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Evaluating ozone depletion from very short-lived halocarbons

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Abstract. A new approach is needed for calculating the ozone depletion potential (ODP) of short-lived gases with mean lifetimes less than 100 days. Clearly, the ozone loss from such gases depends strongly on the location and season of emissions. It is proposed that delivery to the tropical tropopause is a surrogate for the amount of halogen entering the stratosphere. Thus 3-D global models, with accurate simulation of tropospheric chemistry and transport, can calculate the ODP specific to tropical sources (high) and high-latitude sources (low). The ODP of $CH_2BrCH_2CH_3$ from this analysis ranges from 0.0002 to 0.06 depending on the location and season of emissions.

Ozone Depletion Potentials

Since the realization that chlorofluorocarbons (CFC) and halons cause stratospheric ozone destruction there has been an extensive effort to quantify the ozone destruction efficiency of emissions of CFCs and other ozone depleting substances (ODS) using the relative index of ozone depletion potential (ODP) [Wuebbles, 1981; Fisher et al., 1990; WMO, 1999]. The calculation of ODP takes the ratio of integrated ozone depletion following emission of, e.g., a kiloton of the ODS to that following emission of the same mass of CFC-11. Although ODPs are calculated with 2-D stratospheric models, the introduction of semi-empirical ODPs [Solomon et al., 1992] along with the need to evaluate a wide range of compounds has led to an ODP formulation that involves a series of factors: the steady-state lifetime (representing the integral of the ODS concentration), the inverse of the molecular weight, the number of halogen atoms per molecule, a factor (< 1) reflecting the release of halogen radicals, and an α factor describing the relative ozone depletion efficiency for different halogens (e.g., 54 for Br) [Solomon and Wuebbles, 1995].

For short-lived ODS the difficulty in evaluating an ODP lies with calculation of the integrated amount of ODS that enters the stratosphere. The 2-D models used in ODP calculations, by their formulation, lack the tropospheric transport processes, e.g., weather patterns, that control the distribution of short-lived compounds. Alternatively, the use of a steady-state lifetime is also flawed: (1) this lifetime is not unique and depends on the emission pattern, and (2) the mean atmospheric abundance (represented by a given steady-state lifetime) does not accurately describe the amount of ODS in the stratosphere. It is necessary to use 3-D chemistry-transport models (CTM) with a good representation of tropospheric mixing and chemistry in order

to describe the fraction of the short-lived ODS that gets into the stratosphere and participates in ozone depletion. Using such a CTM, we show that the ODP of short-lived compounds depends strongly on the location and season of emissions.

Trace gases are injected into the stratosphere with the bulk flow of air entering through the tropical tropopause, rising at tropical latitudes, spreading to mid and high latitudes, descending and returning to the troposphere [Brewer, 1949; Holton et al., 1995]. This pattern is supported also by modern measurements [Boering et al., 1996; Mote et al., 1996] that show a regular rate of injection of tropospheric air over the year with some fluctuations that could be accounted for here. Thus the concentration of an ODS at the tropical tropopause is an accurate measure of the flux into the stratosphere. Although events showing mixing of mid-latitude tropospheric air into the lowest part of the stratosphere are observed, the statistical evidence from trace gas correlations e.g., [Boering et al., 1996] shows this to be an insignificant source of stratospheric air.

Thus, we evaluate the key factor in the ODP, the delivery of the ODS to the stratosphere, by integrating the ODS concentration in the upper tropical troposphere (f_{utt}). For a long-lived CFC, this mixing ratio as a function of time following emission, $f_{utt}(t)$, is equivalent to a uniform tropospheric mixing ratio, $f_{trop}(t)$, that decays with the steady-state lifetime T_{SS} [Prather, 1996]. The initial value, $f_{trop}(t=0)$, is calculated by distributing the emission according to the steady-state pattern for that CFC and results in a uniform tropospheric value, f_{mix} (i.e., a 23-kiloton emission of CFC-11 gives f_{mix} of 1 ppt). Although f_{utt} behaves irregularly in the first few years as the CFC mixes throughout the atmosphere and T_{SS} is slightly different than the actual decay time, the integral in Eq. 2, below, is exactly equal to $f_{mix} \times T_{SS}$.

