An expanded definition of the odd oxygen family for tropospheric ozone budgets: Implications for ozone lifetime and stratospheric influence

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Key Points:

- Standard model definitions of the odd oxygen family do not properly account for tropospheric ozone sources and sinks
- An expanded odd oxygen definition provides a more consistent accounting relating ozone to molecular oxygen and water
- The new odd oxygen family implies a longer global mean lifetime for tropospheric ozone and a greater contribution from the stratosphere

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Abstract

Models of tropospheric ozone commonly define an "odd oxygen" family (O_x), comprising ozone and species with which it rapidly cycles, in order to compute tropospheric ozone budgets and lifetimes. A major O_x loss is the $O(^1D)+H_2O \rightarrow 2OH$ reaction, but this may not be an actual loss because the resulting hydrogen oxide (HO_x) radicals regenerate ozone in the presence of nitrogen oxides. Here we introduce an expanded odd oxygen family, $O_y \equiv O_x + O_z$, to include both O_x and an additional subfamily, O_z, consisting of HO_x and its reservoirs. We incorporate this new accounting into the GEOS-Chem model, revealing a longer global mean ozone lifetime (73 davs vs. 24 days) and greater stratospheric contribution (26% vs. 9%) under present-day conditions than derived from the standard O_x budget. Tracking the O_y budget may provide better understanding of the discrepancies between global models in their computations of ozone sources and sinks.

Plain Language Summary

Ozone in the lower atmosphere (troposphere) is a greenhouse gas, a strong oxidant, and a surface air pollutant. It is produced chemically in the atmosphere from gaseous precursors that have both natural and anthropogenic sources. While the amount of ozone in the troposphere is easily measured, the processes by which it is produced and lost are not, so we need global models to estimate these processes and their contributions to the ozone budget. This paper describes a new way of accounting for the budget of ozone in models, including the cycling with radicals, thus relating the production and loss of ozone to molecular oxygen (the ultimate source and sink). By implementing our method in a global model, we show that ozone has a much longer effective global mean lifetime than previously thought, extending the global influence of sources. We also find that downwelling of natural ozone from the stratosphere is more important for the tropospheric ozone budget than previously thought.

1 Introduction

Tropospheric ozone (O_3) is an important atmospheric oxidant and greenhouse gas (Monks et al., 2015), and is estimated to be responsible for over one million respiratory deaths annually (Malley et al., 2017). It is produced within the troposphere by photo-

chemical oxidation of volatile organic compounds (VOCs) including methane (CH_4) and carbon monoxide (CO) in the presence of nitrogen oxide radicals ($NO_x \equiv NO + NO_2$). These precursors have both natural and anthropogenic sources. Ozone is also transported from the stratosphere where it is produced naturally by photolysis of oxygen. Loss of ozone from the troposphere takes place by chemical reactions and by deposition to the surface.

There is considerable interest in understanding the factors controlling tropospheric ozone and quantifying anthropogenic influence. In doing so one needs to account for the chemical cycling of ozone with various trace species that do not actually affect the ozone budget. It is standard to define an "odd oxygen" (O_x) chemical family, including ozone and the minor species with which it cycles, as the relevant entity for computing the sources and sinks of ozone in the troposphere. A common definition of odd oxygen to account for cycling with NO_x and its reservoirs is (Wang et al., 1998a):

$$O_x \equiv O_3 + O + O(^1D) + NO_2 + 2NO_3 + 3N_2O_5 + HNO_3 + HNO_4 + PANs \quad (1)$$

where PANs refer to peroxyacyl nitrates and $O(^1D)$ is the excited state of the oxygen atom. Tropospheric ozone budgets are thus computed in global models on the basis of O_x production and loss, ignoring chemical cycling within the family (Myhre et al., 2013; Prather et al., 2001; Wu et al., 2007; Young et al., 2018). Source attribution of ozone is based on production and loss of O_x (Butler et al., 2018; Derwent et al., 2015; Emmons et al., 2012). Ozone typically accounts for over 99% of O_x, so the budget of ozone is effectively that of O_x.

The definition of O_x depends on the model chemical mechanism, and has evolved over time with the complexity of models. In the GEOS-Chem global model, for example, the recent expansions of organic nitrate chemistry (Fisher et al., 2016) and halogen chemistry (Sherwen et al., 2016) have added a number of terms to the O_x family (Hu et al., 2017). Differences in mechanisms aside, the definition of O_x is not always consistent across models, which causes ambiguities in model intercomparisons (Wu et al., 2007; Young et al., 2018).

