

# Isoprene Oxidation Mechanisms: Modelling OH and HO<sub>2</sub>

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## Introduction

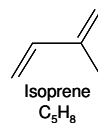
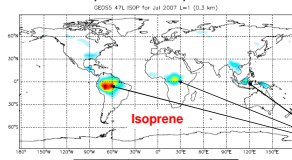
Tropical forests emit significant amounts of volatile organic compounds (VOCs)  
 Isoprene is the dominant reactive VOC emitted into the atmosphere<sup>1</sup>  
 Isoprene and other VOCs are removed from the atmosphere by oxidation processes  
 Atmospheric oxidation is largely controlled by OH and HO<sub>2</sub> radicals – HO<sub>x</sub>  
 ⇒ Isoprene and VOC emissions have a significant impact on HO<sub>x</sub>  
 ⇒ Isoprene and VOC emissions affected by changes to land use  
 ⇒ Changes to HO<sub>x</sub> chemistry affect radiatively active gases such as O<sub>3</sub> and CH<sub>4</sub>

Isoprene reacts rapidly with OH  
 ⇒ Low OH concentrations predicted in regions with high isoprene emissions

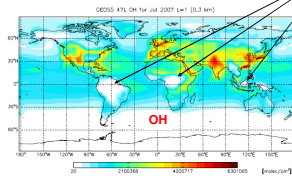
GABRIEL project in Amazonia observed unexpectedly high OH over forested regions<sup>2</sup>  
 ⇒ OH concentrations cannot be explained by current level of understanding  
 ⇒ OH concentrations underpredicted by box models and global models<sup>3,4</sup>

Several experimental and theoretical studies suggest potential additional OH sources in isoprene oxidation<sup>5-8</sup>

2007 GEOS-Chem (GEOS5 v8-02-03) surface concentrations



High isoprene concentrations expected to titrate OH in low NO<sub>x</sub> regions



Benchmark GEOS-Chem simulations predict low OH concentrations in regions of high isoprene and low NO<sub>x</sub>

**Isoprene oxidation mechanisms tested against observations of OH and HO<sub>2</sub> during Oxidant and Particle Photochemical Processes (OP3) to improve understanding of atmospheric oxidation in tropical forest regions**

## OP3 Field Campaign

Oxidant and Particle Photochemical Processes, Borneo 2008  
 Ground, tower and aircraft measurements<sup>9</sup>  
 ⇒ O<sub>3</sub>, CO, NO, NO<sub>2</sub>, VOCs, OH, HO<sub>2</sub>, RO<sub>2</sub>, j(NO<sub>2</sub>), j(O<sup>1</sup>D)



OH and HO<sub>2</sub> measured by low pressure Laser Induced Fluorescence (LIF)<sup>10,11</sup>  
 ⇒ Fluorescence Assay by Gas Expansion (FAGE)  
 ⇒ On-resonance detection of OH at ~ 308 nm  
 ⇒ HO<sub>2</sub> converted by chemical titration to OH

## Model Approach

Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC)<sup>12,13</sup>  
 ⇒ Flexible zero-dimensional box model constrained to observations  
 ⇒ Photolysis rates from TUV with cloud correction factors from observed j(NO<sub>2</sub>)  
 ⇒ Model run forwards to steady state to calculate concentrations of OH and HO<sub>2</sub>

Chemistry described by the Master Chemical Mechanism (MCM) v3.1  
 ⇒ Near explicit degradation schemes<sup>14,15</sup>  
 ⇒ Use of Kinetic Pre-Processor (KPP) enables easy integration of different chemical schemes<sup>16</sup>

## Model Performance

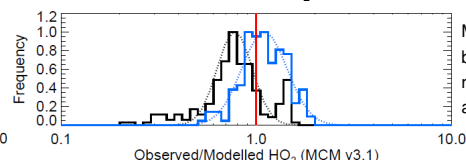
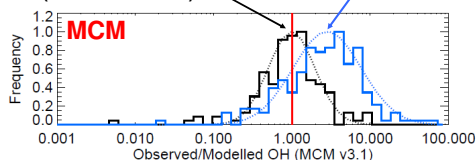
MCM chemistry significantly underpredicts OH<sup>11</sup>  
 ⇒ Probability distribution functions of observed to modelled ratios of OH show significant differences for data points with isoprene above and below 15 ppt  
 ⇒ Model failure for OH is worse for data points with high isoprene concentrations  
 ⇒ No dependence of observed to modelled ratio for HO<sub>2</sub> on isoprene