$$f_{utt}(t) \xrightarrow{CFC \text{ limit}} f(t)_{trop} \xrightarrow{CFC \text{ limit}} f_{mix} \times e^{(-t/T_{SS})} \quad (1)$$

$$ODP \propto \int_0^{\infty} f_{utt}(t) dt \xrightarrow{CFC \text{ limit}} f_{mix} \times T_{SS} \quad (2)$$

Following the initial calculation of ODPs for Group I (CFCs) and Group II (halons) compounds in the Montreal Protocol (1987), the category of ODS expanded to short-lived CFC substitutes including hydrochlorofluorocarbons and to even very short-lived halocarbons such as n-propyl bromide (n-PB, C_3H_7Br). These substitutes are destroyed primarily in the troposphere, reacting with OH radicals or directly photolyzing. For some of these gases, such as CHF_2Cl (global mean lifetime ~ 12 yr) and CH_3CCl_3 (~ 5 yr), tropospheric losses are slow compared with mixing times, and the above approximations for CFCs hold. Even

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for gases with mean lifetimes of ~ 1 yr, such as CH_3Br , the CFC analogy holds providing one is careful to use the steady-state lifetime rather than the e-fold time [Prather, 1997]. In these cases the effective delivery of halogens to the stratosphere depends little on the circumstances of surface emissions.

Very Short-Lived Gases

On the other hand, very short-lived gases, such as n-PB (global mean lifetime ~ 11 days [Wuebbles *et al.*, 1999]), react so rapidly with OH that the emitted gas never becomes well mixed in the troposphere. The CFC approximation (Eq. 1) does not hold: $f_{utt}(0)$ cannot be approximated by f_{mix} , and further, T_{SS} varies greatly with location of emissions. The amount of halocarbon reaching the stratosphere depends strongly on where and when it was emitted. We use a 3-D tropospheric CTM to predict the fraction of very short-lived gases that reach the stratosphere based on latitude and season of emission. Such where/when factors become important for these gases, varying the ODP (Eq. 2) by factors of 100 or more.

For the very short-lived gases, it is still useful to define certain universal "constants" for each compound relating atmospheric burden to mixing ratio and describing a time constant. Consider a thought experiment in which the troposphere mixes instantly and lower stratospheric loss is rapid compared with transport. The latter assumption is typical of bromocarbons [Schauffler *et al.*, 1999]. These assumptions allow us to calculate (1) an f_{mix} in parallel to CFCs above, and (2) a "well mixed" lifetime, T_{mix} , calculated by integrating loss rates assuming a globally uniform tropospheric distribution. Where T_{mix} ranges from 2 to 100 days, stratospheric loss (not included) accounts for at most a few percent of the total. T_{mix} can also be derived empirically by scaling the OH lifetime against that of CH_3CCl_3 at 277K. (New work revises the optimal scaling temperature to 272K [Spivakovsky *et al.*, 2000]). This definition of T_{mix} provides the most convenient yardstick in comparing the short-lived gases, since the steady-state lifetimes depend on emissions and the natural-mode decay times would emphasize stratospheric turnover times [Prather, 1997].

In this thought experiment the ODP is calculated in parallel with the CFCs (Eq. 2) replacing T_{SS} with T_{mix} : $ODP_{mix} \propto f_{mix} \times T_{mix}$. In actuality, there is no unique ODP for the very short-lived gases. From its emission near the surface, the gas is destroyed rapidly compared with tropospheric mixing times, and only a fraction survives transport into the tropics and convective lofting to the tropopause. The ODP for a specific emission pattern X, ODP_X , depends on the where/when of emissions, and is calculated by integrating the full transient response of the air entering the stratosphere, $f_{utt}(t)$.

$$ODP_X \propto \int_0^{\infty} f_{utt}(t) dt \quad (3)$$

ODP Versus Emission Latitude

Our calculation of $f_{utt}(t)$ uses the low-resolution UCI tropospheric CTM (8° lat. by 10° lon. by 9 layers), which includes tropospheric mixing by advection, convection, and horizontal diffusion [Prather *et al.*, 1987]. The meteorology

is derived from the Goddard Institute for Space Science General Circulation Model version II. Tropospheric OH fields (5-day means) are from Spivakovsky *et al.* [1990]. This model is dated, but still typical of modern CTMs with explicit convection [Jacob *et al.*, 1997].