Ultimately, since ozone originates from molecular oxygen (O_2), chemical production and loss of O_x should correspond to loss and production of O_2. This kind of accounting is generally not performed, however, which can lead to erroneous conclusions. The

dominant global O_x sink typically listed in global budgets is

$$O(^1D) + H_2O \rightarrow 2OH \quad (2)$$

but the OH produced in reaction (2) oxidizes CO and VOCs to generate peroxy radicals that may react with NO to return ozone. Thus, reaction (2) may not be an actual sink of O_x if sufficient NO_x is present. This has practical implications for source attribution. For example, it is typically reported that input from the stratosphere is only a minor source of global tropospheric ozone because it amounts to less than 15% of the source from peroxy + NO reactions (Young et al., 2018). However, the stratospheric contribution could be interpreted as larger if one tracks the sources of the peroxy radicals involved in tropospheric ozone production.

A solution, as pointed out above, would be to define O_x such that its chemical production and loss correspond to loss and production of O_2. However, this would not recognize the critical role played by NO_x. For example, the photolysis of formaldehyde by the radical pathway

$$HCHO + h\nu \xrightarrow{2O_2} CO + 2HO_2 \quad (3)$$

would be viewed as a source of O_x because it converts O_2 to peroxy radicals, but it does not actually make ozone unless NO_x is present.

We propose here an expanded definition of the odd oxygen family, $O_y \equiv O_x + O_z$, to enable rigorous accounting of tropospheric ozone budgets. Here O_z includes OH, peroxy radicals, halogen atoms, and their reservoirs. It is analogous to the HO_y chemical family that includes $HO_x \equiv$ OH + peroxy radicals and peroxide reservoirs (Prather & Jacob, 1997), but with halogen species added because of their interconversion with HO_x (Simpson et al., 2015). The coupling between O_x and O_z is described by cycling terms within the O_y family, while the sources and sinks of O_y all involve conversion to/from O_2 and H_2O. The O_y framework provides an alternative interpretation of the sources and sinks of tropospheric ozone and a novel perspective on ozone source attribution and lifetime.

2 Current computation of odd oxygen budgets in ozone models

Global 3-D models resolving the coupling between chemistry and transport have become standard tools for understanding the factors controlling tropospheric ozone (Denman et al., 2007; Lamarque et al., 2013; Young et al., 2013, 2018). These models are gen-

erally able to reproduce the broad spatial and seasonal patterns of tropospheric ozone. They all find that the global ozone budget is dominated by O_x production and loss within the troposphere, and that stratospheric influx and deposition to the surface are relatively minor terms. However, there is a factor of two disagreement between models in global O_x production and loss rates, a situation that has not improved over the last decade (Wu et al., 2007; Young et al., 2018). This suggests that the models may agree in their simulations of ozone concentrations for the wrong reasons, and raises questions about their ability to properly describe ozone chemistry and quantify the relative importance of different ozone sources.

Part of the discrepancy between models may simply be due to inconsistencies in the species included in odd oxygen budgets (Young et al., 2018). While the definition given by equation (1) is commonly used (Banerjee et al., 2016; Finney et al., 2016; Mauzerall et al., 2000; Wang et al., 1998b; Wu et al., 2007), some studies do not include HNO_3 or PANs in the O_x accounting (Bey et al., 2001; Crutzen et al., 1999; Stevenson et al., 2006). Others include additional organic nitrates and/or halogen oxides and their reservoirs, reflecting both more comprehensive mechanisms and more detailed accounting (Hu et al., 2017; Sudo et al., 2002; von Kuhlmann et al., 2003). Many studies fail to report the precise list of species included in their odd oxygen budgets.

