

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

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6                     **Key Points:**

- 7                     • Standard model definitions of the odd oxygen family do not properly account for  
8                     tropospheric ozone sources and sinks
- 9                     • An expanded odd oxygen definition provides a more consistent accounting relat-  
10                    ing ozone to molecular oxygen and water
- 11                    • This new odd oxygen family implies a longer lifetime for tropospheric ozone and  
12                    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 much longer global mean lifetime of ozone (72 days vs. 24 days) and greater stratospheric contribution (27% vs. 9%) than derived from the standard  $O_x$  budget. Tracking the  $O_y$  budget may provide better understanding of the large 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 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, 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 volatile organic compounds (VOCs) and carbon monoxide (CO) in the presence of ni-

43 trogen oxide radicals ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ). These precursors have both natural and an-  
 44 thropogenic sources. Ozone is also transported from the stratosphere where it is produced  
 45 naturally by photolysis of oxygen. Loss of ozone from the troposphere takes place by chem-  
 46 ical reactions and by deposition to the surface.

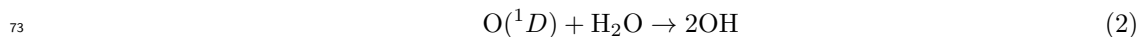
47 There is considerable interest in understanding the factors controlling tropospheric  
 48 ozone and quantifying anthropogenic influence. In doing so one needs to account for the  
 49 chemical cycling of ozone with various trace species that do not actually affect the ozone  
 50 budget. It is standard to define an "odd oxygen" ( $\text{O}_x$ ) chemical family, including ozone  
 51 and the minor species with which it cycles, as the relevant entity for computing the sources  
 52 and sinks of ozone in the troposphere. A common definition of odd oxygen to account  
 53 for cycling with  $\text{NO}_x$  and its reservoirs is (Wang et al., 1998a):

$$54 \quad \text{O}_x \equiv \text{O}_3 + \text{O} + \text{O}(^1D) + \text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{HNO}_4 + \text{PANs} \quad (1)$$

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

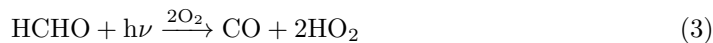
62 The definition of  $\text{O}_x$  depends on the model chemical mechanism, and has evolved  
 63 over time with the complexity of models. In the GEOS-Chem global model, for exam-  
 64 ple, the recent expansion of organic nitrate chemistry (Fisher et al., 2016) and halogen  
 65 chemistry (Sherwen et al., 2016) have added a number of terms to the  $\text{O}_x$  family (Hu  
 66 et al., 2017). Differences in mechanisms aside, the definition of  $\text{O}_x$  is not always consis-  
 67 tent across models, which causes ambiguities in model intercomparisons (Wu et al., 2007;  
 68 Young et al., 2018).

69 Ultimately, since ozone originates from molecular oxygen ( $\text{O}_2$ ), chemical produc-  
 70 tion and loss of  $\text{O}_x$  should correspond to loss and production of  $\text{O}_2$ . This kind of account-  
 71 ing is generally not performed, however, which can lead to erroneous conclusions. The  
 72 dominant global  $\text{O}_x$  sink typically listed in global budgets is



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

82 A solution, as pointed out above, would be to define  $O_x$  such that its chemical pro-  
 83 duction and loss correspond to loss and production of  $O_2$ . However, this would not rec-  
 84 ognize the critical role played by  $NO_x$ . For example, the photolysis of formaldehyde by  
 85 the radical pathway



