

Isoprene Oxidation Mechanisms: Modelling OH and HO₂

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Introduction

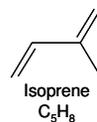
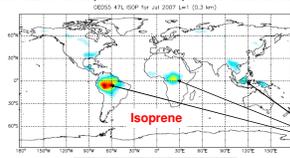
Tropical forests emit significant amounts of volatile organic compounds (VOCs)
 Isoprene is the dominant reactive VOC emitted into the atmosphere¹
 Isoprene and other VOCs are removed from the atmosphere by oxidation processes
 Atmospheric oxidation is largely controlled by OH and HO₂ radicals – HO_x
 ⇒ Isoprene and VOC emissions have a significant impact on HO_x
 ⇒ Isoprene and VOC emissions affected by changes to land use
 ⇒ Changes to HO_x chemistry affect radiatively active gases such as O₃ and CH₄

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

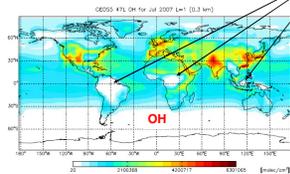
GABRIEL project in Amazonia observed unexpectedly high OH over forested regions²
 ⇒ OH concentrations cannot be explained by current level of understanding
 ⇒ OH concentrations underpredicted by box models and global models^{3,4}

Several experimental and theoretical studies suggest potential additional OH sources in isoprene oxidation⁵⁻⁸

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



High isoprene concentrations expected to titrate OH in low NO_x regions



Benchmark GEOS-Chem simulations predict low OH concentrations in regions of high isoprene and low NO_x

Isoprene oxidation mechanisms tested against observations of OH and HO₂ 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 measurements⁹
 ⇒ O₃, CO, NO, NO₂, VOCs, OH, HO₂, RO₂, j(NO₂), j(O¹D)



OH and HO₂ measured by low pressure Laser Induced Fluorescence (LIF)^{10,11}
 ⇒ Fluorescence Assay by Gas Expansion (FAGE)
 ⇒ On-resonance detection of OH at ~ 308 nm
 ⇒ HO₂ converted by chemical titration to OH

Model Approach

Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC)^{12,13}
 ⇒ Flexible zero-dimensional box model constrained to observations
 ⇒ Photolysis rates from TUV with cloud correction factors from observed j(NO₂)
 ⇒ Model run forwards to steady state to calculate concentrations of OH and HO₂

Chemistry described by the Master Chemical Mechanism (MCM) v3.1
 ⇒ Near explicit degradation schemes^{14,15}
 ⇒ Use of Kinetic Pre-Processor (KPP) enables easy integration of different chemical schemes¹⁶

Model Performance

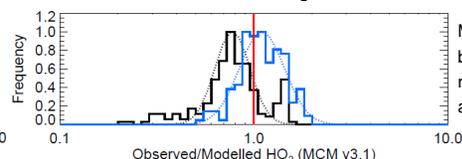
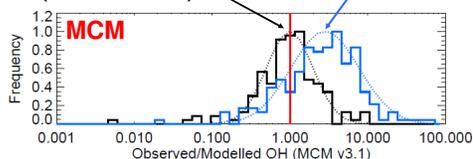
MCM chemistry significantly underpredicts OH¹¹
 ⇒ Probability distribution functions of observed to modelled ratios of OH show significant differences for data points with isoprene above and below 15 ppt
 ⇒ Model failure for OH is worse for data points with high isoprene concentrations
 ⇒ No dependence of observed to modelled ratio for HO₂ on isoprene

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

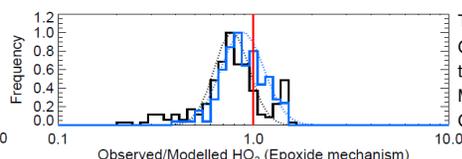
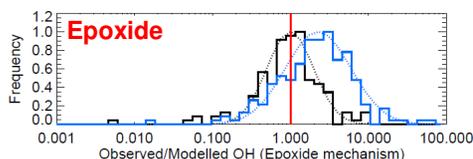
Air masses influenced by isoprene show significant model underestimate for OH (obs:mod ratio ~5)

Experimental and theoretical studies suggest several potential sources of OH

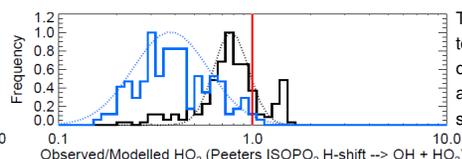
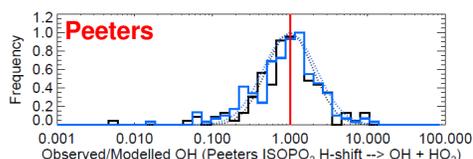
- ⇒ Direct production of OH from isoprene + OH⁴
- ⇒ Conversion of HO₂ to OH by an unknown species¹⁷
- ⇒ H-shifts in ISOPO₂ radicals to produce OH and HO₂⁷
- ⇒ Production of OH from HO₂ + RO₂⁵
- ⇒ Epoxide formation, with production of OH⁶



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 HO₂.



The epoxide mechanism⁶ currently available for use in GEOS-Chem shows little difference for OH compared to the MCM. Differences observed for HO₂ compared to the MCM result from differences in k_{HO2+ISOPO2} between the GEOS-Chem mechanism and the MCM.



The Peeters mechanism⁷ 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 HO₂ leading to a significant model overestimate for HO₂.

Probability distribution functions of observed to modelled ratios of OH (right hand panels) and HO₂ (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 HO₂ during OP3

Conclusions

Isoprene oxidation is poorly understood and misrepresented in models
 ⇒ Leads to poor replication of OH observations in high isoprene low NO_x environments
 ⇒ Could have important consequences for global modelling of radiatively active gases such as O₃ and CH₄

⇒ MCM chemistry significantly underpredicts OH observations during OP3
 ⇒ Standard chemistry scheme in GEOS-Chem does not provide an accurate description of HO_x concentrations in high isoprene and low NO_x regions
 ⇒ Epoxide scheme⁶ currently available for use in GEOS-Chem has little impact on modelled OH concentrations but does improve HO₂
 ⇒ Peeters mechanism⁷ gives significant improvements to the modelled OH but results in model overprediction of HO₂

Thus far we have been unable to successfully model OH and HO₂ during OP3 using isoprene oxidation mechanisms available in the literature

Further laboratory studies of isoprene oxidation chemistry are required

Acknowledgements

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