The coefficients applied to O_x species are another source of ambiguity. Consider the cycling of NO_2 with HNO_3 by the following abridged mechanism:

$$NO_2 + OH + M \rightarrow HNO_3 + M \tag{4}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{5}$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \tag{6}$$

$$N_2O_5 + H_2O \xrightarrow{\text{aerosol}} 2HNO_3 \tag{7}$$

$$HNO_3 + h\nu \rightarrow NO_2 + OH \tag{8}$$

$$HNO_3 + OH \rightarrow NO_3 + H_2O \tag{9}$$

$$NO_3 + h\nu \xrightarrow{O_2} NO_2 + OH \tag{10}$$

HNO_3 is traditionally considered to carry one O_x equivalent (cf. equation (1)) so that cycling by reactions (4) and (8) conserves O_x. In that case reaction (7) is a sink of O_x, and reaction (9) is a source of O_x. But one could just as appropriately consider HNO_3 to carry 1.5 O_x equivalents so that reaction (7) conserves O_x and reaction (4) is a source

of O_x. Alternatively, one could consider HNO_3 to carry two O_x equivalents so that reaction (9) conserves O_x. The ambiguity is caused by the exclusion of OH from the O_x family. If OH were counted as 0.5 equivalents of an expanded odd oxygen family, with HNO_3 counted as 1.5 equivalents, then reactions (4)-(10) would all conserve the family and any ambiguity would disappear.

Indeed, the commonly used definitions of odd oxygen do not account for the cycling between O_x and HO_x radicals, and therefore offer only a limited perspective on ozone sources and sinks. By the definition in equation (1), the largest tropospheric sink of O_x is reaction (2), while the dominant sources of O_x are

$$HO_2 + NO \rightarrow NO_2 + OH \tag{11}$$

$$RO_2 + NO \rightarrow NO_2 + RO \tag{12}$$

where RO_2 denotes organic peroxy radicals. This is how global tropospheric ozone budgets are presented in the literature (Stevenson et al., 2006; Sudo et al., 2002; Young et al., 2013). However, reaction (2) is in fact the major source of OH to the troposphere, and most of this OH goes on to form HO_2 and RO_2:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2 \tag{13}$$

$$OH + RH \xrightarrow{O_2} RO_2 + H_2O \tag{14}$$

where RH denotes a generic VOC. The O_x and HO_x families are therefore coupled, and reactions (2), (11), and (12) cannot be considered true sinks and sources of odd oxygen; rather, they form part of a larger cycle between the O_x family and the HO_x radical family.

Tropospheric ozone budgets using the standard definition of O_x may thus be interpreted to overstate the importance of reactions (11) and (12) for ozone production, and understate the importance of primary sources, in particular transport from the stratosphere. The same problem applies to model studies where O_x is "tagged" during its production to investigate ozone sources (Butler et al., 2018; Derwent et al., 2015; Emmons et al., 2012; Nagashima et al., 2010; Sudo & Akimoto, 2007). These studies tag ozone either by the origin of the NO involved in reactions (11) and (12) (such as fossil fuel, lightning, etc.) or the location from which O_x originates (continental boundary layer, stratosphere, etc.). The first approach does not resolve the origin of the HO_x required for ozone

formation, and the second approach underestimates the effective lifetime of ozone by not accounting for its cycling with HO_x.

3 An expanded odd oxygen family

To overcome the inconsistencies described above, an alternative treatment of the odd oxygen budget should reference production and loss to O_2 and H_2O, the main forms of tropospheric oxygen and hydrogen, while also recognizing the importance of NO_x in converting peroxy radicals to ozone. To that end, we propose an expanded odd oxygen family, $O_y \equiv O_x + O_z$, as the sum of O_x and a reservoir O_z that includes HO_x radicals, atomic halogen radicals, and their reservoirs. This new formulation is analogous to other extended atmospheric chemical families used to denote cycling between species and their reservoirs, for example $NO_y \equiv NO_x + NO_z$ where the NO_z reservoir includes HNO_3, PANs, etc. Specifically, the reservoir species in O_z include OH (generated mostly by O_x loss from reaction (2)), peroxy radicals (which cycle with OH and regenerate O_x by reactions (11) and (12)), and their reservoirs. O_z would be identical to the commonly defined HO_y family (Jaeglé et al., 2001) were it not for necessary accounting of tropospheric halogens and their cycling with HO_x (Simpson et al., 2015).

