



Supporting Online Material for

Nitrous Oxide (N₂O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century

A. R. Ravishankara,* John S. Daniel, Robert W. Portmann

*To whom correspondence should be addressed. E-mail: A.R.Ravishankara@noaa.gov

Published 27 August 2009 on *Science Express*
DOI: 10.1126/science.1176985

This PDF file includes:

Materials and Methods
SOM Text
Figs. S1 and S2
References

Supporting Online Material

Nitrous Oxide (N₂O): The dominant ozone depleting substance emitted in the 21st Century

A. R. Ravishankara, John S. Daniel, and Robert W. Portmann
Chemical Sciences Division, Earth System Research Laboratory
National Oceanic and Atmospheric Administration
325 Broadway, Boulder CO 80305

The following supplementary material provides additional details about our ozone depletion potential, ODP, calculations, factors affecting the ODP of N₂O, uncertainties unique to the calculation of the ODP of N₂O, our method of inferring N₂O emissions, and a comparison of the contributions of the sectoral N₂O emissions with the emissions of methyl bromide.

ODP Calculation and Important Factors

The Ozone Depletion Potential (ODP) of some ozone depleting substance, ODS, is defined by the time-integrated change of global ozone due to a unit mass emission of the ODS relative to that of CFC-11. We use steady state calculations to compute the ozone changes since our model incorporates a mixing ratio lower boundary condition rather than an emission boundary condition. The ODP of compound X relative to the reference gas CFC-11 is computed using the formula

$$ODP_X = \frac{m_{CFC11} \times \Delta\mu_{CFC11} \times \tau_X \times [\Delta O_3]_X}{m_X \times \Delta\mu_X \times \tau_{CFC11} \times [\Delta O_3]_{CFC11}}$$

where τ is the atmospheric lifetime, ΔO_3 is the change in globally averaged column ozone computed by the model, $\Delta\mu$ is the change in the mixing ratio boundary

condition, and m is the molecular weight of the ODS. The $\Delta\mu$'s should be small enough that the ozone change is linear in $\Delta\mu$.

In the ODP calculations we use the model calculated lifetimes for N₂O (98 years), CFC-11 (44 years), and CFC-12 (78 years) and the currently accepted value for HCFC-22 (12 years), whose loss is primarily due to reaction with tropospheric OH. (See below for a discussion of choice of lifetimes.) The perturbations used in the calculation are 100 pptv for the halocarbons and 50 ppbv for N₂O. All ODPs are computed with respect to ozone changes induced by CFC-11 at 2000 Cl_y levels and background aerosol loading. The calculated values are shown in Table SI-1.

SIT-1: ODPs vs. year of emission and aerosol level

	1959		2000	
	Background	Volcanic	Background	Volcanic
CFC-11	1.02	1.86	1.00 ¹	1.39
N ₂ O	0.026	0.019	0.017	0.009

¹All ODPs are referenced to ozone depletion by CFC-11 for background sulfate loading and Cl_y values in 2000.

The ODP of CFC-11 is nearly independent of Cl_y levels but does increase with volcanic loading, as expected, due to the greater activation of chlorine. N₂O, on the other hand, has a higher ODP when Cl_y levels are lower (55% larger for 1959 vs. 2000 Cl_y). The ODP of N₂O is also greatly reduced during times of high volcanic loading. All these changes are consistent with the anticipated roles of heterogeneous reactions on nitrogen and chlorine species and on the buffering effect between NO_x and chlorine radicals.

The vertical distribution of ozone depletion calculated by our model is shown in Fig. S1. The curves are in density units, rather than the percentage contributions that are often presented. To put these depletions in perspective, the right hand panel shows the global average ozone profile in this model. N₂O-induced ozone depletion maximizes in the middle stratosphere just above the ozone maximum while CFC-11-induced losses maximize in the lower stratosphere and upper stratosphere (the

upper stratospheric peak is more evident when viewed as a percentage change). In the lower stratosphere, there are ozone increases from N_2O increases due to enhanced UV radiation from the ozone decreases above. This “self-healing” effect is most important at tropical latitudes (not shown). Also, in the lower stratosphere at middle and high latitudes there are complex interactions between chlorine and nitrogen radicals and reservoirs that impact the ozone changes.

