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$_2$O $\to$ 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, $O_x \equiv O_x + O_\gamma$, to include both $O_x$ and an additional subfamily, $O_\gamma$, 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 days vs. 24 days) and greater stratospheric contribution (26% vs. 9%) under present-day conditions than derived from the standard $O_x$ budget. Tracking the $O_\gamma$ 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 photochemical oxidation of carbon monoxide (CO), methane (CH$_4$), and other volatile organic compounds (VOCs) 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)

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

(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 \( \text{O}_x \) 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 \( \text{O}_x \) (Butler et al., 2018; Derwent et al., 2015; Emmons et al., 2012). Ozone typically accounts for over 99% of \( \text{O}_x \), so the budget of ozone is effectively that of \( \text{O}_x \).

The definition of \( \text{O}_x \) 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; Wang et al., 2019; Zhu et al., 2019) have added a number of terms to the \( \text{O}_x \) family (Hu et al., 2017). Differences in mechanisms aside, the definition of \( \text{O}_x \) 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 (\( \text{O}_2 \)), chemical production and loss of \( \text{O}_x \) should correspond to loss and production of \( \text{O}_2 \). This kind of accounting is generally not performed, however, which can lead to erroneous conclusions. The dominant global \( \text{O}_x \) sink typically listed in global budgets is

\[
\text{O}^1D + \text{H}_2\text{O} \rightarrow 2\text{OH},
\]

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 \( \text{O}_x \) 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 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 \( \text{O}_x \) such that its chemical production and loss correspond to loss and production of \( \text{O}_2 \). However, this would not recognize the critical role played by NO\(_x\). For example, the photolysis of formaldehyde by the radical pathway

\[
\text{HCHO} + \text{hv} \rightarrow \text{CO} + 2\text{HO}_2
\]

would be viewed as a source of \( \text{O}_x \) because it converts \( \text{O}_2 \) 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, \( \text{O}_y \equiv \text{O}_x + \text{O}_z \), to enable rigorous accounting of tropospheric ozone budgets. Here \( \text{O}_z \) includes HO\(_x\) radicals (\( \equiv \text{OH} + \) peroxy radicals), halogen atoms, and their reservoirs. It is analogous to the HO\(_y\) chemical family that includes HO\(_x\) and its peroxide reservoirs (Prather & Jacob, 1997) but with halogen species added because of their interconversion with HO\(_x\) (Simpson et al., 2015). The coupling between \( \text{O}_x \) and \( \text{O}_z \) is described by cycling terms within the \( \text{O}_y \) family, while the sources and sinks of \( \text{O}_z \) all involve conversion to/from \( \text{O}_x \) and \( \text{H}_2\text{O} \). The \( \text{O}_y \) 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 are 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 generally able to reproduce the broad spatial and seasonal patterns of tropospheric ozone. They all find that the global ozone budget is dominated by \( \text{O}_x \) 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 \( \text{O}_x \) 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 HNO₃ or PANs in the Oₓ 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 Oₓ species are another source of ambiguity. Consider the cycling of NO₂ with HNO₃ by the following abridged mechanism:

\[
\begin{align*}
\text{NO}_2 + \text{OH} + \text{M} & \rightarrow \text{HNO}_3 + \text{M}, \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2, \\
\text{NO}_3 + \text{NO}_2 + \text{M} & \rightarrow \text{N}_2\text{O}_5 + \text{M}, \\
\text{N}_2\text{O}_3 + \text{H}_2\text{O}_{\text{aerosol}} & \rightarrow 2\text{HNO}_3, \\
\text{HNO}_3 + h\nu & \rightarrow \text{NO}_2 + \text{OH}, \\
\text{HNO}_3 + \text{OH} & \rightarrow \text{NO}_3 + \text{H}_2\text{O}, \\
\text{NO}_3 + h\nu & \rightarrow \text{O}_2 + \text{NO}_2 + \text{OH}. 
\end{align*}
\]

