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A new diagnostic for tropospheric ozone production

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Abstract

Tropospheric ozone is important for the Earth’s climate and air quality. It is produced during the oxidation of organics in the presence of nitrogen oxides. Due to the range of organic species emitted and the chain like nature of their oxidation, this chemistry is complex and understanding the role of different processes (emission, deposition, chemistry) is difficult. We demonstrate a new methodology for diagnosing ozone production based on the processing of bonds contained within emitted molecules, the fate of which is determined by the conservation of spin of the bonding electrons. Using this methodology to diagnose ozone production in the GEOS-Chem chemical transport model, we demonstrate its advantages over the standard diagnostic. We show that the number of bonds emitted, their chemistry and lifetime, and feedbacks on OH are all important in determining the ozone production within the model and its sensitivity to changes. This insight may allow future model-model comparisons to better identify the root causes of model differences.

1. Introduction

The chemistry of the troposphere is one of oxidation [Levy, 1973; Kroll et al., 2011]. Organic compounds together with nitrogen and sulfur containing molecules are emitted into the troposphere where they are oxidised into compounds which can either be: absorbed by the biosphere; are involatile enough to form aerosols; can deposit to the surface; or be taken up by clouds and rained out. The oxidation of these compounds is significantly slower than might be expected based on the atmospheric composition of 20% molecular oxygen (O₂). The inefficiency of ground state O₂ as an atmospheric oxidant is due to its electronic structure. With two unpaired electrons it is a spin-triplet (total spin quantum number S=1, giving a term symbol of ³Σ⁺). In
contrast, virtually all trace chemicals emitted into the atmosphere contain only paired electrons and are thus spin-singlets (S=0). From a simplistic perspective (i.e. ignoring nuclear spin interactions, inter-system crossings, nuclear dipole effects etc.) the spin selection rule, $\Delta S=0$, means that the reaction of ground state O$_2$ with most emitted compounds is effectively spin forbidden. Electronically excited O$_2$ ($^1\Delta_g$ or $^1\Sigma_g^+$) is a spin singlet and is more reactive in the atmosphere but low concentrations limit its role [Larson and Marley, 1999]. Instead, atmospheric oxidation proceeds predominantly via reactions with spin-doublet oxygen-derived species (S=½), notably the hydroxyl (OH) and peroxy radicals (RO$_2$ = HO$_2$, CH$_3$O$_2$, C$_2$H$_5$O$_2$, etc.), or spin-singlet species (e.g. ozone (O$_3$)).

One of the few spin-triplet species in the atmosphere other than O$_2$ is the ground state of atomic oxygen (O($^3$P)), which readily undergoes a spin allowed reaction with O$_2$ to produce the spin-singlet O$_3$ molecule. This spin allowed reaction is responsible for the creation of O$_3$ in both the stratosphere, where it forms the protective O$_3$ layer, and the troposphere. The ability of O$_3$ to oxidise other spin-singlet species makes it a powerful oxidant, and it is thus considered a pollutant with negative health effects. Sources of O($^3$P) within the troposphere are limited because solar photons at sufficiently short wavelengths to directly photolyse O$_2$ to O($^3$P) are essentially unavailable.

Aside from the photolysis of O$_3$ itself, the only other significant source of tropospheric O($^3$P) is the photolysis of nitrogen dioxide (NO$_2$) [Crutzen, 1971]. Nitrogen oxides are emitted into the troposphere as nitrogen oxide (NO), which can be oxidised to NO$_2$ by O$_3$ and other oxidants. A large thermodynamic energy barrier prevents oxidation of NO to NO$_2$ by the OH radical [Nguyen et al., 1998], and therefore NO oxidation occurs through reaction with either O$_3$ or RO$_2$. In terms of O$_3$ production, the oxidation of NO by O$_3$ forms a null cycle. Thus only the reaction of NO with RO$_2$ leads to a net production of O$_3$.

Exploring the distribution, source and sinks of tropospheric O$_3$ is a central theme of atmospheric science. Chemical transport models (online and offline) are essential tools enabling this understanding but their validity needs to be continually assessed. Model-model comparison exercises are commonly performed to assess performance, and comparisons of modelled O$_3$ budgets traditionally form part of this assessment [Stevenson et al., 2006; Wu et al., 2007; Wild, 2007; Young et al., 2013]. Ozone production is diagnosed from the flux of NO to NO$_2$ via reaction with each of the
speciated RO2 in the model’s chemical schemes. This approach provides information on the relative importance of the different RO2 in the fast NO + RO2 reactions within the model, but gives very little detail on how the longer time scale model processes (emissions, chemistry, deposition) influence O3 production. Thus exploring the reasons that models differ in their O3 production is difficult and progress has been slow.

A new diagnostic framework that links large scale model drivers such as emission, chemistry, and deposition to O3 production would allow an improved assessment of why model ozone budgets differ. We attempt to provide such a framework here.