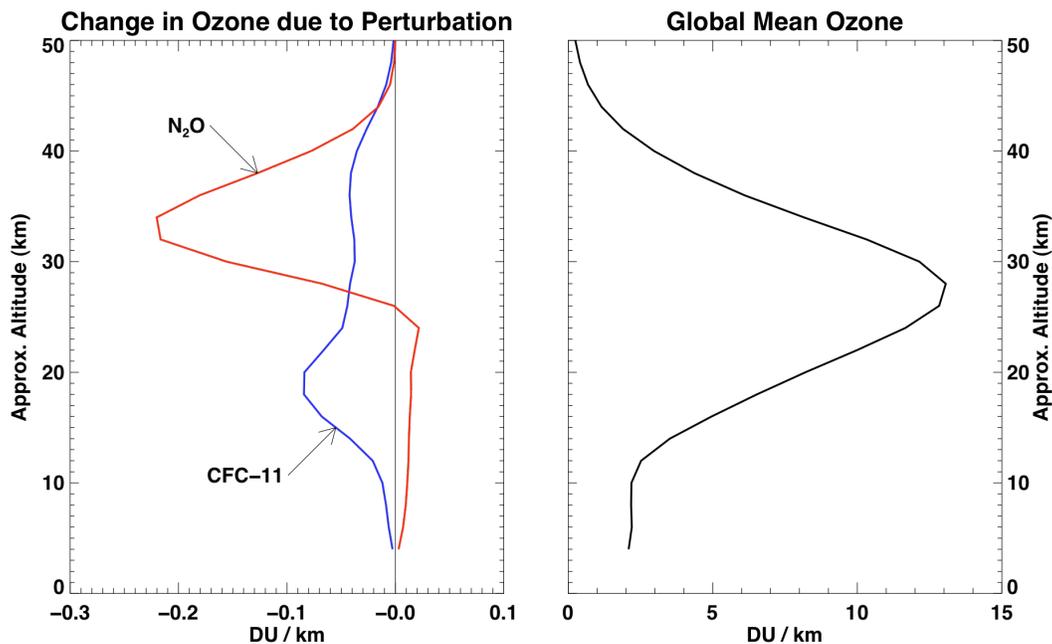


Fig. S1 The change in global average ozone due to a 100 pptv increase in CFC-11 and a 50 ppbv increase in N_2O for year 2000 levels of source gases and background aerosol conditions. The global average ozone profile for the same conditions is also shown.

Uncertainties in ODP estimate

Our calculated ODPs of CFC-12 and HCFC-22, using the same model as used for the N_2O calculation, agree well with the ODPs listed in the Montreal Protocol (1). Nevertheless, in addition to the uncertainties associated with the calculation of ODPs of chlorine-containing source gases, the N_2O ODP value does have important

and unique dependencies on sulfate and Cl_y levels. Because of the dependence on Cl_y levels, we have chosen to use the ODP calculated at today's levels in order to provide a conservative estimate of the future impact of N_2O on ozone. We also use the ODP for background aerosol conditions because of the temporary duration of elevated sulfate levels from volcanic eruptions.

N_2O , unlike Cl_y , does not cause enhanced ozone depletion in polar springtime (e.g., the ozone hole) and thus will not produce the extremely low ozone levels that enhanced Cl_y does. This spatial difference leads to a somewhat higher uncertainty in the ODP of N_2O than for chlorocarbon ODPs since there is less cancellation of errors in the calculated ozone depletion.

Inferred N_2O Emissions

We infer annual anthropogenic N_2O emissions from the highest and lowest mixing ratio projections of the A1B, A1T, A1FI, A2, and B1 SRES scenarios (2). We assume natural emissions account for 270 ppbv of atmospheric N_2O , the value observed during the preindustrial era (3), and that growth above that level is attributed to human activity. Total emissions are then inferred using a 1-box model and assuming an atmospheric lifetime of 125 years for N_2O (Volk et al., 1997) from the equation

$$E_{t-1} = \frac{\mu_t - \mu_{t-1} \exp\left(-\frac{1}{\tau_{N_2O}}\right)}{f \tau_{N_2O} \left(1 - \exp\left(-\frac{1}{\tau_{N_2O}}\right)\right)} \quad (\text{SOM 1})$$