HNO₃ is customarily considered to carry one Oₓ equivalent (cf. equation (1)) so that cycling by reactions (4) and (8) conserves Oₓ. In that case reaction (7) is a sink of Oₓ, and reaction (9) is a source of Oₓ. But one could just as appropriately consider HNO₃ to carry 1.5 Oₓ equivalents so that reaction (7) conserves Oₓ and reaction (4) is a source of Oₓ. Alternatively, one could consider HNO₃ to carry two Oₓ equivalents so that reaction (9) conserves Oₓ. The ambiguity is caused by the exclusion of OH from the Oₓ family. If OH were counted as 0.5 equivalents of an expanded odd oxygen family, with HNO₃ 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 Oₓ and HOₓ radicals and, therefore, offer only a limited perspective on ozone sources and sinks. By the definition in equation (1), the largest tropospheric sink of Oₓ is reaction (2), while the dominant sources of Oₓ are

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH}, \\
\text{RO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{RO},
\end{align*}
\]

where RO₂ 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 HO₂ and RO₂:

\[
\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{O}_2 \text{HO}_2 + \text{CO}_2, \\
\text{OH} + \text{RH} & \rightarrow \text{RO}_2 + \text{H}_2\text{O}_2,
\end{align*}
\]

where RH denotes a generic VOC. The Oₓ and HOₓ 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 Oₓ family and the HOₓ radical family.

Tropospheric ozone budgets using the standard definition of Oₓ 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 Oₓ 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; Wang et al., 1998b). These studies tag ozone either by the origin of the NO involved in reactions (11) and (12) (such as fossil fuel and lightning) or the location from which Oₓ originates (continental boundary layer, stratosphere, etc.). The first approach does not resolve the origin of the HOₓ required for ozone formation, and the second approach underestimates the effective lifetime of ozone by not accounting for its cycling with HOₓ.
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, \( O_x \equiv O_2 + O_y \), as the sum of \( O_2 \) and a reservoir \( O_y \) that includes \( NO_x \) 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 \( NO_x \) reservoir includes, for example, HNO3 and PANs. Specifically, the reservoir species in \( O_2 \) include OH (generated 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. \( O_x \) would be identical to the commonly defined \( HO_x \) family (Jaeglé et al., 2001) were it not for necessary accounting of tropospheric halogens and their cycling with \( HO_x \) (Evans et al., 2003; 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 \( (O_y) \) 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 \( O_y \) families depends on the chemical mechanism. In the mechanism used by the GEOS-Chem model version 11-02d, \( O_x \) and \( O_y \) are defined as follows:

\[
O_x \equiv O_3 + O + O(1D) + NO_2 + 2NO_3 + 3N_2O_5 + HNO_3 + HNO_4 + PANS + RONO_2 + CR + XO + XNO_2 + 2XNO_3 + \sum_{n=2}^{5} nX_2O_n + 2OXO, \tag{15}
\]

\[
O_y \equiv 0.5x(H + OH + HO_2 + RO_2 + HNO_2 + HNO_3 + HNO_4 + PANS + RONO_2 + X + XO + XNO_2 + XNO_3 + OXO) + H_2O_2 + ROOH + X_2 + HOX + X_2O_n. \tag{16}
\]

Here \( X \) denotes halogen atoms (Cl, Br, and I), and \( CR \) 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 peroxyacetyl nitrates (PANs), organic peroxy radicals (\( RO_x \)), and organic peroxides (\( ROOH \)). Alkyl and alkoxy radicals would need to be included in \( O_y \) 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 \( O_y \), 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 \( O_y (RO_2) \) and one of \( O_y (NO_2) \); PANs thus represent \( 1O_x + 0.5O_y \). Similarly, HNO3 includes \( 1O_x + 0.5O_y \). This solves the theoretical problem posed in section 2, as production/loss of HNO3 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).