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

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

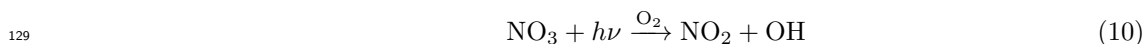
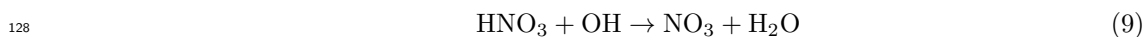
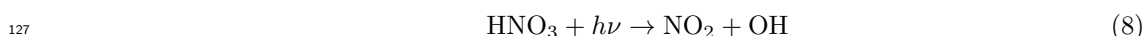
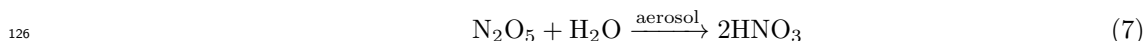
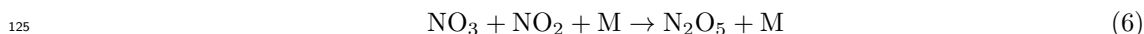
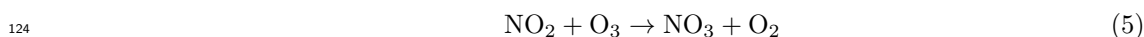
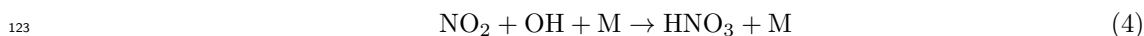
## 99 **2 Current computation of odd oxygen budgets in ozone models**

100 Global 3-D models resolving the coupling between chemistry and transport have  
 101 become standard tools for understanding the factors controlling tropospheric ozone (Den-  
 102 man et al., 2007; Lamarque et al., 2013; Young et al., 2013, 2018). These models are gen-  
 103 erally able to reproduce the broad spatial and seasonal patterns of tropospheric ozone.  
 104 They all find that the global ozone budget is dominated by  $O_x$  production and loss within

105 the troposphere, and that stratospheric influx and deposition to the surface are relatively  
 106 minor terms. However, there is a factor of two disagreement between models in global  
 107  $O_x$  production and loss rates, a situation that has not improved over the last decade (Wu  
 108 et al., 2007; Young et al., 2018). This suggests that the models may agree in their sim-  
 109 ulations of ozone concentrations for the wrong reasons, and raises questions about their  
 110 ability to properly describe ozone chemistry and quantify the relative importance of dif-  
 111 ferent ozone sources.

112 Part of the discrepancy between models may simply be due to inconsistencies in  
 113 the species included in odd oxygen budgets (Young et al., 2018). While the definition  
 114 given by equation (1) is commonly used (Banerjee et al., 2016; Finney et al., 2016; Mauzer-  
 115 all et al., 2000; Wang et al., 1998b; Wu et al., 2007), some studies do not include  $HNO_3$   
 116 or PANs in the  $O_x$  accounting (Bey et al., 2001; Crutzen et al., 1999; Stevenson et al.,  
 117 2006). Others include additional organic nitrates and/or halogen oxides and their reser-  
 118 voirs, reflecting both more comprehensive mechanisms and more detailed accounting (Hu  
 119 et al., 2017; Sudo et al., 2002; von Kuhlmann et al., 2003). Many studies fail to report  
 120 the precise list of species included in their odd oxygen budgets.

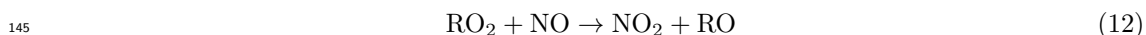
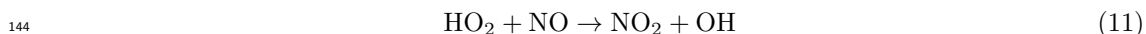
121 The coefficients applied to  $O_x$  species are another source of ambiguity. Consider  
 122 the cycling of  $NO_2$  with  $HNO_3$  by the following abridged mechanism:



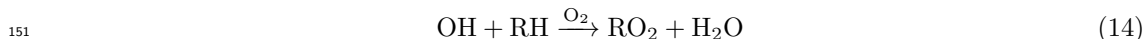
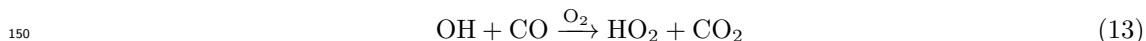
131  $HNO_3$  is traditionally considered to carry one  $O_x$  equivalent (cf. equation (1)) so that  
 132 cycling by reactions (4) and (8) conserves  $O_x$ . In that case reaction (7) is a sink of  $O_x$ ,  
 133 and reaction (9) is a source of  $O_x$ . But one could just as appropriately consider  $HNO_3$   
 134 to carry 1.5  $O_x$  equivalents so that reaction (7) conserves  $O_x$  and reaction (4) is a source  
 135 of  $O_x$ . Or one could consider  $HNO_3$  to carry two  $O_x$  equivalents so that reaction (9) con-  
 136 serves  $O_x$ . The ambiguity is caused by the exclusion of OH from the  $O_x$  family. If OH

137 were counted as 0.5 equivalents of an expanded odd oxygen family, with HNO<sub>3</sub> counted  
 138 as 1.5 equivalents, then reactions (4)-(10) would all conserve the family and any ambi-  
 139 guity would disappear.

140 Indeed, the commonly used definitions of odd oxygen are fundamentally lacking  
 141 because they fail to account for the cycling between O<sub>x</sub> and HO<sub>x</sub> radicals. By the def-  
 142 inition in equation (1), the largest tropospheric sink of O<sub>x</sub> is reaction (2), while the dom-  
 143 inant sources of O<sub>x</sub> are



146 where RO<sub>2</sub> denotes organic peroxy radicals. This is how global tropospheric ozone bud-  
 147 gets are presented in the literature (Stevenson et al., 2006; Sudo et al., 2002; Young et  
 148 al., 2013). However, reaction (2) is in fact the major source of OH to the troposphere,  
 149 and most of this OH goes on to form HO<sub>2</sub> and RO<sub>2</sub>:



152 where RH denotes a generic VOC. The O<sub>x</sub> and HO<sub>x</sub> families are therefore coupled, and  
 153 reactions (2), (11), and (12) cannot be considered true sinks and sources of odd oxygen;  
 154 rather, they form part of a larger cycle between the O<sub>x</sub> family and the HO<sub>x</sub> radical fam-  
 155 ily.

156 Tropospheric ozone budgets using the standard definition of O<sub>x</sub> thus overstate the  
 157 importance of reactions (11) and (12) for ozone production, and understate the impor-  
 158 tance of primary sources, in particular transport from the stratosphere. The same prob-  
 159 lem applies to model studies where O<sub>x</sub> is "tagged" during its production to investigate  
 160 ozone sources (Butler et al., 2018; Derwent et al., 2015; Emmons et al., 2012; Nagashima  
 161 et al., 2010; Sudo & Akimoto, 2007). These studies tag ozone either by the origin of the  
 162 NO involved in reactions (11) and (12) (such as fossil fuel, lightning, etc.) or the loca-  
 163 tion from which O<sub>x</sub> originates (continental boundary layer, stratosphere, etc.). The first  
 164 approach does not resolve the origin of the HO<sub>x</sub> required for ozone formation, and the  
 165 second approach underestimates the effective lifetime of ozone by not accounting for its  
 166 cycling with HO<sub>x</sub>.

### 3 An expanded odd oxygen family

To overcome the inconsistencies described above, a proper 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 11-2d (Sherwen et al., 2016),  $O_x$  and  $O_z$  are defined as follows:

$$O_x \equiv O_3 + O + O(^1D) + NO_2 + 2NO_3 + 3N_2O_5 + HNO_3 + HNO_4 + PANs + RONO_2 + CI + XO + XNO_2 + 2XNO_3 + \sum_{n=2}^5 nX_2O_n + 2OXO \quad (15)$$

$$O_z \equiv 0.5 \times (H + OH + HO_2 + RO_2 + HNO_2 + HNO_3 + HNO_4 + PANs + RONO_2 + X + XO + XNO_2 + XNO_3 + OXO) + H_2O_2 + ROOH + X_2 + HOX + \sum_{n=2}^5 X_2O_n \quad (16)$$

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.