where E_{t-1} is the emission in kg assumed constant throughout year $t-1$, μ_t is the N_2O mixing ratio at the beginning of year t , τ_{N_2O} is the lifetime of N_2O , and f relates the number of kg of N_2O to the number of ppb in the atmosphere (assumed to be 7.75×10^9 kg/ppb). A shorter lifetime would lead to larger emissions (see below). This method leads to total emissions slightly lower for the 1990s than suggested by IPCC (3) (16.0 vs. 17.7 TgN/yr) but in good agreement with those of Huang et al. (4)

and Hirsch et al. (5). Inferred anthropogenic emissions for the 1990s are also slightly lower than those of IPCC (3) (5.4 vs. 6.7 TgN/yr).

Comparison of influence of sectoral N₂O emissions with that of methyl bromide

One of the primary anthropogenic emissions of N₂O is associated with food production, where the agricultural practice of nitrogen fertilization leads to its emission. Therefore, it is interesting to compare the ODP-weighted emissions of N₂O from different sources with those of methyl bromide, which also has agricultural and food transport usage (Fig. S2). Clearly, N₂O emissions are much larger than those of methyl bromide. Indeed, most of the individual sectors of N₂O emissions are larger than the combined emissions of methyl bromide due to fumigation and use as feedstock.

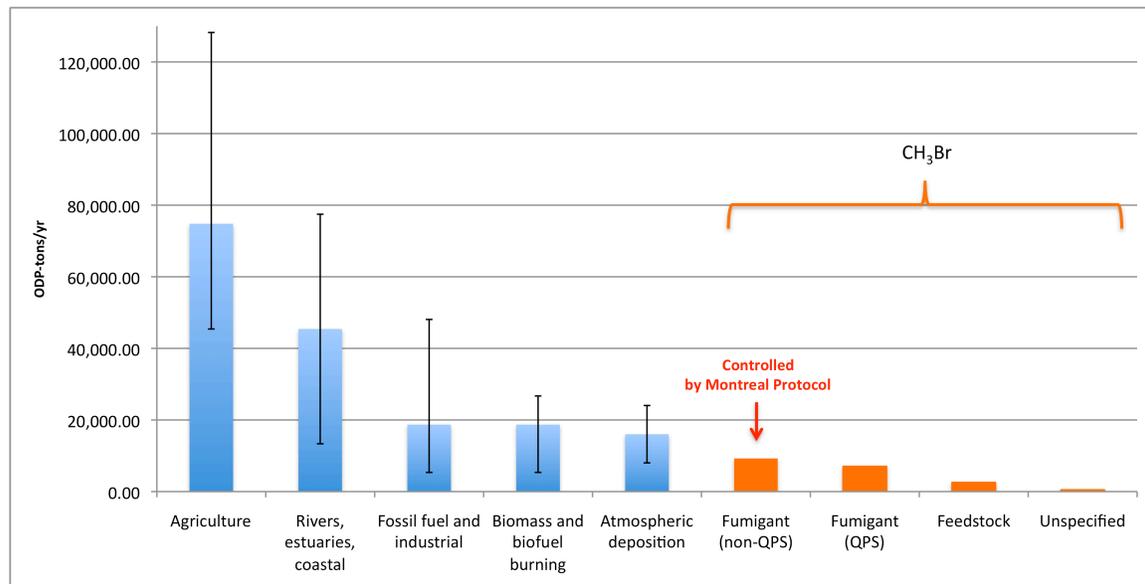


Fig. S2. Comparison of the ODP-weighted emissions of N₂O from various sectors with the ODP-weighted production of methyl bromide. The contribution of N₂O emissions from the agricultural sector far exceeds the contribution of methyl bromide. Indeed, most of the sectors of N₂O emissions outweigh the contribution of methyl bromide. Methyl bromide production estimates are for 2005 and are taken from UNEP MBTOC report (6); N₂O emissions come from IPCC report, Chapter 7 (7), and represent annual emission estimates for the 1990s.

