

New insights in isoprene photooxidation: from chamber studies to global model

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Introduction

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- Low NO_x : very poor understanding due to experimental challenges
- Aerosol: what are the gas-phase precursors of isoprene-originating aerosols

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Unfortunately, everything is intermingled: isoprene still accounts for a very large fraction of the uncertainty in atmospheric chemistry (past-present-future)

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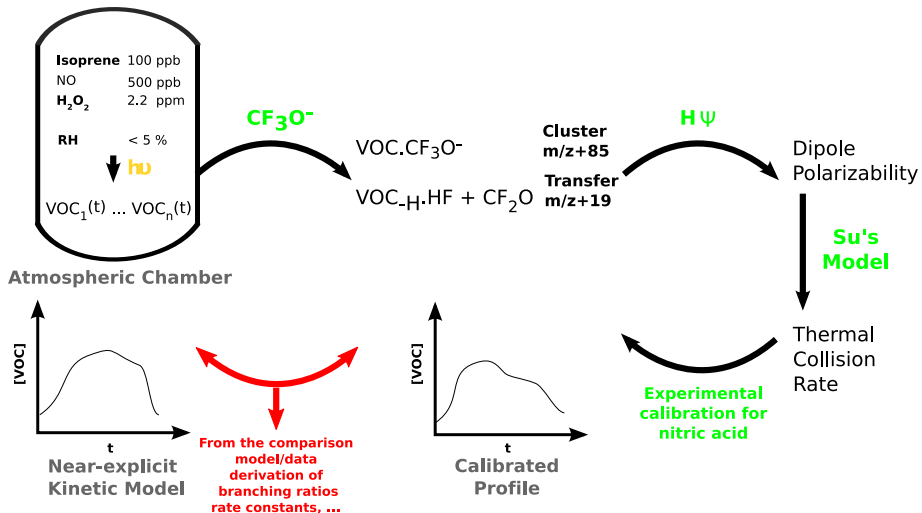
Climate change : CO₂ vs Temperature influence

Outline

1 Chamber studies

2 GEOS-Chem

Framework



Crouse et al. 2006, Paulot et al. 2009

Advantages

- Fast and direct measurements of a wide range of VOC (organic nitrates, small carboxylic acids, organic peroxides)
- Measurement of inorganic species: HONO, HO₂NO₂, H₂O₂, HNO₃, N₂O₅ (indirect) → strong constraints to derive a mechanism

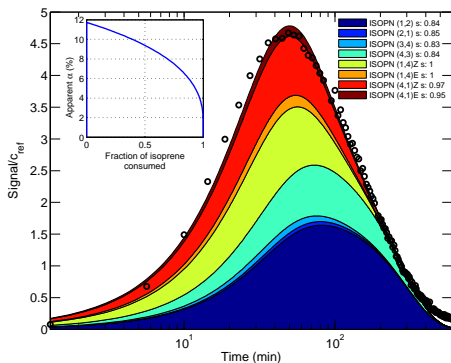


Figure: Isoprene nitrate

Major conclusions

- δ hydroxy channel
 - Constraints on $\sim 30\%$ of the carbon
 - Formation of large acids

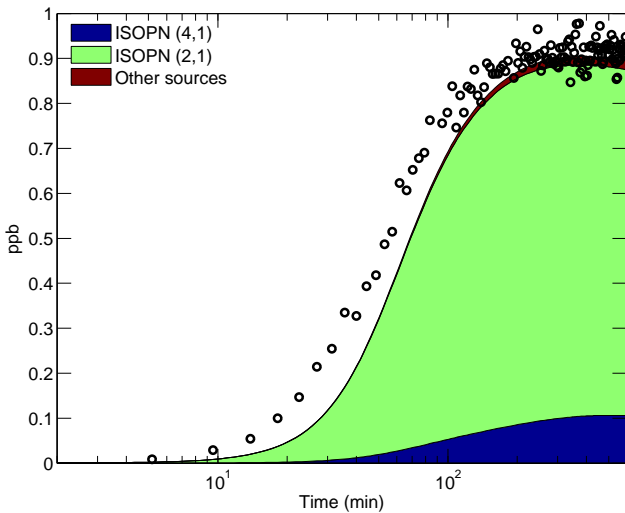
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 - Overall yield: $12 \pm 3\%$
 - Large discrepancy between the β ($\sim 6.7\%$) and δ hydroxychannels ($\sim 24\%$)
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 - MVK and MACR nitrates are formed with yields exceeding 10%
 - MVK nitrate and propanone nitrate ($\sim 1\%$) are very long-lived