The rate of production of tropospheric O3 is limited by the rate of oxidation of NO to NO2, which is in turn limited by the rate of production of peroxy radicals (RO2). Peroxy radicals form through association reactions of hydrogen (H) atoms or alkyl radicals (both spin-doublets, S=½) with O2, forming a highly reactive spin-doublet radical on an oxygen atom. This spin allowed reaction converts spin-triplet O2 that cannot react with spin-singlet pollutants into a spin-doublet O2 containing species that can. As such the formation of RO2 is central to the atmosphere’s oxidation capacity, and its production is limited by the rate of production of H atoms or alkyl radicals. Thus the maximum potential rate of tropospheric O3 production is equal to the rate at which H atoms and alkyl radicals are produced.

Hydrogen atoms and alkyl radicals are predominantly produced via the spin allowed breaking of the spin-pairing between the two electrons in a C or H containing covalent bond (S=0), such as those in hydrocarbons. These spin-pairings can be broken in the atmosphere either chemically or photolytically, with the products necessarily conserving spin. The breaking of a covalent bond by a photon (s=1) can result in two products with S=½ or two products with S=0. Likewise, oxidation by a radical (S = ½) will result in one product with S=0 and one with S=½, because the unpaired electron on the radical reactant pairs with one of the covalent bond electrons to produce a spin-singlet.

Although the majority of RO2 is formed from emitted C or H containing covalent bonds, there are a few notable exceptions. Hydrogen atoms can also be produced through the oxidation of CO to CO2 by OH. During this reaction the coordinate bond
between the C and O atom is broken and the H atom is produced via the breaking of the O-H bond. The other notable exception is the oxidation of an SO\textsubscript{2} lone pair of electrons to SO\textsubscript{3} by OH, where again the H atom produced comes from the OH. In both of these exceptions a spin-singlet electron pairing (CO coordinate bond or SO\textsubscript{2} lone pair) is broken during the production of the H atom, and we can therefore consider these reactions as similar to the breaking of C or H containing covalent bond. For simplicity these spin-singlet electron pairings that can be broken in the troposphere to produce either a H atom or alkyl radical will be referred to as “oxidisable bonds” (C-C, C-H, C=C, CO coordinate bond, S:).

Tropospheric O\textsubscript{3} production occurs through the oxidation of NO by RO\textsubscript{2}. Following the above rationale, these RO\textsubscript{2} are produced during the spin allowed breaking of oxidisable bonds predominantly contained within emitted VOCs. This perspective allows us to build a new metric for the production of tropospheric O\textsubscript{3} based around the spin conserving properties of oxidisable bond breaking. In the extreme case, all oxidisable bonds are photolysed to produce two spin-doublet RO\textsubscript{2} products, which then react exclusively with NO to generate O\textsubscript{3}. Thus at steady state, the maximum rate of O\textsubscript{3} production is equal to the rate of production of RO\textsubscript{2}, which is equal to twice the rate of destruction of the number of oxidisable bonds. This in turn is equal to twice the rate of emission of oxidisable bonds. Deviation from this maximum is determined by:

- The relative importance of processes that produce spin-singlet vs. spin-doublet products during oxidisable bond breaking;
- The fraction of spin-doublet products from oxidisable bond breaking which form RO\textsubscript{2};
- The fraction of RO\textsubscript{2} that go on to oxidize NO to NO\textsubscript{2}.

To illustrate this Fig. 1 shows the tropospheric oxidation of a methane (CH\textsubscript{4}) molecule through various steps to either a carbon dioxide (CO\textsubscript{2}) molecule or a species that is deposited (CH\textsubscript{3}OOH, CH\textsubscript{2}O, CH\textsubscript{3}NO\textsubscript{3}). Methane contains 4 x C-H oxidisable bonds (8 paired bonding-electrons) and as the oxidation proceeds, the number of oxidisable bonds decays to zero. Figure 1 highlights the steps in the tropospheric CH\textsubscript{4} oxidation mechanism that form spin-doublet products, with between 1 and 5 RO\textsubscript{2} produced depending on the oxidation pathway. This compares with the theoretical maximum of 8 if all the original C-H bonds were photolysed to yield 2 spin-doublet products.
Figure 1. Peroxy radical production during the tropospheric oxidation of CH₄.

Moving from left to right, the oxidisable bonds (emitted = red, produced = blue) present in CH₄ are removed via a range of tropospheric processes, indicated by the coloured arrows. The large numbers across top of the figure indicate the number of oxidisable bonds at each stage of this oxidation. The production of RO₂ is indicated by the +1/+2 numbers with the associated process arrows for producing 1 or 2 RO₂ respectively.