Note on N₂O lifetimes

We use the 2D model-estimated lifetimes in the ODP calculations (e.g., 98 years for N₂O), and to infer N₂O emissions we use a lifetime value of 125 years, which is based on stratospheric observations (8) and has been used to infer N₂O emissions from a global network of observations (4). The shorter value in the ODP calculation was used to maximize internal consistency in the ODP estimate and the longer lifetime was used to estimate emissions in order to obtain conservative estimates.

From SOMF- 1 it is clear that an assumed shorter (longer) N₂O lifetime will lead to larger (smaller) inferred annual emissions. Therefore, by using an estimated lifetime that is somewhat higher than used in IPCC (3) and WMO/UNEP (9), we obtain annual emissions that are somewhat conservative. The lifetime used here is not an upper limit, however.

In the 2D model calculation there is, in general, a negative relationship between the lifetime for a gas and the steady state ozone depletion caused by an increase of that gas (this is a complex relationship and is dependent on the loss region for the gas being in stratosphere). Thus, when computing the ODP, it is preferable to use the model lifetime estimates even if they are somewhat different than the accepted values. IPCC 2007 (3) adopted a value of 114 years for the N₂O lifetime, about 14% larger than our model estimated value. Using the IPCC value would increase our ODP estimates by this same percentage. However, since the model lifetime for CFC-11 is likely too low by about the same fraction as the N₂O lifetime, there is a further cancelation of errors if the model lifetimes are used throughout as we have done.

Role of methane changes on ozone depletion

Several studies have shown that changes in methane in the 21st century will also affect the evolution of ozone (11). Methane's influence on ozone is very dependent on altitude. In the troposphere and lower stratosphere it induces ozone production via "smog chemistry" (10)), while at higher altitudes it causes ozone losses through

the HO_x radicals produced in its degradation to CO (and from the water produced as a byproduct). The net effect is generally a gain in column ozone due to methane increases, both in the stratospheric column and total column (11). Thus, unlike for N₂O, a calculated ODP for methane would likely be negative. Nevertheless, CH₄ should be considered when estimating the long-term changes in ozone. In addition to these effects of methane on ozone, there could also be a coupling between methane (and its breakdown products) and the effectiveness of NO_x on ozone destruction. These higher order effects could affect the ODP of N₂O during the 21st century. We have not estimated the magnitude of these effects but believe them to be small compared with the other uncertainties discussed in the paper (especially the emission estimates).

References

1. The Montreal Protocol on Substances that Deplete the Ozone Layer (1987).
2. N. Nakicenovic, Swart, R., Ed., *IPCC (Intergovernmental Panel on Climate Change) Emission Scenarios. A special report of working Group III of the Intergovernmental Panel on Climate Change*, (Cambridge, U. K. and New York, N.Y., 2000).
3. P. Forster, Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., and Van Dorland, R., 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).
4. J. Huang, Golombek, A., Prinn, R., Weiss, R., Fraser, P., Simmonds, P., Dlugokencky, E.J., Hall, B., Elkins, J., Steele, P., Langenfelds, R., Krummel, P., Dutton, G., Porter, L., *Journal of Geophysical Research* **113**, doi:10.1029/2007JD009381 (2008).
5. A. I. Hirsh, Michalak, A.M., Bruhwiler, L.M., Peters, W., Dlugokencky, E.J., Tans, P. P., *Global Biogeochemical Cycles* **20**, doi:10.1029/2004GB002443. (2006).
6. UNEP, "2006 Report of the Methyl Bromide Technical Options Committee," (UNEP Ozone Secretariat, 2006).
7. K. L. Denman, Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E., Hauglustine D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., Dias, P. L. d-S., Wofsy, S. C., Zhang, X., 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).
8. C. M. Volk, J. W. Elkins, D. W. Fahey, G. S. Dutton, J. M. Gilligan, M. Loewenstein, J. R. Podolske, K. R. Chan, and M. R. Gunson, *J. Geophys. Res.* **102**, 25 (1997).
 9. WMO, "WMO (World meteorological Organization), 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).
 10. R. P. Wayne, *Chemistry of Atmosphere, Third Edition*. (Oxford University Press, Oxford, UK, 2000), pp. 775.
 11. L. K. Randeniya, Vohralik, P.F., Plumb, I.C., *Geophys. Res. Lett.*, **29**, 10.1029/2001GL014295. (2002).