In our definition of the expanded odd oxygen family O_y, odd oxygen (O_x) follows a standard definition and includes all minor species that cycle with ozone, while the odd oxygen reservoir (O_z) includes all species that cycle with HO_x radicals to produce ozone in the presence of NO_x. The ensemble of model species to be included in the O_x and O_z families depends on the chemical mechanism. In the mechanism used by the GEOS-Chem model version 12.0, O_x and O_z are defined as follows:

$$\begin{aligned} O_x \equiv\ & O_3 + O + O(^1D) + NO_2 + 2NO_3 + 3N_2O_5 + HNO_3 + HNO_4 + PANs + RONO_2 \\ & + CI + XO + XNO_2 + 2XNO_3 + \sum_{n=2}^{5} nX_2O_n + 2OXO \qquad (15) \\ O_z \equiv\ & 0.5 \times (H + OH + HO_2 + RO_2 + HNO_2 + HNO_3 + HNO_4 + PANs + RONO_2 + X \\ & + XO + XNO_2 + XNO_3 + OXO) + H_2O_2 + ROOH + X_2 + HOX + X_2O_n \qquad (16) \end{aligned}$$

Here X denotes halogen atoms (Cl, Br, I) and CI denotes Criegee intermediates (produced from ozonolysis of VOCs). $RONO_2$ includes various organic nitrates simulated explicitly or in lumped form (Fisher et al., 2016) and the same holds for peroxyacylnitrates (PANs), organic peroxy radicals (RO_2), and organic peroxides (ROOH). Alkyl and alkoxy

radicals would need to be included in O_z if they were explicit species in the mechanism, but GEOS-Chem (like most models) treats them implicitly as in steady state.

Coefficients in equations (15) and (16) are from standard accounting of reaction stoichiometry. To conserve O_y in reaction (2), OH must carry a coefficient of 0.5, and the same coefficient then applies to peroxy radicals and related species. A number of species must be included in both O_x and O_z, which again follows from the accounting. For example, the thermal dissociation of PANs $\rightarrow RO_2 + NO_2$ results in the formation of 0.5 equivalents of O_z (RO_2) and one of O_x (NO_2); PANs thus represent $1O_x + 0.5O_z$. Similarly, HNO_3 includes $1O_x + 0.5O_z$. This solves the theoretical problem posed in Section 2, as production/loss of HNO_3 by reactions (4)-(10) now conserves the O_y family regardless of chemical pathway.

4 Application to a global budget of tropospheric ozone

Figure 1 presents a schematic for the global tropospheric ozone budget using the expanded odd oxygen (O_y) family, and Table 1 gives the dominant pathways and global annual rates as inferred from a GEOS-Chem model simulation. A brief description of the GEOS-Chem simulation is provided in footnote to Table 1; more detail is given for example in Hu et al. (2017).

The sources of tropospheric O_y include transport from the stratosphere and photolysis of carbonyls. Additional sources of O_y can include photolysis of oxygen in the upper troposphere (Prather, 2009) and direct emission of NO_2 and halogens, but these are too minor in GEOS-Chem to appear in Table 1. The sinks of O_y include terminal chemical losses to O_2 and H_2O and irreversible deposition of O_y components to the surface. Reactions (2), (11), and (12) are cycling terms within the O_y family. Because reactions (11) and (12) conserve O_z while also generating O_x, NO acts as an amplifier for O_x production, augmenting the amount of O_y produced from the primary sources.

The expanded odd oxygen family has implications for understanding the effective lifetime of tropospheric ozone and the contributions from different sources. We can define a chain length N, or O_x production efficiency per unit O_z, as the number of times a unit of O_z is converted to O_x before it is removed by a terminal sink:

$$N = \frac{R_B}{R_G + R_H} = \frac{5300}{2600 + 550} = 1.68 \tag{17}$$

Table 1. Global tropospheric ozone budget described by the expanded odd oxygen family O_y[a]