The principal atmospheric source of oxidisable bonds is the emission of C-H, C-C and C=C bonds in hydrocarbons, with the only other significant sources being the emission of CO and the chemical production of CO and H₂ during hydrocarbon oxidation. Over a long enough timescale, the global atmosphere can be considered to be in a chemical steady state, where the rate of loss of oxidisable bonds is balanced by the rate of production or emission. Thus the O₃ production rate can be described by equation (1), where the O₃ production metric \( P_{O_3} \) is equal to the number of spin-paired electrons in oxidisable bonds (i.e. twice the sum of the number of oxidisable bonds emitted (\( E_{bonds} \)) and chemically produced (\( P_{bonds} \)), multiplied by the number of spin-doublet radicals produced per oxidisable bond break divided by the maximum of 2 (\( F_{radical} \)), multiplied by the fraction of the radicals produced which are RO₂ (\( F_{RO_2} \)), multiplied by the fraction of RO₂ that goes on to react with an NO to produce an O₃
molecule (FNO). A small correction (I) for the production of RO₂ via reactions of spin-doublet radicals other than those that result in the breaking of oxidisable spin-pairings (e.g. O₃ + OH → HO₂ + O₂) is included.

\[ P_sO_3 = \left( (2 \times (F_{bonds} + P_{bonds}) \times F_{radicals} \times F_{RO_2}) + I \right) \times F_{NO} \]  

3. Implementation

We use the GEOS-Chem model to evaluate this new O₃ production diagnostic. GEOS-Chem is a global chemical transport model of tropospheric chemistry, aerosol and transport (www.geos-chem.org version 9-02). The model is forced by assimilated meteorological and surface fields (GEOS-5) from NASA’s Global Modelling and Assimilation Office, and was run at 4°x5° spatial resolution. The model chemistry scheme includes Oₓ, HOₓ, NOₓ, BrOₓ and VOC chemistry as described in Mao et al. [2013] as are the emissions. The new \( P_sO_3 \) diagnostic has been implemented via the tracking of reactions by type in the GEOS-Chem chemical mechanism file (further details given in the SI). This tracking of reactions enables the fate of all oxidisable bonds as well as the production and loss of all RO₂ within the model to be determined using the standard GEOS-Chem production and loss diagnostic tools. Model simulations were run for 2 years (July 1st 2005 – July 1st 2007) with the first year used as a spin up and the diagnostics performed on the second year.

The standard GEOS-Chem diagnostic for O₃ production (\( PO_3 \)) is shown on the left side of Table 1. This emphasizes the very fast cycling between NO and NO₂, but provides little in terms of higher process level information. The right side of Table 1 shows the new budget for \( P_sO_3 \), which tracks the processing of oxidisable bonds within the model. Both diagnostic methods give the same final answer but our new methodology provides more process level detail. Figure 2 illustrates this new process based approach, showing the flow of emitted oxidisable spin-paired electrons (bonds) to O₃ and the magnitude of the various mechanisms that contribute to and compete with O₃ production. The annual oxidisable bond emission of 389 T mol yr⁻¹ has the potential to create 778 T mol yr⁻¹ of radicals. If all oxidisable bonds were broken by photons to produce two radical products the RO₂ production would be 778 T mol yr⁻¹.

If the oxidisable bonds were instead broken via radical reaction (e.g. OH) then RO₂ production would be 389 T mol yr⁻¹. The various oxidisable bond breaking / removal
pathways within the model result in the production of 280 T mol yr\(^{-1}\) of RO\(_2\), with the remainder largely producing stable spin singlet products.

Of the 280 T mol yr\(^{-1}\) RO\(_2\) produced, 112 T mol yr\(^{-1}\) reacts with NO to produce O\(_3\). The remainder is lost through the reaction or deposition of RO\(_2\) reservoir species (RO\(_2y\) = RO\(_2\) + peroxides + peroxy-acetyl nitrates). For example the production of methylperoxide (CH\(_3\)O\(_2\) + HO\(_2\) = CH\(_3\)OOH) results in the loss of 2 RO\(_2\)’s. However, the reaction of methylperoxide with OH can re-release CH\(_3\)O\(_2\) (CH\(_3\)OOH + OH = CH\(_3\)O\(_2\) + H\(_2\)O). Thus, the production of methylperoxide represents the loss of a HO\(_2\) and the movement of a CH\(_3\)O\(_2\) into a peroxide RO\(_2y\) reservoir species. The deposition of a peroxide molecule is thus the loss of a RO\(_2y\) reservoir species. Notable in Fig. 2 is that the role of PAN and nitrate removal of global RO\(_2y\) is negligible, instead being dominated by peroxide production and loss and the reaction of RO\(_2\) with O\(_3\).

<table>
<thead>
<tr>
<th>PO(_3) / T mol Yr(^{-1})</th>
<th>PO(<em>3) / T mol Yr(^{-1}) (except F(</em>{Radicals}), F(<em>{RO2}) and F(</em>{NO}) which are all unitless)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + HO(_2) → NO(_2)</td>
<td>E(_{bonds})</td>
</tr>
<tr>
<td>NO + CH(_3)O(_2) → NO(_2)</td>
<td>P(_{bonds})</td>
</tr>
<tr>
<td>Other RO(_2) + NO → NO(_2)</td>
<td>F(_{Radicals})</td>
</tr>
<tr>
<td>Other</td>
<td>F(_{RO2})</td>
</tr>
<tr>
<td></td>
<td>Inorganic RO(_2) source</td>
</tr>
<tr>
<td></td>
<td>F(_{NO})</td>
</tr>
<tr>
<td>PO(_3)</td>
<td>112</td>
</tr>
<tr>
<td>P(_3)O(_3)</td>
<td>112</td>
</tr>
</tbody>
</table>

