Uncertainties in isoprene photochemistry and emissions: implications for the oxidative capacity of past and present atmospheres


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1. How has the atmospheric oxidative capacity varied over Earth's history? What are the dominant controlling factors?

Murray et al. (2014), Table 1

<table>
<thead>
<tr>
<th>Last Glacial Maximum [LGM, 19-23 ka]</th>
<th>ΔOH</th>
<th>Pre-industrial</th>
<th>ΔOH</th>
<th>Present-day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-60 to +56 %</td>
<td></td>
<td>-30 to +60 %</td>
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</tbody>
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2. What drove past natural variations in atmospheric CH₄ concentration?

Last Glacial Maximum 350 ppbv

Pre-industrial 700 ppbv

Wetland emissions source vs. OH sink

3. How can we reduce the uncertainties of anthropogenic radiative forcing estimates?

Uncertainties largely due to those in radiative forcing of short-lived climate forcers.

IPCC AR5 SPM (2013)
Recent developments in isoprene emissions & photochemistry

(1) The sensitivity of plant isoprene emissions to atmospheric [CO₂]

(2) The isoprene photo-oxidation scheme & heterogeneous HO₂ uptake

- OH-recycling in high-isoprene, low-NOₓ regions?
- Efficacy of HO₂ uptake by aerosols?
  (Paulot et al., 2009a, b)
  (Mao et al., 2013c)

How do these recent developments affect existing model estimates of the oxidative capacity of LGM and preindustrial atmospheres?
ICECAP: simulating the chemical composition of past atmospheres

Method: Perform sensitivity experiments using the ICE age Chemistry And Proxies (ICECAP) climate-biosphere-chemistry model framework, testing 3 different chemistry schemes, with or without considering the CO$_2$-sensitivity of plant isoprene emissions.
The new isoprene photochemistry scheme leads to higher OH, which is dampened by the new HO\textsubscript{2} uptake scheme.

C1: old isoprene + HO\textsubscript{2} uptake
C2: new isoprene + old HO\textsubscript{2} uptake
C3: new isoprene + new HO\textsubscript{2} uptake

The 2 LGM scenarios differ in the degree of cooling of tropical SSTs.

For a given climate scenario, the largest source of uncertainties in global mean OH arises from different isoprene chemical schemes.

Achakulwisut \textit{et al.}, in review
Sensitivity of OH to uncertainties in isoprene emissions

Consideration of CO$_2$-sensitivity leads to higher isoprene emissions in the past, resulting in reduced global OH.

Achakulwisut et al., in review
Sensitivity of changes in OH relative to the Preindustrial

Percent change in OH relative to the respective Preindustrial scenario (%)

Under the old isoprene chemistry scheme, changes in global OH relative to the Preindustrial are highly sensitive to uncertainties in isoprene emissions.

C1: old isoprene + HO₂ uptake

Achakulwisut et al., in review
Changes in global OH relative to the Preindustrial do not exceed 10% under the new isoprene chemistry scheme.

C2: new isoprene + old HO₂ uptake

C3: new isoprene + new HO₂ uptake

Achkulwisut et al., in review
Changes in SOA relative to Preindustrial are highly sensitive to estimates of the global isoprene burdens.

Our results suggest that SOA reductions may have amplified regional warming in the present but minimized regional cooling at the LGM, relative to the preindustrial.
1. Changes in the tropospheric ozone burden relative to the Preindustrial are insensitive to the uncertainties tested in this study. Relative to the preindustrial, the absolute magnitude of the RF from the change in tropospheric ozone at the LGM may be comparable to that of the present day.

2. We find little variability in the implied LGM-preindustrial difference in methane emissions with respect to the uncertainties in isoprene photochemistry and emissions tested in this study. But values are larger than those estimated from wetland emissions models.

3. The linear relationship between tropospheric mean OH and tropospheric mean ozone photolysis rates, water vapor, and total emissions of NO$_x$ and reactive carbon – first reported in Murray et al. (2014) – does not hold across all periods with the new isoprene photo-oxidation mechanism.