As a proxy for very short-lived ODS—few of which have well defined chemical rates—four hydrocarbons are studied: ethane, propane, n-butane, and ethene. Reaction with OH is the only tropospheric loss and typical rate coefficients at 298 K are 0.24, 1.1, 2.5, and $8.2 \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively [Atkinson, 1990; DeMore *et al.*, 1997]. In the model's top layer, a uniform loss frequency for each compound rapidly removes the gas from the stratosphere. For these gases T_{mix} is calculated as 93, 18.5, 7.4, and 2.1 days, respectively.

To study the impact of an emission's location and seasonality on the ODP, a range of emission patterns (X) was chosen. Uniform emission per unit area for latitude bands 8°S – 8°N , 32°N – 40°N , 40°N – 48°N , 48°N – 56°N , and 56°N – 64°N assume no specific matching to industrial regions. The collective bands 40°S – 64°S and 40°N – 64°N are also compared. Seasonality was studied with 90-day emissions starting Jun 1 or Dec 1. In all cases the same amount was emitted uniformly over the first 90 days of each experiment. The concentration, $f_{utt}(t)$, in the upper tropical troposphere (defined as the average over 16°S to 16°N latitude and 10 to 18 km altitude) is shown for propane ($T_{mix} = 18.5$ d) for the different X (Jun 1) in Figure 1.

In general f_{utt} rises during the first 90 days of emissions and falls rapidly following cessation of emissions. The maxima of $f_{utt}(t)$ for these patterns range over a factor of 100. The high-latitude X are smallest during summer because the gas is rapidly destroyed in northern mid latitudes before reaching the tropics. For Dec 1 emissions (not shown) the f_{utt} from tropical emissions changes only slightly, but the value from northern latitudes becomes much larger with less

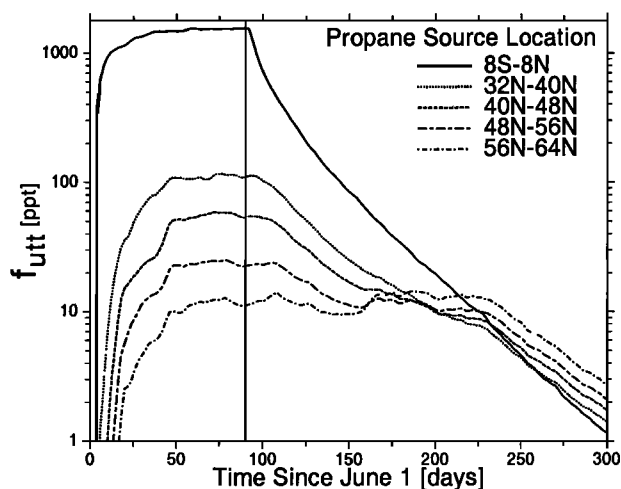


Figure 1. Modeled propane ($T_{mix} = 18.5$ d) mixing ratio in the upper tropical troposphere (f_{utt}) versus time since emission for different source latitudes X. The mixing ratio is averaged over 16°S – 16°N latitude, 10–18 km, and all longitudes. A total source of 5×10^{11} moles, equivalent to 2825 ppt if well mixed throughout the atmosphere, was emitted at a uniform rate starting June 1 and ending 90 days later (vertical line). Shown are results for X = 8°S – 8°N (solid), 32°N – 40°N (dotted), 40°N – 48°N (dashed), 48°N – 56°N (short-long dashes), and 56°N – 64°N (dot dash).

difference between latitude bands. This behavior is typical for the other 3 gases studied. The area under each curve is proportional to ODP_X and generally determined by the first 6 months following emission. (N.B., the scale in Figure 1 is logarithmic.)

The log of the ratio, ODP_X/ODP_{mix} , of ODP derived from different emission patterns (Eq. 3) to that assuming a well mixed gas is plotted against T_{mix} in Figure 2. The individual points for each gas represent the different X described above. For gases with $T_{mix} > 100$ d (beyond range of figure), the points for different X clearly converge; but for the 4 gases shown with $T_{mix} < 100$ d, this figure demonstrates the breakdown of the well mixed assumption that would have all points fall on the zero (log) line. As T_{mix} becomes shorter, the spread in ODP_X becomes much larger. For $T_{mix} = 93$ d, ODP_X varies by less than a factor of ten over the range of X considered; whereas for $T_{mix} = 2.1$ d ODP_X varies by nearly a factor of 10^4 .