Table 1. Comparison of ozone production diagnostics for GEOS-Chem base simulation. Standard model PO\(_3\) diagnostics (left column) show reactions responsible for NO to NO\(_2\) conversions but provide little process level information. The new P\(_3\)O\(_3\) (right) provides increased information on the processes controlling O\(_3\) production within the model.
Figure 2. Flow of oxidisable bonds to O$_3$ production in the GEOS-Chem base simulation. Arrows are coloured according to process and the arrow thickness is proportional to the flux through that channel. Spin-paired electrons are input as oxidisable bonds into the model (left arrow), with the potential to create 778 T mol yr$^{-1}$ of radicals. The actual fate of these bonds is shown in the central arrow, producing 280 T mol yr$^{-1}$ of RO$_2$, of which 112 T mol yr$^{-1}$ reacts with NO to produce O$_3$ (right arrow).

### 3.1 Emitted oxidisable bonds

The fuel for tropospheric oxidation chemistry is the emission of oxidisable bonds, predominantly in the form of hydrocarbons. The production of tropospheric O$_3$ from the spin-paired bonding electrons emitted into the standard GEOS-Chem model occurs with an efficiency of 14% (112 T mol yr$^{-1}$ molecules of O$_3$ produced / 778 T mol yr$^{-1}$ spin-paired electrons emitted as oxidisable bonds, Fig.2). These spin-paired bonding electrons are predominantly emitted in the form of CH$_4$, isoprene (C$_5$H$_8$) and CO (37%, 28%, and 9% respectively). Oxidisable bonds produced during chemical reactions ($P_{bonds}$), account for 15% of the net source. Figure 3 shows emissions of CO and hydrocarbons in the standard GEOS-Chem simulation in terms of mass of carbon per compound, number of oxidisable bonds per compound and as number of bonds in different oxidisable bond types. The commonly used carbon mass approach splits emissions approximately equally between each of the major sources (CH$_4$ (29%),
Isoprene (32%) and CO (30%). In contrast, the oxidisable bonds accounting approach apportions hydrocarbon emissions 44%, 33% and 11% for CH$_4$, isoprene and CO respectively. This highlights the high number of oxidisable bonds per carbon atom in CH$_4$ (4) compared to isoprene (2.8) and CO (1). Thus efforts to consider emissions on a per-bond basis may provide more insight into chemical processes, as it is these bonds that ultimately determine the chain-like chemistry rather than the mass of carbon atoms. This helps to emphasise the relative importance of CH$_4$ emissions on global tropospheric chemistry compared with other emissions such as isoprene or CO. The type of oxidisable bond emitted is overwhelmingly C-H (71%).

Figure 3. Pie charts showing hydrocarbon emissions in the base GEOS-Chem simulation. Emissions split by carbon mass (left), number of oxidisable bonds (centre) and bond type (right).

The total emission and production of oxidisable bonds has the potential to create 778 T mol yr$^{-1}$ of radicals. However, only 6% of the oxidisable spin-pairings are broken to give the maximum 2 spin-doublet products (e.g. radical channel of CH$_2$O photolysis). The majority (68%) are oxidized via reaction with a spin-doublet species (OH) to produce 1 spin-singlet and 1 spin-doublet product (e.g. OH + VOC). The remaining 26% of spin-paired electrons are removed to form two spin-singlets (e.g. the non-radical channel of CH$_2$O photolysis). Thus, of the 778 Tmol yr$^{-1}$ spin-paired electrons emitted or produced only 265 T mol yr$^{-1}$ (34%) are converted into RO$_2$, with an additional 15 T mol yr$^{-1}$ produced from reactions such as O$_3$ + OH $\rightarrow$ HO$_2$ + O$_2$ (I). The efficiency of O$_3$ production from the available oxidisable bonds is further reduced as only 40% of the 280 T mol yr$^{-1}$ of RO$_2$ produced react with NO to produce NO$_2$. The remainder is lost either through the self-reaction of RO$_2$ or via loss through deposition or reaction of RO$_2$, reservoir species (e.g. peroxides). Thus overall 14% of the emitted bonding electrons go on to make O$_3$. This new O$_3$ production diagnostic shows the impact of processes such as emission, deposition and chemical mechanism, providing significantly more detail than the
standard PO\textsubscript{3} diagnostic approach (Table 1). We now explore the sensitivity of model O\textsubscript{3} production to changing emissions of NO\textsubscript{x} and VOC from the perspective of the two diagnostic methods.