**Air masses not influenced by isoprene show good model agreement for OH (obs:mod ratio ~1)**

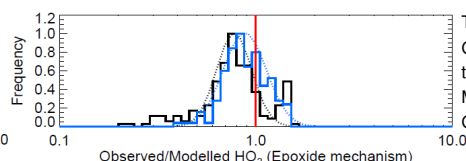
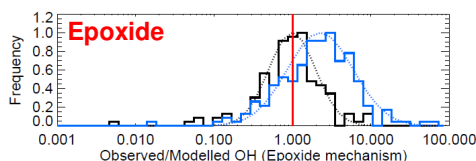
**Air masses influenced by isoprene show significant model underestimate for OH (obs:mod ratio ~5)**

Experimental and theoretical studies suggest several potential sources of OH

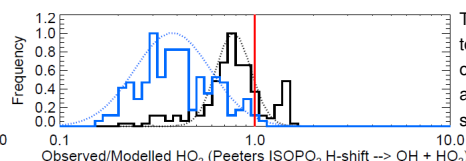
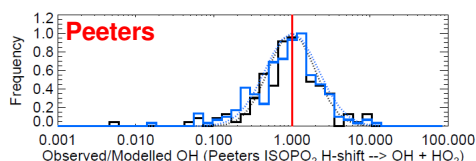
- ⇒ Direct production of OH from isoprene + OH<sup>4</sup>
- ⇒ Conversion of HO<sub>2</sub> to OH by an unknown species<sup>17</sup>
- ⇒ H-shifts in ISOPO<sub>2</sub> radicals to produce OH and HO<sub>2</sub><sup>7</sup>
- ⇒ Production of OH from HO<sub>2</sub> + RO<sub>2</sub><sup>5</sup>
- ⇒ Epoxide formation, with production of OH<sup>6</sup>



MCM chemistry underpredicts OH for air masses impacted by isoprene, but shows good model agreement (obs:mod ratio ~ 1) for OH for air masses not impacted by isoprene and for HO<sub>2</sub>.



The epoxide mechanism<sup>6</sup> currently available for use in GEOS-Chem shows little difference for OH compared to the MCM. Differences observed for HO<sub>2</sub> compared to the MCM result from differences in k<sub>HO2+ISOPO2</sub> between the GEOS-Chem mechanism and the MCM.



The Peeters mechanism<sup>7</sup> gives a significant improvement to the modelled OH, showing good agreement between the observed and modelled OH. However, this mechanism also produces large amounts of HO<sub>2</sub> leading to a significant model overestimate for HO<sub>2</sub>.

Probability distribution functions of observed to modelled ratios of OH (right hand panels) and HO<sub>2</sub> (left hand panels) for data points with isoprene below 15 ppt (black) and isoprene above 15 ppt (blue). The red line indicates an observed to modelled ratio of 1.

**Mechanisms investigated thus far cannot successfully reproduce observations of both OH and HO<sub>2</sub> during OP3**

## Conclusions

Isoprene oxidation is poorly understood and misrepresented in models  
 ⇒ Leads to poor replication of OH observations in high isoprene low NO<sub>x</sub> environments  
 ⇒ Could have important consequences for global modelling of radiatively active gases such as O<sub>3</sub> and CH<sub>4</sub>

⇒ MCM chemistry significantly underpredicts OH observations during OP3  
 ⇒ Standard chemistry scheme in GEOS-Chem does not provide an accurate description of HO<sub>x</sub> concentrations in high isoprene and low NO<sub>x</sub> regions  
 ⇒ Epoxide scheme<sup>6</sup> currently available for use in GEOS-Chem has little impact on modelled OH concentrations but does improve HO<sub>2</sub>  
 ⇒ Peeters mechanism<sup>7</sup> gives significant improvements to the modelled OH but results in model overprediction of HO<sub>2</sub>

Thus far we have been unable to successfully model OH and HO<sub>2</sub> during OP3 using isoprene oxidation mechanisms available in the literature

**Further laboratory studies of isoprene oxidation chemistry are required**

## Acknowledgements

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