Calculations based on a mixed-gas assumption for a gas with $T_{mix} \sim 11$ d would tend to overestimate, by up to a factor of 100, the impact of these emissions. High-latitude emissions in winter have greater impact than summer. Summer emissions show the greatest sensitivity to the source latitude. For equatorial emissions ODP_{mix} underestimates ODP_X by a factor of 2–4.

As an example, we calculate bounds on the ODP of n-PB for the range of emission patterns studied here. Assuming that n-PB and halon-1211 (CF_2ClBr) have similar impact on ozone once in the stratosphere, we compute a scaled ODP_{mix} for n-PB of 0.02. Using the range of values in Figure 2, we then derive a range in ODP that varies from as little as 0.0002 for summer emissions at $56^\circ N$ – $64^\circ N$ to as large as 0.06 for tropical emissions. This range is consistent with Wuebbles et al. [1999] calculated ODP of 0.026 for globally uniform emissions using a 2-D model.

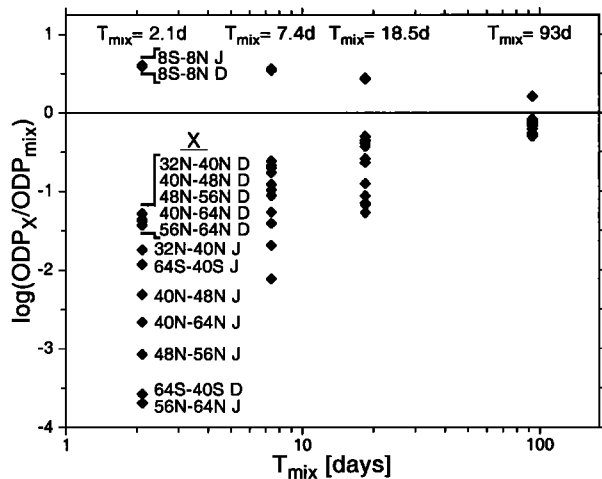


Figure 2. The log of the ratio ODP_X/ODP_{mix} as a function of the well mixed lifetime T_{mix} (days) for 4 very short-lived gases. This ratio compares latitudinal emission patterns X (labeled for $T_{mix} = 2.1$ d) to the well mixed approximation (see text). The relative ordering of this ratio is the same for all 4 gases. The letter D (or J) refers to 90-day emissions starting Dec 1 (Jun 1).

Conclusions

Very short-lived ODS, such as C_2HCl_3 (~ 7 days [WMO, 1999]) and C_3H_7Br (~ 11 days), can deliver ozone-depleting halogens to the stratosphere. Quantitative evaluation of their ODPs, however, must extend beyond the traditional approach using a mean atmospheric lifetime [Solomon and Wuebbles, 1995]. These gases will never become well mixed in the troposphere, and the fraction of emissions involved in ozone depletion depends vitally on the location and season of the source. Such differences may complicate policy since industrialized countries in mid to high latitudes would have much smaller ODPs for emissions than would developing economies in equatorial regions.

This paper examines the delivery of the primary halocarbon to the tropical tropopause and thence into the stratosphere. We introduce a clear diagnostic, Figure 2, pointing out the dependence of the ODP on the location and season of emission. One remaining uncertainty is whether the degradation products of the halocarbon still pose a threat to stratospheric ozone. Provided such compounds are water soluble, they will be scavenged efficiently from the atmosphere on time scales of a week [Giorgi and Chameides, 1986] and with much greater efficiency by the condensation in deep convection in the tropics [Jaegle et al., 1997; Cohan et al., 1999]. Thus we expect that ODPs calculated in this manner for compounds with lifetimes even less than 10 days are appropriate and reasonably accurate.

If, however, the degradation products form an insoluble oxygenated halocarbon, the secondary delivery of halogens to the stratosphere could be disproportionately important. No such products have been identified yet. A more detailed treatment of tropospheric chemistry, including wet removal processes, would be necessary to evaluate the importance of these products.

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