4 Model sensitivities

Understanding model response to changing emissions is an important tool for considering policy interventions. The major controls on O\textsubscript{3} production are emissions of NO\textsubscript{x} and VOCs. We show in Fig. 2 that from the perspective of global O\textsubscript{3} production, oxidisable bond emissions are dominated by CH\textsubscript{4} and isoprene. Figure 4 shows the impact of changing emissions of NO\textsubscript{x}, isoprene and CH\textsubscript{4} on O\textsubscript{3} production from both the perspective of this new methodology and the conventional NO+RO\textsubscript{2} diagnostic approach. The following sections investigate these model responses and use the new diagnostic to provide insight into the processes driving the observed response in O\textsubscript{3} production.
Figure 4. Understanding the effect of NO\textsubscript{x} and VOC emissions on ozone production at the process level. Stack plots showing fractional change in model PO\textsubscript{3} compared to base simulation and associated contributions from the current PO\textsubscript{3} (i) and new P\textsubscript{s}O\textsubscript{3} (ii) diagnostic parameters under changing NO\textsubscript{x} emissions (a), effective CH\textsubscript{4} emission (b) and isoprene emission (c).

4.1 NO\textsubscript{x} emissions

Figure 4a diagnoses the relative response of GEOS-Chem O\textsubscript{3} production to changing NO\textsubscript{x} emissions, using simulations where NO\textsubscript{x} emissions from anthropogenic, biomass burning, biofuels, soil and lighting sources were multiplied by factors of 0.5 - 2. Increasing NO\textsubscript{x} emissions increases O\textsubscript{3} production. The standard RO\textsubscript{2}+NO diagnostic (Fig. 4a(i)) shows that fractional contributions to the total change in PO\textsubscript{3} from HO\textsubscript{2} (67%), methyl-peroxy (MO\textsubscript{2}) (25%), and other RO\textsubscript{2} (8%) remain approximately constant across the NO\textsubscript{x} emission range investigated. This diagnostic provides little detail on the processes driving the change in O\textsubscript{3} production under changing NO\textsubscript{x} emissions. In contrast, Fig. 4a(ii) is based on the new P\textsubscript{s}O\textsubscript{3} diagnostic and shows a range of process level changes occurring as NO\textsubscript{x} emissions change.

4.1.1 Impact of changing NO\textsubscript{x} emission on F\textsubscript{NO}

Unsurprisingly, as NO\textsubscript{x} emissions increase the fraction of RO\textsubscript{2} reacting with NO to produce NO\textsubscript{2} (F\textsubscript{NO}) increases (red section in Fig. 4a(ii)). However, this impact only accounts for around 40% of the increase in P\textsubscript{s}O\textsubscript{3}. Figure 5a shows the fractional change in all the P\textsubscript{s}O\textsubscript{3} efficiency parameters and the global mean NO\textsubscript{x} concentration as a function of the changing NO\textsubscript{x} emission. As NO\textsubscript{x} emissions increase the increase...
in NO$_x$ concentration in the model is somewhat dampened. Halving the NO$_x$ emission leads to NO$_x$ burdens dropping by ~35%, and doubling leads to an increase of 95%.

This dampening is due to the impact of NO$_x$ emissions on OH (see section 4.1.2), which is the dominant sink for NO$_x$. Increasing NO$_x$ increases OH concentrations, which in turn shortens the NO$_x$ lifetime thus dampening the response of concentration to emission.

![Figure 5. Fractional change in new P$_x$O$_y$ diagnostic parameters from base run against changing NO$_x$ emission (a); effective CH$_4$ emission (b); and isoprene emission (c).](image)
distribution of $F_{NO}$ values across all model grid boxes for the base simulation and the
half and doubled NO$_x$ emission simulations (black, blue and red lines respectively).

For example, in a grid-box in the continental boundary layer where RO$_2$ reacts
overwhelmingly with NO, doubling the NO$_x$ emission may move $F_{NO}$ from 0.90 to
0.95 but it can’t double it. Similarly, in the remote boundary layer where RO$_2$ reacts
overwhelmingly with other RO$_2$ doubling NO$_x$ emissions may move $F_{NO}$ from 0.3 to
0.4 but again it doesn’t double. Thus the geographical spread of NO$_x$ chemistry limits
the change in $F_{NO}$ caused by changing NO$_x$ emissions. The spatial variability in the
new $P,O_3$ diagnostic parameters shows that this approach has significant potential in
the analysis of regional O$_3$ budgets as well as global.

![Graph showing distribution of $F_{NO}$ values](image)

**Figure 6.** Effect of NO$_x$ emission on distribution of $F_{NO}$ values (log scale). $F_{NO}$ values for each model grid box in the base and NO$_x$ emission x 0.5 and x 2 simulations, split into 50 x 0.02 width bins.