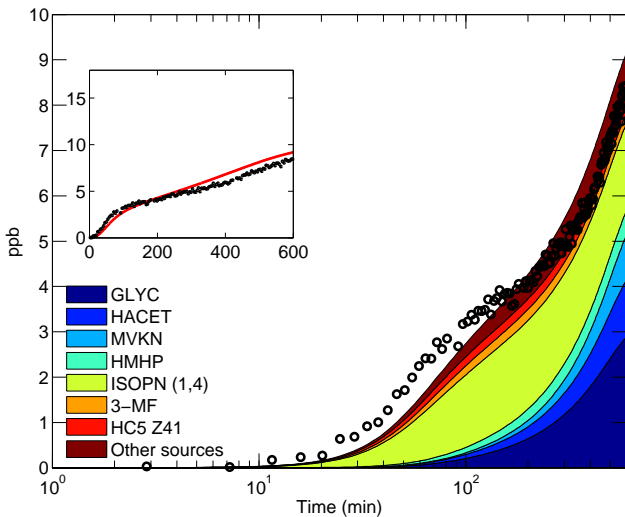
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- Large formation of small carboxylic acid
 - Glycolaldehyde and hydroxyacetone (Butkovskaya 2006)
 - Isoprene nitrates

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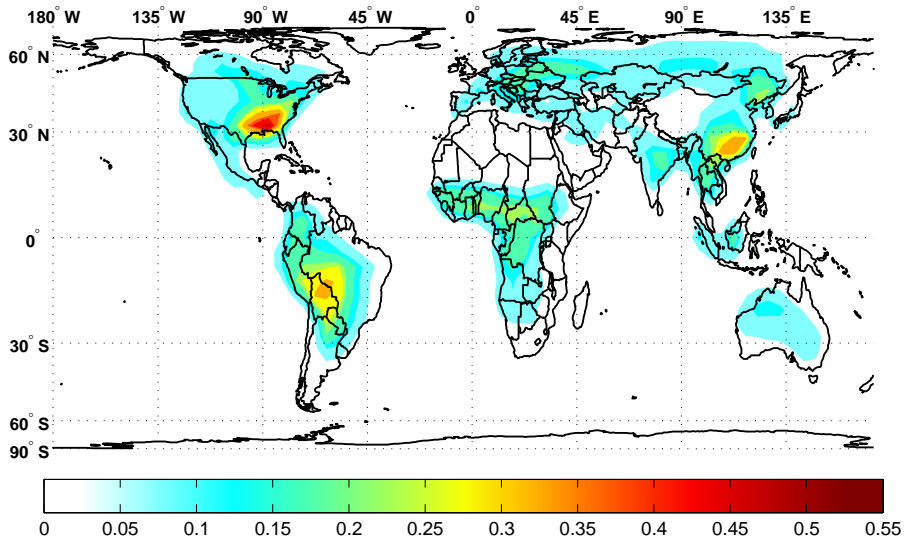


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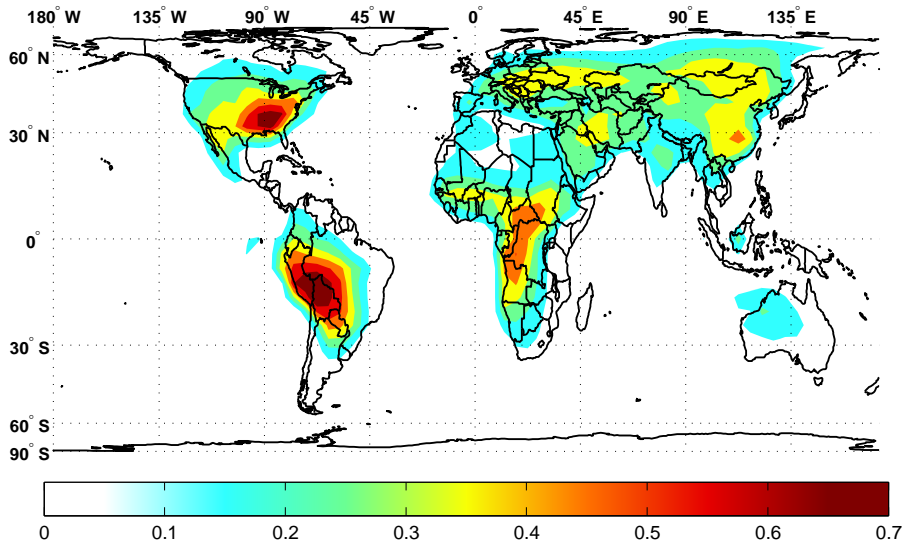
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Summer NH Isoprene nitrate



Formic acid Northern Hemisphere summer



Work in progress and acknowledgements

- Low NO_x chemistry: isoprene (Paulot et al. in review) and atmospheric relevant products: MVK, MACR, MBO, ... (Crouse et al. in preparation)
 - Fate of the peroxides
 - OH recycling

Current chemical schemes are very wrong over tropical regions (not specific to GEOS-Chem).

- Compare model with CIMS measurements collected during INTEX-B, TC4 and ARCTAS.

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John D. Crouse, Henrik G. Kjaergaard (University of Otago, New Zealand), Jesse H. Kroll (now at MIT), John H. Seinfeld, Paul O. Wennberg

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