O_x (mass: 380 Tg O_3 equivalents)					
Sources [Tg O_3 equivalents a^{-1}]	*5800*		*Sinks* [Tg O_3 equivalents a^{-1}]	*5800*	
A. Primary	500		C. Conversion to O_z	2310	
Transport from stratosphere		100%	$O^1D + H_2O \rightarrow 2OH$		96%
B. Production from O_z	5300		D. Conversion to O_2	2540	
$NO + HO_2 \rightarrow NO_2 + OH$		67%	$O_3 + HO_2 \rightarrow OH + O_2$		46%
$NO + RO_2 \rightarrow NO_2 + RO$		33%	$O_3 + OH \rightarrow HO_2 + O_2$		28%
			$IO + HO_2 \rightarrow HOI + O_2$		13%
			$BrO + HO_2 \rightarrow HOBr + O_2$		7%
			E. Deposition	950	
			O_3 deposition		84%
			HNO_3 deposition		14%
O_z (mass: 8.3 Tg O_3 equivalents)					
Sources [Tg O_3 equivalents a^{-1}]	*3150*		*Sinks* [Tg O_3 equivalents a^{-1}]	*3150*	
F. Primary	840		G. Conversion to H_2O	2600	
$CH_2O + h\nu \xrightarrow{2O_2} 2HO_2 + CO$		78%	$CH_3OOH + OH \rightarrow H_2O +$ products[b]		39%
Other carbonyl photolysis		19%	$OH + HO_2 \rightarrow O_2 + H_2O$		23%
C. Production from O_x	2310		$H_2O_2 + OH \rightarrow HO_2 + H_2O$		13%
$O^1D + H_2O \rightarrow 2OH$		96%	HO_2 uptake by aerosol[c]		11%
			$ROOH + OH \rightarrow H_2O + RO_2$		8%
			H. Deposition	550	
			H_2O_2 deposition		69%
			CH_3OOH deposition		13%
			HNO_3 deposition		12%

[a]Global annual mean budget from the GEOS-Chem model version 11-2d (Sherwen et al., 2016) in a 1-year simulation for 2016 (after a 1-year initialization through 2015). The expanded odd oxygen family $O_y \equiv O_x + O_z$ includes the commonly defined odd oxygen family (O_x) and its reservoirs (O_z), as defined in GEOS-Chem by equations (15-16). Total production and loss rates are given in Tg O_3 a^{-1} by applying the molar mass of O_3 to all component species. Percentages contributed by the major pathways are indicated; additional minor pathways contributing less than 3% are not listed. The GEOS-Chem simulation was performed at 2°×2.5° horizontal resolution with 47 vertical layers, driven by Goddard Earth Observing System - Fast Processing (GEOS-FP) meteorological fields. Detailed chemistry is included for the troposphere only (as diagnosed from the local tropopause). Ozone transport from the stratosphere is specified in this simulation with the Synoz flux boundary condition (McLinden et al., 2000) so that the influx of stratospheric ozone is precisely known. This simulation uses biogenic emissions from MEGAN v2.1 (Guenther et al., 2012), biomass burning emissions from GFED4 (Giglio et al., 2013), and anthropogenic emissions from EDGAR v4.2 overwritten by regional inventories for Asia (Li et al., 2017), the United States (USA EPA NEI-2011), and Canada (CAC), with additional NO_x emissions from lightning (Murray et al., 2012), soils (Hudman et al., 2012), aircraft (Stettler et al., 2011), and ships (Holmes et al., 2014; Vinken et al., 2011). For further details on the GEOS-Chem simulation of tropospheric ozone see for example Sherwen et al. (2016) and Hu et al. (2017).

[b]Depending on the branch the products may be either CH_3O_2 or CH_2O and OH.

[c]Catalytic conversion to H_2O by transition metal ions (Mao, Jacob, & Travis, 2013).

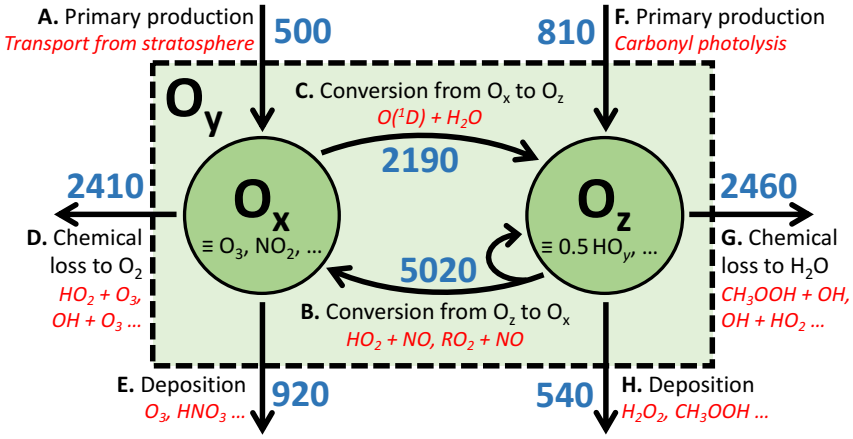

Figure 1. Sources and sinks of the expanded tropospheric odd oxygen family O_y and its components O_x and O_z. Source and sink processes are shown as black arrows. Their global annual rates computed with the GEOS-Chem model (Tg O_3 equivalents a^{-1}) are shown in blue. Major pathways contributing to the rates are shown in red. Table 1 gives a more detailed accounting of the pathways, and equations (15)-(16) give complete definitions of O_x and O_z for the GEOS-Chem chemical mechanism. Conversion of O_z to O_x by (B) conserves O_z, as indicated by the return arrow, and thus serves as a secondary source of O_y to balance the O_y budget.

where R_i denotes the rate of process i as shown in Figure 1 and Table 1. Because $N > 1$, the conversion from O_x to O_z by reaction (2) is a net source of O_x rather than a sink, in contrast to how it is generally presented in tropospheric ozone budgets.