4.1.2 Impact of changing NO$_x$ emission on $E_{bonds}$

Figure 4a(ii) shows that 60% of the response in $P,O_3$ to changing NO$_x$ emission is due
to factors other than $F_{NO}$, with 40% of the increase due to changes in the emissions
($E_{bonds}$: 32%) and chemical production ($P_{bonds}$: 8%) of oxidizable bonds. This increase
in $E_{bonds}$ is surprising given VOC emissions are unchanged in these simulations.
However, increasing NO$_x$ emissions results in an increased OH concentration in the
model, which then leads to an increase in CH$_4$ oxidation. GEOS-Chem fixes CH$_4$
concentrations resulting in an increase in the effective CH$_4$ emissions as OH
concentrations increase, causing an increase in the total bond emission ($E_{\text{bonds}}$). Figure
7 shows the response of model global mean OH concentration and effective CH$_4$ bond
emission as a function of global mean NO$_x$ concentration across the simulations where
the base NO$_x$ emissions are multiplied by factors from 0.5 to 2. More CH$_4$ oxidation
also leads to more CH$_2$O production and in turn more CO production ($P_{\text{CO}}$),
accounting for a significant fraction of the increase in this term.

Figure 7. Global mean OH concentration and effective CH$_4$ emission as a
function of [NO$_x$]. Plot shows effective CH$_4$ emission tracks OH concentration in
simulations where the NO$_x$ emission was increased or decreased from the base
simulation. Note X-axis log scale.

4.1.3 Impact of changing NO$_x$ emission on $F_{\text{radicals}}$, $F_{\text{RO2}}$ and $I$
The fraction of radicals produced from bond oxidation ($F_{\text{radicals}}$) and the fraction of
those radicals which are RO$_2$ ($F_{\text{RO2}}$) show slight positive increase with NO$_x$ emission,
accounting for 9% and 6% of the change in $P_{\text{O}_3}$ respectively. This reflects changes in
the partitioning of the fate of the oxidisable bonds, and is largely due to the changes in
OH. As OH increases with NO$_x$ emission, the rate of chemical oxidation of bonds
increases at the expense of other losses, in particular deposition. The inorganic RO$_2$
source term ($I$) also correlates with NO$_x$ emission, as it is largely determined by the
concentrations of OH and O$_3$. This change accounts for 5% of the observed change in $P_sO_3$.

Thus, with this new diagnostic methodology it is evident that only 40% of the model O$_3$ production response to changing NO$_x$ emission is due to the direct effect of increasing NO concentration on the rate of RO$_2$ + NO reactions. Another 40% is due to fixing the concentration of CH$_4$ within the model, with the final 20% due to the increased OH competing for the available oxidisable bonds.

### 4.2 Changing effective CH$_4$ emissions

Figure 4b shows the effect on the O$_3$ production diagnostic of varying the prescribed CH$_4$ concentrations by factors of between 0.5 and 2 from the base simulation. The CH$_4$ emission rate (plotted) is diagnosed from the loss rate of CH$_4$ to reaction with OH, the only CH$_4$ loss in the model. We describe this as the effective CH$_4$ emission.

As effective CH$_4$ emission increases, O$_3$ production also increases. The standard diagnostic (Fig.4b(i)) shows that this increase occurs through an increased rate of reaction of HO$_2$ and CH$_3$O$_2$ with NO, as would be expected as these are the RO$_2$ produced during CH$_4$ oxidation. The rate of other RO$_2$ + NO reactions actually decreases slightly as CH$_4$ emissions increase, due to lower OH concentrations and increased competition for NO from HO$_2$ and CH$_3$O$_2$. The new diagnostic (Fig.4b(ii)), however, shows the increase in O$_3$ production with increasing effective CH$_4$ emission is not simply a result of more HO$_2$ and MO$_2$.

#### 4.2.1 Impact of changing effective CH$_4$ emission on $F_{NO}$

The observed change in $P_sO_3$ is around one third smaller than would be expected from the increase in the oxidisable bond emission ($E_{bonds}$) and bond production ($P_{bonds}$) terms alone. This is due to a countering decrease in the other efficiency parameters with increasing effective CH$_4$ emission. Figure 5b shows the fractional change in all the efficiency parameters as a function of the changing effective CH$_4$ emission. The decrease in the fraction of RO$_2$ reacting with NO to produce NO$_2$ ($F_{NO}$) is driven by increasing O$_3$ concentrations, which push the NO/NO$_2$ ratio towards NO$_2$. This reduces the availability of NO to react with RO$_2$ thereby reducing O$_3$ production. This shift in the NO/NO$_2$ ratio also increases NO$_x$ loss within the model with increasing CH$_4$ emission, as the increased CH$_4$ oxidation increases RO$_2$ concentrations resulting
in larger losses of NO₂ via compounds such as peroxyacetyl nitrate (PAN) and peroxy nitric acid (PNA).

### 4.2.2 Impact of changing effective CH₄ emission on Eₚonds

As CH₄ is the largest single source of oxidisable bonds (Fig. 3), increasing the effective CH₄ emission results in an increase in Eₚonds. Changing the fraction of total emitted oxidisable bonds from CH₄ does however have significant consequences on the loss mechanisms of these bonds, which influences the other efficiency parameters. The pie charts in Fig. 8 show the split of oxidisable bond loss mechanisms in the base simulation and those with the CH₄ concentration fields multiplied by 0.5 and 2. As the effective CH₄ emission increases the fraction of bonds lost via OH decreases, despite the actual number of oxidisable bonds lost to OH increasing. A larger fraction of bonds are therefore lost via the other mechanisms shown in Fig. 8 rather than reaction with OH. As CH₄ removal occurs predominantly in the free troposphere, increasing the effective CH₄ emission also results in a reduction in the fraction of oxidisable bonds lost via deposition. The largest fractional increase in bond loss mechanism with increasing effective CH₄ emission is for photolysis, with the increase in the “other” fraction due to increased loss of bonds to the stratosphere with increasing CH₄. The fraction of bonds lost via other chemistry (e.g. non-OH radical oxidation and RO₂ self reactions) remains approximately constant across the effective CH₄ emission scenarios investigated.

