decrease the effectiveness of NO<sub>x</sub> emissions by sequestering the catalytically active NO<sub>x</sub> in HNO<sub>3</sub>. Such an influence has been observed following Mt. Pinatubo eruption (14). Therefore, we anticipate that the ODP of N<sub>2</sub>O 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 Mt. Pinatubo (15) (see SOM).

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 because 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<sub>2</sub>O 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<sub>2</sub>O were a significant fraction of the ODP-weighted emissions of CFC-11, CFC-12, and CFC-113 even in 1987, just prior to the adoption of the Montreal Protocol. 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<sub>2</sub>O's ODP is only 0.017, roughly one sixtieth of CFC-11's, the large anthropogenic emissions of N<sub>2</sub>O more than make up for its small ODP, making anthropogenic N<sub>2</sub>O emissions the single most important of the anthropogenic ODS emissions today, Fig. 1. For example, the global anthropogenic emission of N<sub>2</sub>O 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 tonnes per year compared to slightly more than a million tonnes 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 20<sup>th</sup> and all of the 21<sup>st</sup> centuries (see SOM for details of the calculation). Recent estimates of expected future N<sub>2</sub>O emissions under various greenhouse gas mitigation requirements continue to show that N<sub>2</sub>O emissions are unlikely to be lower than today, even under the most stringent reduction requirements (16). It is clear that N<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O are not particularly sensitive to the uncertainties in the total anthropogenic emission rate or to the uncertainties in specific sectoral emissions. (See SOM)

It should be noted that the largest uncertainty in ODP-weighted emission comparisons comes from the uncertainties in the emission estimates of N<sub>2</sub>O, rather than in the calculated ODP. The magnitudes of the sectoral emissions of N<sub>2</sub>O, mostly from agricultural practices and from industrial sources, are highly uncertain; but the total human-caused emissions are constrained by observed increases in N<sub>2</sub>O concentrations and N<sub>2</sub>O's lifetime. IPCC AR4 estimates (17) a total annual emission during the 1990s of 17.7 TgN, of which 6.7 TgN (10.5 million metric tons N<sub>2</sub>O) 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<sub>2</sub>O to climate forcing with the contributions of other major greenhouse gases. The bottom panel of Figure 2 shows the CO<sub>2</sub> equivalent (100-year GWP weighted) emissions of various non-CO<sub>2</sub> greenhouse gases. Among these gases N<sub>2</sub>O'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<sub>2</sub>O emissions show that N<sub>2</sub>O is an important gas for both future ozone and climate. They also support, and now quantify, previous suggestions that reductions in N<sub>2</sub>O emissions would benefit both the ozone layer and climate (10). Numerous N<sub>2</sub>O mitigation options are currently available. Examples include more efficient use of fertilizer on cropland (18) and the capture and destruction of byproduct N<sub>2</sub>O emissions in chemical processes (e.g., manufacturing adipic and nitric acids) (19). It may be more desirable to reduce non-industrial N<sub>2</sub>O emissions when its ozone layer depletion impact is considered in addition to its impact on climate.

The WMO/UNEP 2007 assessment 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, i.e., the so-called banks. However, much of the banked halocarbons reside in applications that are generally not cost-effective to recover (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 AR4 emission estimates for N<sub>2</sub>O, the total 2010 projected banks (3) of ODSs are equivalent to roughly 17 years of continued anthropogenic emissions of N<sub>2</sub>O at today's rate. Thus, while policy decisions regarding banks of Halons and CFCs do represent the largest option for ozone protection today, the effect of N<sub>2</sub>O 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, while reductions in N<sub>2</sub>O emissions have the ability to continue providing benefits into the future.

A few other points are worthy of note. (1) Increases in anthropogenic N<sub>2</sub>O emissions or decreases due to abatement strategies would affect a number of issues of importance to stratospheric ozone: (a) it would affect the date for the recovery of the ozone layer; (b) 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; (c) it would have implications for the recovery of the polar ozone hole that might differ from that of global ozone. (2) N<sub>2</sub>O could be an unintended byproduct of enhanced crop growth for biofuel production (20) or iron fertilization to mitigate CO<sub>2</sub> emissions (21). 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.* (20) For historical reasons, it is interesting to compare ozone depletion caused by anthropogenic N<sub>2</sub>O emissions with that from the original projections for 500 US supersonic transport (7), SSTs. The total increase in stratospheric NO<sub>x</sub> by that fleet of SSTs is comparable to that from today's total anthropogenic N<sub>2</sub>O emission, indicative of the significance of anthropogenic N<sub>2</sub>O.