197 Coefficients in equations (15) and (16) are from standard accounting of reaction  
 198 stoichiometry. To conserve  $O_y$  in reaction (2), OH must carry a coefficient of 0.5, and  
 199 the same coefficient then applies to peroxy radicals and related species. A number of species  
 200 must be included in both  $O_x$  and  $O_z$ , which again follows from the accounting. For ex-  
 201 ample, the thermal dissociation of PANs  $\rightarrow$  RO<sub>2</sub> + NO<sub>2</sub> results in the formation of 0.5  
 202 equivalents of  $O_z$  (RO<sub>2</sub>) and one of  $O_x$  (NO<sub>2</sub>); PANs thus represent  $1O_x + 0.5O_z$ . Sim-  
 203 ilarly, HNO<sub>3</sub> includes  $1O_x + 0.5O_z$ . This solves the theoretical problem posed in Sec-  
 204 tion 2, as production/loss of HNO<sub>3</sub> by reactions (4)-(10) now conserves the  $O_y$  family  
 205 regardless of chemical pathway.

#### 206 4 Application to a global budget of tropospheric ozone

207 Figure 1 presents a schematic for the tropospheric ozone budget using the expanded  
 208 odd oxygen ( $O_y$ ) family, and Table 1 gives the dominant pathways and global annual rates  
 209 as inferred from a GEOS-Chem model simulation. A brief description of the GEOS-Chem  
 210 simulation is given in footnote to Table 1; more detail is given for example in Hu et al.  
 211 (2017).

212 The sources of tropospheric  $O_y$  include transport from the stratosphere and pho-  
 213 tolysis of carbonyls. The sinks of  $O_y$  include terminal chemical losses to O<sub>2</sub> and H<sub>2</sub>O,  
 214 and irreversible deposition of  $O_y$  components to the surface. Reactions (2), (11), and (12)  
 215 are cycling terms within the  $O_y$  family. Because reactions (11) and (12) conserve  $O_z$  while  
 216 also generating  $O_x$ , NO acts as an amplifier for  $O_x$  production, augmenting the amount  
 217 of  $O_y$  produced from the primary sources.

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

$$222 \quad N = \frac{R_B}{R_G + R_H} = \frac{5020}{2460 + 540} = 1.67 \quad (17)$$

223 where  $R_i$  denotes the rate of process  $i$  as shown in Figure 1 and Table 1. Because  $N >$   
 224 1, the conversion from  $O_x$  to  $O_z$  by reaction (2) is a net source of  $O_x$  rather than a sink,  
 225 in contrast to how it is generally presented in tropospheric ozone budgets.



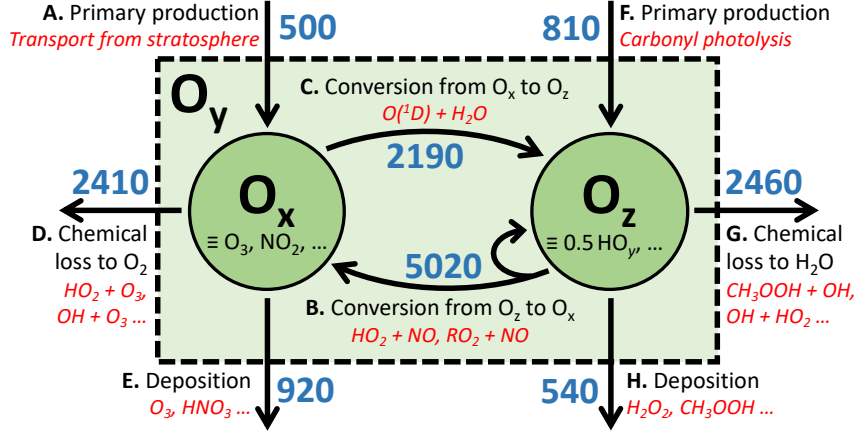
**Table 1.** Global tropospheric ozone budget described by the expanded odd oxygen family  $O_y$ <sup>a</sup>