![Figure 8. Oxidisable bond loss mechanisms under changing CH₄ emissions. Pie charts showing fractional loss mechanisms for oxidisable bonds in model simulations with 0.5 x CH₄ concentration field (a), base simulation (b) and 2 x CH₄ concentration field.](image)
4.2.3 Impact of changing effective CH₄ emission on $F_{\text{radicals}}$, $F_{\text{RO2}}$ and $I$

The fraction of oxidisable bonds that goes on to produce radicals ($F_{\text{radicals}}$) and the fraction of these that are RO₂ ($F_{\text{RO2}}$) also decrease with increasing effective CH₄ emissions. This is due to decreasing global OH concentration resulting from increased loss by reaction with CH₄ and a decreasing NO concentration. This favours bond loss via pathways such as deposition rather than those that produce RO₂. These changes are predominantly due to the chemistry of CH₂O. As shown in Fig. 1, the oxidation of CH₂O occurs either via reaction with OH or photolysis, with OH reaction yielding 1 RO₂ from the net breaking of 2 spin-singlet bonds, and the two photolysis channels yielding either 0 x RO₂ (spin-singlet products molecular channel) or 2 x RO₂ (spin-doublet products radical channel), with the molecular channel being dominant. The reduction in OH concentration with increasing CH₄ means photolysis increases its competition as a bond loss mechanism, which has the effect of reducing the average RO₂ production per CH₂O oxidised. The increase in the fraction of total bonds lost through the CH₂O photolysis as CH₄ increases thus results in a reduction in both $F_{\text{radicals}}$ and $F_{\text{RO2}}$. The reduction in $F_{\text{radicals}}$ due to changing CH₂O fate, however, is largely offset by a reduction in the fraction of bonds lost via deposition as CH₄ increases. This is due to the long lifetime of CH₄ compared with the majority of other sources of oxidisable bonds, resulting in oxidation increasing fractionally in the free troposphere where deposition is a less significant loss mechanism than in the boundary layer.

4.3 Changing isoprene emission

The species through which the oxidisable bonds are emitted has a significant impact on $O_3$ production, due to their subsequent removal mechanisms. For example, in a simulation where the only emission of oxidisable bonds is CO, $F_{\text{radicals}}$ is 0.5 and $F_{\text{RO2}}$ is 1 as the only CO sink is reaction with OH to produce one HO₂ (OH + CO $\rightarrow$ HO₂ + CO₂). The CO coordinate bond, which in theory has the potential to produce 2 radicals, only produces 1 radical, which is an RO₂. Isoprene has the most complex chemistry in the model and is the second largest source of bonds into the atmosphere (Fig. 3). Figure 4c shows the response of the two $O_3$ production diagnostics to varying the isoprene emission within the model. The standard diagnostic (Fig.4c(i)) shows that the most significant increase in $PO_3$ from
increasing isoprene emissions is from NO + HO\(_2\) and non-MO\(_2\) peroxy radicals, with a smaller increase from MO\(_2\). The new \(P,\text{O}_3\) diagnostic (Fig.4c(ii)) again provides more insight, showing significant offsetting of around a half between the terms.

### 4.3.1 Impact of changing isoprene emission on \(F_{\text{NO}}\)

The increased isoprene emission leads to a similar change in the magnitude of the total number of oxidisable bonds emitted (\(E_{\text{bonds}}\)) as the simulations in which effective CH\(_4\) emission were varied. However, the countering decrease in all of the efficiency parameters is much larger for isoprene than for CH\(_4\). Figure 5c shows the fractional change in the new \(P,\text{O}_3\) ozone production diagnostic parameters as a function of isoprene emissions compared to the base simulation. The change in \(F_{\text{NO}}\) is due to both a decrease in global mean NO\(_x\) concentrations with increasing isoprene and the spatial distribution of isoprene emissions. With the majority of global isoprene emissions being in regions with low NO\(_x\) emissions, and thus low values of \(F_{\text{NO}}\), Figure 9 shows a decrease in global mean NO\(_x\), and global mean OH, concentrations with increasing isoprene emissions, however, the effect is less than that seen when CH\(_4\) is responsible for the same increase in oxidisable bond emission. This is due in a large part to the spatial scales over which the two compounds impact.