## References and Notes

1. The Montreal Protocol on Substances that Deplete the Ozone Layer (1987).
2. The Vienna Convention for the Protection of the Ozone Layer (1985).
3. Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project- Report No. 50'' Global Ozone Research and Monitoring Project-Report No. 37 (World Meteorological Organization, 2007).
4. D. J. Wuebbles, *J. Geophys. Res.* **88**, 1433 (1983).
5. P. J. Crutzen, *Q.J.R.Meteorol. Soc.* **96**, 320 (1970).
6. H. S. Johnston, *Science* **173**, 517 (1971).
7. R. P. Wayne, *Chemistry of Atmosphere, Third Edition.* (Oxford University Press, Oxford, UK, 2000), pp. 775.
8. M. P. Chipperfield and W. Feng, *Geophys. Res. Lett.* **30**, 1389 (2003).
9. D. Kinnison, H. Johnston, D. Wuebbles, *J. Geophys. Res.* **93(D11)**, 14 (1988).
10. L. K. Randeniya, P.F. Vohralik, I.C.Plumb, *Geophys. Res. Lett.*, **29**, 10.1029/2001GL014295. (2002).
11. S. Solomon, *et al.*, *Geophys. Res. Lett.* **25**, 1871 (1998).
12. S. Solomon, M. Mills, L. E. Heidt, W. H. Pollock, A. F. Tuck, *J. Geophys. Res.* **97**, 825 (1992).
13. R. W. Portmann and S.Solomon, , *Geophys. Res. Lett.* **34**, 10.1029/2006GL028252 (2007).
14. L. J. Mickley, J. P. D.Abbatt, J. E. Frederick, J. M. Russell III, *J. Geophys. Res.* **102(D19)**, 23 (1997).

15. L. Thomason and Th. Peter, "SPARC Assessment of stratospheric aerosol properties" (2006).
16. D. P. van Vuuren, *et al.*, *Climatic Change* **81**, 119 (2007).
17. P. Forster, V. Ramaswamy, *et al.*, in *The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller, Ed. (Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007).
18. P. Smith, D. Martino, *et al.*, "Agriculture. In Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change" (2007).
19. L. Bernstein, J. Roy, *et al.*, "Industry. In Climate Change 2007: Mitigation. Contribution of Working Group III" (2007).
20. P. J. Crutzen, A. R. Mosier, K. A. Smith, W. Winiwarter, *Atmos. Chem. Phys.* **8**, 389 (2008).
21. X. Jin and N. Gruber, *Geophys. Res. Lett.*, **30(24)**, 2249 (2003).
22. S. Solomon, D. Qin, *et al.*, *IPCC, 2007: Climate Change 2007: The physical basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. (Cambridge university Press, Cambridge, UK and New York, NY, USA, 2007), pp. 996.
23. G. J. M. Velders, D. W. Fahey, J. S. Daniel, M. McFarland, and S. O. Andersen, *PNAS* **106**, 10949 (2009).
24. We are extremely grateful to Susan Solomon for helpful discussion, suggestions for improving the paper, and encouragement. We also thank Steven Montzka for helpful suggestions, and Steven Montzka and Geoff Dutton of the Global Monitoring Division/Earth System Research Laboratory for providing us with mixing ratio observations from which we could infer emission data for several ODSs in 2008 and for helpful discussions. This work was supported in part by NOAA's Climate Goal Program.

### Supporting Online Material

[www.sciencemag.org/cgi/content/full/1176985/DC1](http://www.sciencemag.org/cgi/content/full/1176985/DC1)

Materials and Methods

SOM Text

Figs. S1 to S2

References

28 May 2009; accepted 12 August 2009

Published online 27 August 2009; 10.1126/science.1176985

Include this information when citing this paper.

**Fig. 1.** Comparison of annual N<sub>2</sub>O ODP-weighted emissions from the 1990s (IPCC, 2007 (17, 22)) with emissions of other ozone depleting substances in 1987, when the emissions of

chlorine- and bromine-containing ODSs were near their highest level, and for 2008. Emissions during 2008 were inferred from observations taken by the Global Monitoring Division, Earth System Research Laboratory, NOAA for CFC-11, CFC-12, Halon 1211 (H1211), Halon 1301 (H1301) and CH<sub>3</sub>Br; all other emissions are taken from WMO (3)). ODPs for all, except N<sub>2</sub>O, are assumed to be the semi-empirical ODPs from WMO (3). Even at the height of ODS emissions in the 1980s, annual anthropogenic N<sub>2</sub>O emissions were the fourth most significant. Currently, anthropogenic N<sub>2</sub>O emissions represent the largest contribution to ozone depletion. HCFC-22, the most significant CFC replacement, would fall below the 1987 level of CH<sub>3</sub>Br for both time periods if included in the figure.

**Fig. 2.** Historical and projected ODP- and GWP-weighted emissions of the most important ODSs and non-CO<sub>2</sub> greenhouse gases. Non-N<sub>2</sub>O ODS emissions are taken from WMO (3). HFC projections are taken from Velders *et al.* (23), 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<sub>4</sub> emissions represent the range of the SRES A1B, A1T, A1FI, A2, and B1 scenarios (22). The range of anthropogenic N<sub>2</sub>O emissions is inferred from the mixing ratios of these same SRES scenarios (See SOM for details of calculation).