<b><math>O_x</math> (mass: 370 Tg <math>O_3</math> equivalents)</b>			
<i>Sources</i> [Tg $O_3$ equivalents $a^{-1}$ ]	<i>5520</i>	<i>Sinks</i> [Tg $O_3$ equivalents $a^{-1}$ ]	<i>5520</i>
A. Primary	500	C. Conversion to $O_z$	2190
Transport from stratosphere	100%	$O^1D + H_2O \rightarrow 2OH$	96%
B. Production from $O_z$	5020	D. Conversion to $O_2$	2410
$NO + HO_2 \rightarrow NO_2 + OH$	67%	$O_3 + HO_2 \rightarrow OH + O_2$	46%
$NO + RO_2 \rightarrow NO_2 + RO$	33%	$O_3 + OH \rightarrow HO_2 + O_2$	27%
		$IO + HO_2 \rightarrow HOI + O_2$	12%
		$BrO + HO_2 \rightarrow HOBr + O_2$	7%
		E. Deposition	920
		$O_3$ deposition	84%
		$HNO_3$ deposition	14%
<b><math>O_z</math> (mass: 7.8 Tg <math>O_3</math> equivalents)</b>			
<i>Sources</i> [Tg $O_3$ equivalents $a^{-1}$ ]	<i>3000</i>	<i>Sinks</i> [Tg $O_3$ equivalents $a^{-1}$ ]	<i>3000</i>
F. Primary	810	G. Conversion to $H_2O$	2460
$CH_2O + h\nu \xrightarrow{2O_2} 2HO_2 + CO$	78%	$CH_3OOH + OH \rightarrow H_2O + \text{products}^b$	40%
Other carbonyl photolysis	19%	$OH + HO_2 \rightarrow O_2 + H_2O$	22%
C. Production from $O_x$	2190	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	13%
$O^1D + H_2O \rightarrow 2OH$	96%	$HO_2$ uptake by aerosol <sup>c</sup>	11%
		$ROOH + OH \rightarrow H_2O + RO_2$	8%
		H. Deposition	540
		$H_2O_2$ deposition	69%
		$CH_3OOH$ deposition	13%
		$HNO_3$ deposition	12%

<sup>a</sup>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  $4^\circ \times 5^\circ$  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. For further details on the GEOS-Chem simulation of tropospheric ozone see for example Sherwen et al. (2016) and Hu et al. (2017).

<sup>b</sup>Depending on the branch the products may be either  $CH_3O_2$  or  $CH_2O$  and  $OH$ .

<sup>c</sup>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.

226 The tropospheric ozone lifetime is commonly derived as the tropospheric mass  $m_{O_x}$   
 227 of  $O_x$  divided by the  $O_x$  loss rate. Wu et al. (2007) report a range of 19 to 33 days from  
 228 a review of contemporary global models. The corresponding value in our model as cal-  
 229 culated from the values in Table 1 is 24 days. But the conversion from  $O_x$  to  $O_z$  is not  
 230 an actual loss for ozone, and instead amplifies  $O_x$  production when  $N$  is greater than  
 231 1, as is the case on a global average basis. The effective lifetime of ozone must therefore  
 232 be longer.