![Figure 9](attachment:figure9.png)

**Figure 9.** The effect of oxidisable bond parent species on OH, HO\(_2\), O\(_3\) and NO\(_x\) concentrations. Global mean [OH], [HO\(_2\)], [O\(_3\)] and [NO\(_x\)] for simulations where the effective CH\(_4\) emission (solid lines) and isoprene emission (dashed lines) were changed, against model \(E_{\text{bonds}}\). The dashed vertical green line indicates \(E_{\text{bonds}}\) in the base simulation (330 T mol yr\(^{-1}\)).
4.2.2 Impact of changing isoprene emission on $E_{\text{bonds}}$

As isoprene is the second largest source of oxidisable bonds (Fig. 3), increasing the isoprene emission results in a significant increase in $E_{\text{bonds}}$. Differences in both the spatial distribution of emissions and the oxidation chemistry of isoprene and CH$_4$, however, means that the impact of the increases in $E_{\text{bonds}}$ on O$_3$ production are significantly different for the two compounds. This is predominantly because the fraction of oxidisable bonds that are physically deposited for isoprene is high compared to those emitted as CH$_4$. This increase is due to i) the higher solubility of isoprene oxidation products compared to those of CH$_4$, and ii) the higher reactivity of isoprene means its oxidation occurs in the boundary layer where both dry and wet deposition is most effective.

Figure 10 shows the split of oxidisable bond loss mechanisms in the base simulation and those with the isoprene emissions multiplied by 0.5 and 2. The complex myriad of products formed during the isoprene oxidation mechanism also results in the production of many highly oxygenated multifunctional compounds with high Henry’s law solubility constants, meaning they are more readily lost to deposition.

Figure 10. Oxidisable bond loss mechanisms under changing isoprene emissions.

Pie charts showing fractional loss mechanisms for oxidisable bonds in model simulations with 0.5 x isoprene emission (a), base simulation (b) and 2 x isoprene emission (c).

Increasing the isoprene emission also has a slight offsetting impact on the effective CH$_4$ emission, as increased isoprene concentrations decrease OH concentrations, and thus decrease the effective CH$_4$ emission. A doubling in isoprene emission causes a 6% reduction in the effective emission of CH$_4$. 

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4.3.3 Impact of changing isoprene emission on $F_{\text{radicals}}$, $F_{\text{RO2}}$ and $I$

As shown in Fig. 3c(ii), increasing the isoprene emission results in a reduction in all $P_3O_3$ efficiency parameters. The reductions in $F_{\text{radicals}}$ is due to the higher fraction of oxidisable bonds that are lost via non-radical forming pathways (e.g. deposition) for isoprene relative to the other main oxidisable bond emission sources CH$_4$ and CO. The slight decreases of $F_{\text{RO2}}$ and $I$ with increasing isoprene emission are predominantly due to changes in OH and NO$_x$ (Fig. 9).

The complex chemistry of isoprene oxidation combined with the spatial distribution of isoprene emissions means the increase in O$_3$ production due to increases in isoprene emission alone (i.e. if the increase was via CO instead of isoprene).

5. Conclusions

We have shown that this bond-focused approach to O$_3$ production provides a significantly more detailed understanding of the processes involved. The role of modelled VOC emissions and O$_3$ burden has been reported previously [Wild, 2007; Young et al., 2013]. However previous efforts extending this to a general process led approach has not been successful. This new approach provides a tool with which the processes controlling O$_3$ production can be investigated, and a metric by which different emissions can be compared. For example, the differing chemistry of isoprene and CH$_4$ shows that even though their emissions of carbon mass are comparable, the atmosphere responds in different ways, with the isoprene bonds being less effective in producing O$_3$ than CH$_4$ bonds. By quantifying multiple steps in the O$_3$ production process, competing changes in the system become apparent (as shown in Fig. 4b(ii) and c(ii)) and are thus testable. This enables the effect of model approximations on O$_3$ production to be quantified (e.g. the effect of NO$_x$ on CH$_4$ emissions when using CH$_4$ concentration fields).

This new diagnostic also points towards the importance of observational datasets for assessing our understanding of tropospheric chemistry. Although the budget presented in Fig. 2 provides an annually integrated global estimate it points towards local comparisons that can be made to assess model fidelity. Comparisons, both their magnitude and their ratios, between observed and modelled bond concentration, bond emission and loss fluxes (e.g. OH reactivity [Yang et al., 2016] or depositional fluxes
Wesely and Hicks, 2000), and O$_3$ production [Cazorla and Brune, 2010] would all provide comparisons for outputs from the $P,O_3$ diagnostic and help assess model performance.

Another potentially important application is in model-model comparisons. Increases in our understanding of why different models calculate different O$_3$ production and burdens has been slow [Stevenson et al., 2006; Wu et al., 2007; Young et al., 2013]. A comparison between models based on this methodology may well help identify at a process level why models differ in their O$_3$ production. The application of this diagnostic to regional O$_3$ production should also increase insight into the processes controlling model O$_3$. 
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**Author contributions**

All work presented here was conceived by P.M.E. and M.J.E. The implementation, model simulations and analysis were carried out by P.M.E., and the manuscript was written by P.M.E. with substantial input from M.J.E..

**Additional information**

The authors declare no competing financial interests.

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