The global mean lifetime of tropospheric ozone is commonly derived as the tropospheric mass m_{O_x} of O_x divided by the O_x loss rate. Wu et al. (2007) report a range of 19 to 33 days from a review of contemporary global models. The corresponding value in our model as calculated from the values in Table 1 is 24 days. But the conversion from O_x to O_z is not an actual loss for ozone, and instead amplifies O_x production when N is greater than 1, as is the case on a global average basis. The effective lifetime of ozone must therefore be longer.

To gain insight into the effective global mean lifetime of tropospheric ozone, let us consider a simple steady-state analysis of the O_z and O_x budgets in which we express the loss from process i in Figure 1 as a pseudo first-order loss rate constant k_i. The masses

of O_x and O_z are then given by

$$m_{O_x} = \frac{R_A + k_B m_{O_z}}{k_C + k_D + k_E} \tag{18}$$

$$m_{O_z} = \frac{R_F + k_C m_{O_x}}{k_G + k_H} \tag{19}$$

Replacing equations (17) and (19) into (18) we obtain, with the numerical values of Table 1,

$$m_{O_x} = \frac{R_A + N R_F}{k_D + k_E + (1-N)k_C} = \frac{500 + (1.67 \times 810)}{6.6 + 2.5 + (1 - 1.68) \times 6.0} = 380 \text{ Tg} \tag{20}$$

Here the numerator represents the primary sources of ozone (transport from the stratosphere and primary production of HO_x radicals in the presence of NO_x). The denominator gives the effective loss rate constant for ozone and its inverse gives the effective ozone lifetime τ_{O_3}:

$$\tau_{O_x} = \frac{1}{k_D + k_E + (1-N)k_C} = 73 \text{ days} \tag{21}$$

Thus the effective global mean lifetime of ozone is three times as long as obtained from the standard O_x-based calculation. Conversion of O_x to O_z by $O(^1D) + H_2O$ (process C) actually prolongs the ozone lifetime, rather than shortening it, when the recycling of O_z to O_x is efficient ($N > 1$). In fact, when recycling is very efficient such that $N > 1+(k_D+k_E)/k_C$, the denominator of equation (21) becomes negative and there is no steady-state solution for ozone. Instead there is runaway ozone production. A runaway regime would not actually be sustained in the atmosphere because of chemical nonlinearities; in particular, the NO/NO_2 ratio decreases as ozone increases, which then decreases N. But the point is that $O(^1D)+ H_2O$ is not only an ineffective sink but an amplifier for ozone when NO_x is present.

The longer effective global mean lifetime of ozone than previously recognized has implications for the persistence in influence from primary sources. From the numerator of equation (20), the contribution of transport from the stratosphere (process A) to the tropospheric ozone burden is $500/(500+(1.68 \times 840)) = 26\%$. This is much larger than the contribution that would be inferred from the standard O_x budget ($500/(500+5300) = 9\%$, with the 17% difference counted as tropospheric). In other words, the standard budget interprets only directly transported O_x (process A) as stratospheric in origin, while the O_y framework includes the cycling of transported ozone with O_z within its stratospheric component (i.e., the fraction of ozone from process B that originated through processes A and C).