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

$$237 \quad m_{O_x} = \frac{R_A + k_B m_{O_z}}{k_C + k_D + k_E} \quad (18)$$

$$239 \quad m_{O_z} = \frac{R_F + k_C m_{O_x}}{k_G + k_H} \quad (19)$$

240 Replacing equations (17) and (19) into (18) we obtain, with the numerical values of Ta-  
 241 ble 1,

$$242 \quad m_{O_x} = \frac{R_A + NR_F}{k_D + k_E + (1 - N)k_C} = \frac{500 + (1.67 \times 810)}{6.5 + 2.5 + (1 - 1.67) \times 5.9} = 370 \text{ Tg} \quad (20)$$

243 Here the numerator represents the primary sources of ozone (transport from the strato-  
 244 sphere and primary production of HO<sub>x</sub> radicals in the presence of NO<sub>x</sub>). The denom-  
 245 inator gives the effective loss rate constant for ozone and its inverse gives the effective  
 246 ozone lifetime  $\tau_{O_3}$ :

$$247 \quad \tau_{O_x} = \frac{1}{k_D + k_E + (1 - N)k_C} = 72 \text{ days} \quad (21)$$

248 Thus the effective lifetime of ozone is three times as long as obtained from the standard  
 249 O<sub>x</sub>-based calculation. Conversion of O<sub>x</sub> to O<sub>z</sub> by O(<sup>1</sup>D) + H<sub>2</sub>O (process C) actually pro-  
 250 longes the ozone lifetime, rather than shortening it, when the recycling of O<sub>z</sub> to O<sub>x</sub> is ef-  
 251 ficient ( $N > 1$ ). In fact, when recycling is very efficient such that  $N > 1 + (k_D + k_E)/k_C$ ,  
 252 the denominator of equation (21) becomes negative and there is no steady-state solu-  
 253 tion for ozone. Instead there is runaway ozone production. A runaway regime would not  
 254 actually be sustained in the atmosphere because of chemical nonlinearities; in particu-  
 255 lar, the NO/NO<sub>2</sub> ratio decreases as ozone increases, which then decreases N. But the point  
 256 is that O(<sup>1</sup>D) + H<sub>2</sub>O is not only an ineffective sink but an amplifier for ozone when NO<sub>x</sub>  
 257 is present.

258 The longer effective lifetime of ozone than previously recognized has implications  
 259 for the persistence in influence from the primary sources. From the numerator of equa-  
 260 tion (20), the contribution of transport from the stratosphere (process A) to the tropo-  
 261 spheric ozone burden is  $500/(500 + (1.67 \times 810)) = 27\%$ . This is much larger than the  
 262 contribution that would be inferred from the Ox budget ( $500/(500 + 5020) = 9\%$ ).

263 It should be emphasized that the above global budget calculations are intended to  
 264 be merely illustrative because (1) the importance of the different terms in the O<sub>y</sub> bud-  
 265 get may vary considerably across the troposphere, (2) there may be correlations between  
 266 terms that need to be accounted for, (3) there is strong chemical non-linearity within  
 267 the system. Our purpose in this paper was to describe an improved theoretical frame-  
 268 work for thinking about the tropospheric ozone budget. More detailed analysis of the  
 269 implications for understanding the factors controlling tropospheric ozone will be the topic  
 270 of a follow-up paper

## 271 5 Conclusions

272 We have introduced the concept of an expanded odd oxygen family  $O_y \equiv O_x + O_z$  to  
 273 better analyze the tropospheric ozone budget in global models and track the contribu-  
 274 tions of different ozone sources. This new definition, where  $O_z$  mainly includes the hy-  
 275 drogen oxide ( $HO_x$ ) radicals and their reservoirs, accounts for the recycling of  $O_x$  fol-  
 276 lowing conversion to  $O_z$  by the  $O(^1D) + H_2O$  reaction, and provides a better theoret-  
 277 ical foundation for the ozone budget by treating  $O_2$  and  $H_2O$  as terminal sinks of  $O_y$ .  
 278 Application to the global tropospheric ozone budget in the GEOS-Chem model shows  
 279 a much longer effective ozone lifetime (72 days vs. 24 days) and a much larger strato-  
 280 spheric contribution (27% vs. 9%) than diagnosed from the standard definition of odd  
 281 oxygen. Analysis of ozone budgets in the framework of this expanded odd oxygen fam-  
 282 ily may help to understand the large discrepancies between global models in their com-  
 283 putations of ozone sources and sinks.

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