Primary sources of tropospheric \( O_y \) include transport from the stratosphere and photolysis of carbonyls. There are additional primary sources of \( O_y \) from photolysis of oxygen in the upper troposphere (Prather, 2009) and direct emission of \( NO_x \) and halogens (\( HOX, X_2 \)), 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 \( O_x \) family, but reactions (11) and (12) also generate \( O_y \). From that perspective, 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 important 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 \( O_x \), as the number of times a unit of \( O_x \) is converted to \( O_x \) before it is removed by a terminal sink:

\[
N = \frac{R_B}{R_D + R_H} = \frac{5}{600 + 550} = 1.68,
\]

(17)

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 \( O_x \) by reaction (2) is a net source of \( O_x \) on a global scale 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 \( O_x \) is not an actual sink 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 \( O_x \) 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 \( O_x \) are then given by

\[
m_{O_x} = \frac{R_A + k_B m_{O_x}}{k_C + k_D + k_E},
\]

(18)

\[
m_{O_x} = \frac{R_F + k_C m_{O_x}}{k_D + k_H}.
\]

(19)

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

\[
m_{O_x} = \frac{R_A + NR_F}{k_D + k_E + (1-N)k_C} = \frac{500 + (1.68 \times 840)}{6.6 + 2.5 + (1-1.68) \times 6.0} = 380 \text{ Tg}.
\]

(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 \( \tau_{O_x} \).
Thus, the effective global mean lifetime of ozone is 3 times as long as obtained from the standard $O_x$-based calculation. Conversion of $O_2$ to $O_3$ by $O^{(1D)} + H_2O$ (Process C) actually prolongs the ozone lifetime, rather than shortening it, when the recycling of $O_2$ to $O_3$ 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. For example, 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 also 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 $500/(500+(1.68\times840))=26\%$. This
is much larger than the contribution that would be inferred from the standard $O_x$ budget ($500/(500+5,300) \approx 9\%$ with the 17% difference counted as tropospheric). In other words, the standard budget interprets only directly transported ozone (Process A) as stratospheric in origin, while the $O_x$ framework tracks the HO$_x$ radicals produced from the photolysis of that ozone (Process C) and the resulting ozone production (Process B).

The reinterpretation of primary source influence provided by the $O_x$ 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 $O_x$ 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 preindustrial 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 the 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 $O_x$ analysis reveals the importance of direct $O_x$ production and of $O_x$ 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 $O_x$ 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 $O_x$ 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 $O_x$ 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%. 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 $O_x$ 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 nonlinearity within the system. Our purpose here is mainly to describe an improved theoretical framework for thinking about the tropospheric ozone budget. More detailed quantitative analysis of the implications for understanding the factors controlling tropospheric ozone will be discussed in the follow-up paper.

5. Conclusions

We have introduced the concept of an expanded odd oxygen family $O_x \equiv O_x + O_x$ to better analyze the tropospheric ozone budget in global models and track the contributions of different ozone sources. This new definition, where $O_x$ mainly includes the hydrogen oxide (HO$_x$) radicals and their reservoirs, accounts for the recycling of $O_x$ following conversion to $O_x$ by the $O(1D) + H_2O$ reaction and provides a better theoretical
foundation for the ozone budget by tracking the reactive oxygen atoms to their terminal sinks as O$_2$ and H$_2$O. The new framework thus treats the peroxo + NO reactions as an amplifier in the cycling of odd oxygen between O$_2$ and O$_3$, augmenting the O$_3$ from primary sources of stratospheric influx and carbonyl photolysis, whereas the standard definition of odd oxygen would treat the peroxo + NO reactions as a primary ozone source.

While the O$_3$ framework does not fundamentally change the burden or production and loss pathways of tropospheric ozone in models, it provides a novel perspective on the importance and interdependence of specific chemical pathways and offers a complementary method of analysis to the traditional O$_3$ 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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