The reinterpretation of primary source influence provided by the O_y definition has further ramifications on conducting and interpreting perturbation and tagging simulations to study processes controlling tropospheric ozone. Perturbation experiments, in which a precursor or pathway in the ozone system (e.g. anthropogenic NO_x emissions) is perturbed and the resulting simulation compared to an unperturbed baseline, are used to diagnose the complicated nonlinear dependencies of ozone. Quantifying the effects of these perturbations on the broader O_y system can provide valuable new insight into such dependencies. For example, we performed an identical GEOS-Chem simulation to that described in Table 1 but with all anthropogenic emissions turned off and the methane mixing ratio set to 700 ppb to approximate pre-industrial atmospheric conditions. After a year of initialization, we found that the mean tropospheric ozone burden over the following year was 27% below the baseline simulation, similar to the mean decrease of 29% found in the Atmospheric Chemistry and Climate Model Intercomparison Project simulations (Young et al., 2013). Of the processes shown in Figure 1, most dropped by 33-37%, with the exceptions of processes A (held fixed), B (dropped by 41%), and E (dropped by 48%). As a result, N dropped from 1.68 to 1.5 (Equation 17), and ozone lifetime increased from 73 to 77 days (Equation 21), or 24 to 29 days by the standard O_x definition. The standard analysis would focus on the production and loss of O_x to explain this perturbation: a sharp decrease in process B is balanced by a moderate increase in lifetime. The O_y analysis reveals the importance of direct O_z production and of O_y cycling: decreases in both N and process F both serve to reduce the tropospheric ozone burden, balanced by only a slight increase in ozone lifetime.

The expanded odd oxygen family can also be applied to the ozone tagging simulations described in Section 2. Current methods tag only based on direct production of tropospheric O_x via processes A and B. In the O_y framework, odd oxygen would be tagged by its initial source (processes A and F), and could additionally be tagged by how many times it cycles through processes B and C. Because O_y of stratospheric origin retains its stratospheric tag even after cycling through processes C and B, this tagging method inherently acknowledges the longer lifetime and persistence of primary sources described above as a key insight from the expanded odd oxygen family. This could further be coupled with tagging by the source of the NO involved in process B or the locations in which processes A, B, C and F occur.

We incorporated O_y tagging by source (processes A and F) and number of cycles (through process C) into a GEOS-Chem simulation run identically to the one described in Table 1. We find that the new tagging method increases the proportion of total surface ozone with a stratospheric tag from 15% to 30%, and that the global annual average number of cycles through process C undergone by each ozone molecule ranges from 1.25 at the surface to 0.7 at 10 km altitude. Investigating the spatiotemporal variability of these tagged ozone tracers and comparing the distributions of tagged ozone tracers between models might provide another method to diagnose inconsistencies and biases in simulated ozone burdens. More detailed descriptions of the implementation of the expanded odd oxygen family in perturbation and tagging studies will be the subject of a follow-up paper.

It should be emphasized that the above global budget calculations are intended to be merely illustrative because (1) the importance of the different terms in the O_y budget may vary considerably across the troposphere, (2) there may be correlations between terms that need to be accounted for, and (3) there is strong chemical non-linearity within the system. Our purpose in this paper was to describe an improved theoretical framework for thinking about the tropospheric ozone budget. More detailed analysis of the implications for understanding the factors controlling tropospheric ozone, including discussions of the spatial heterogeneity, intercorrelations, and non-linearities of budget terms, will be incorporated into the aforementioned follow-up paper.

5 Conclusions

We have introduced the concept of an expanded odd oxygen family $O_y \equiv O_x + O_z$ to better analyze the tropospheric ozone budget in global models and track the contributions of different ozone sources. This new definition, where O_z mainly includes the hydrogen oxide (HO_x) radicals and their reservoirs, accounts for the recycling of O_x following conversion to O_z by the $O(^1D) + H_2O$ reaction, and provides a better theoretical foundation for the ozone budget by treating O_2 and H_2O as terminal sinks of O_y. The new framework thus treats NO as an amplifier in the cycling of odd oxygen between O_z and O_x, augmenting the O_y from primary sources of stratospheric influx and carbonyl photolysis, whereas the standard definition of odd oxygen emphasizes the role of NO as an ozone source. While the O_y framework does not fundamentally change the burden or production and loss pathways of tropospheric ozone in models, it provides a novel per-

spective on the importance and interdependence of specific chemical pathways, and offers a complementary method of analysis to the traditional O_x family in perturbation and tagging studies. Application to the global tropospheric ozone budget in the GEOS-Chem model reveals a much longer effective ozone lifetime (73 days vs. 24 days) and a much larger stratospheric contribution (26% vs. 9%) under present-day emissions and meteorology than diagnosed from the standard definition of odd oxygen. Analysis of ozone budgets in the framework of this expanded odd oxygen family may help to understand the large discrepancies between global models in their computations of ozone sources and sinks.

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