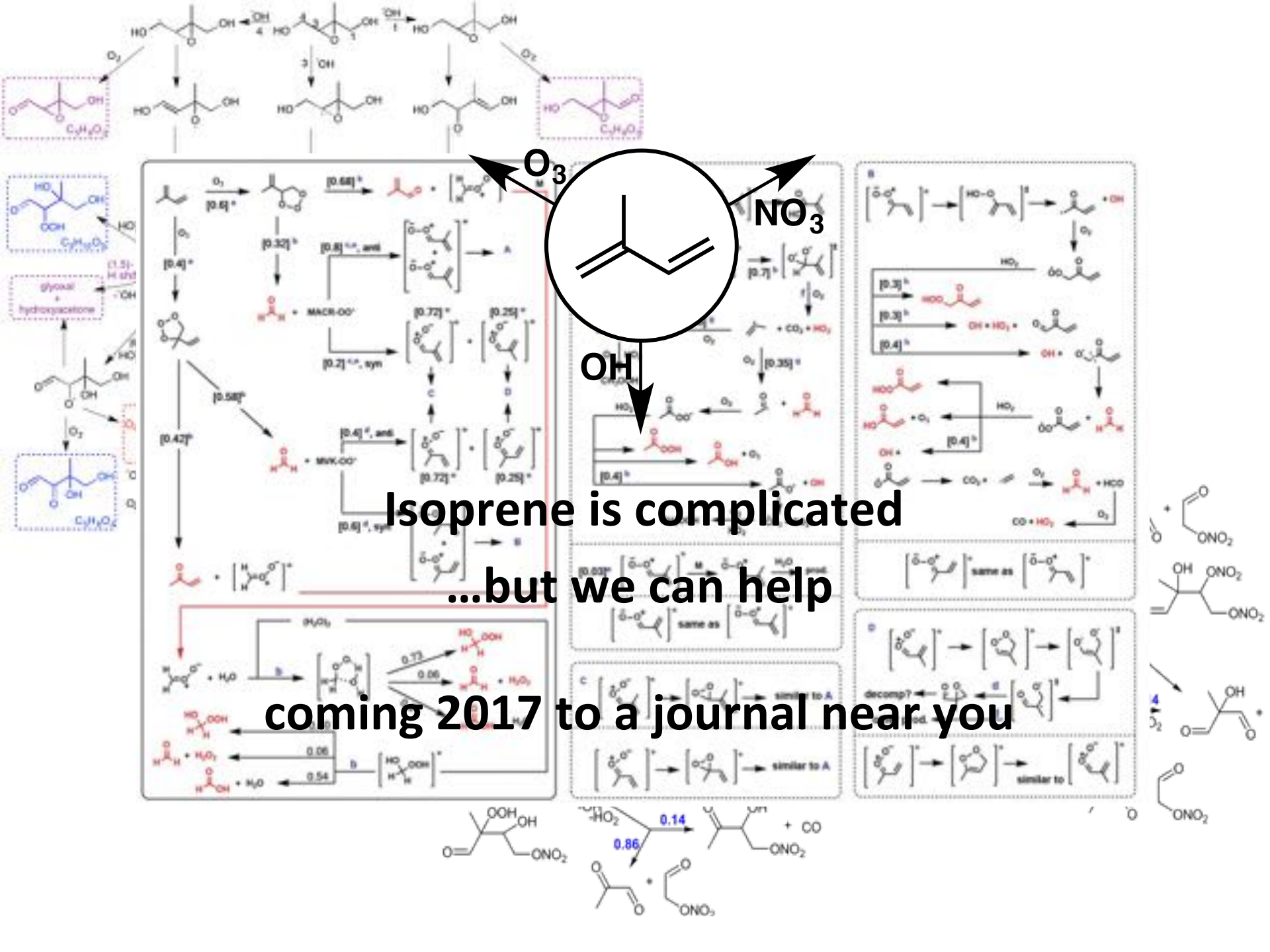
Incorporating recent advances in isoprene photooxidation into GEOS-Chem:

Effects on NO_X, oxidant, and VOC budgets

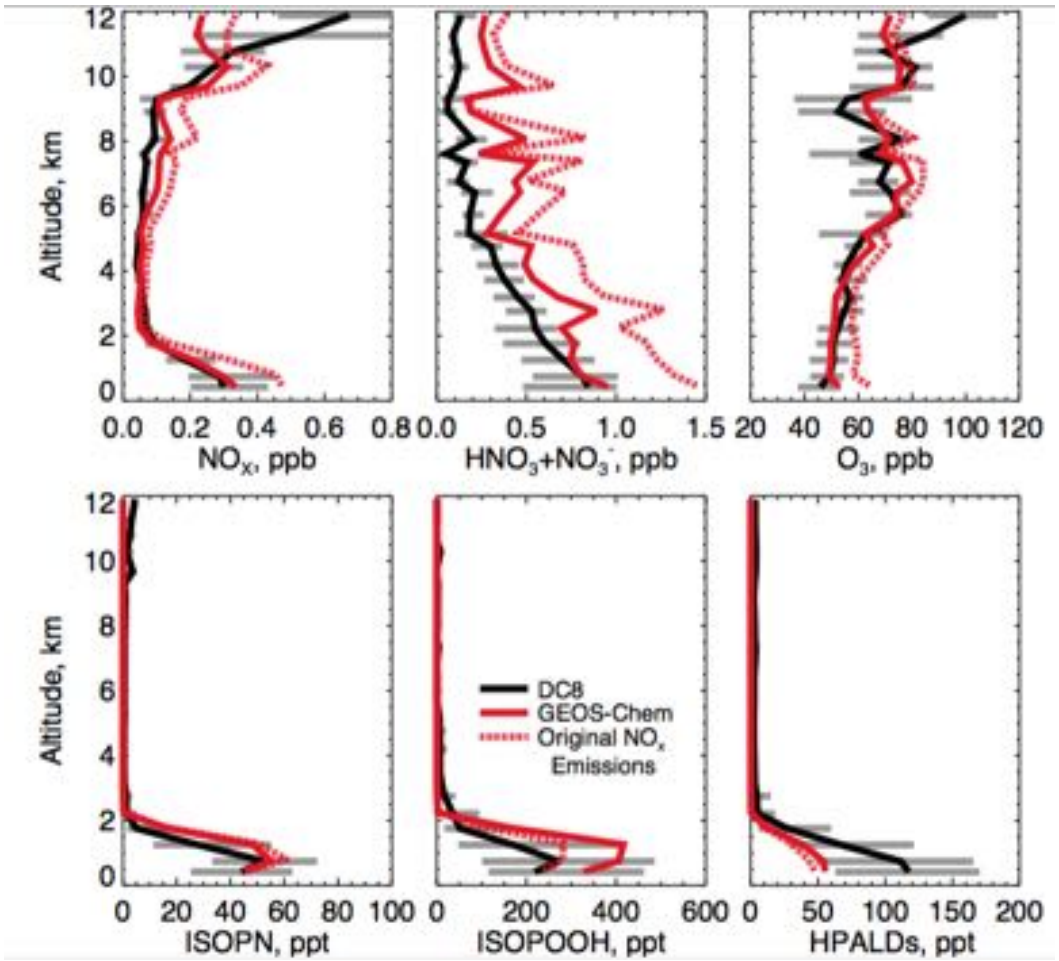
Kelvin H. Bates

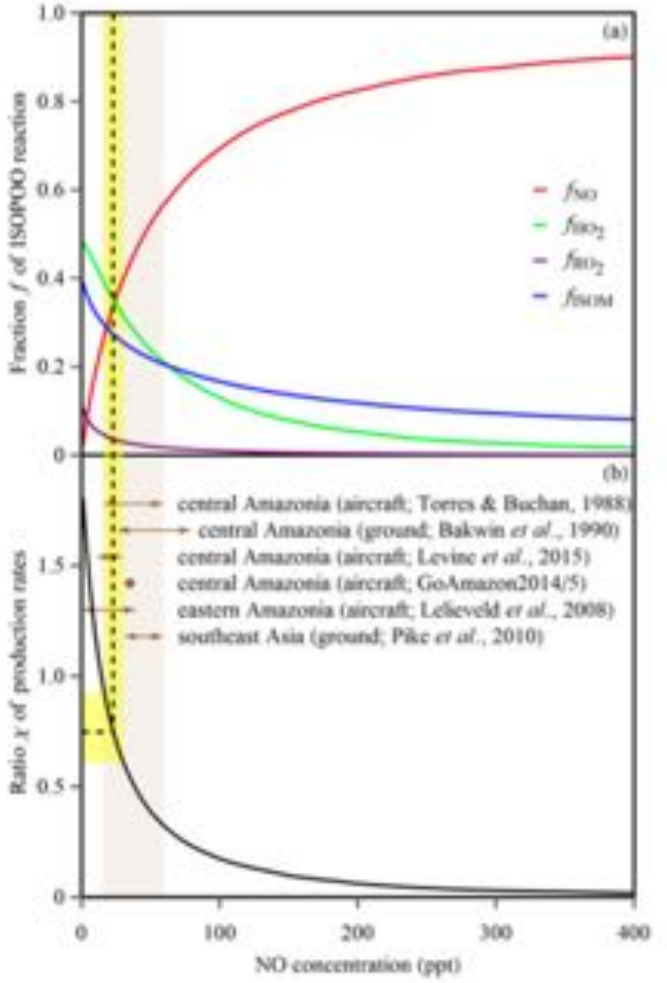
Caltech

with Renee C. McVay, Alex P. Teng, John D. Crounse, Tran B. Nguyen, Eric Praske, Rebecca H. Schwantes, Jason M. St Clair, Hannah M. Allen, John H. Seinfeld, and Paul O. Wennberg


O_3
NO_3
OH
Isoprene is complicated
…but we can help
coming 2017 to a journal near you

State of the Models

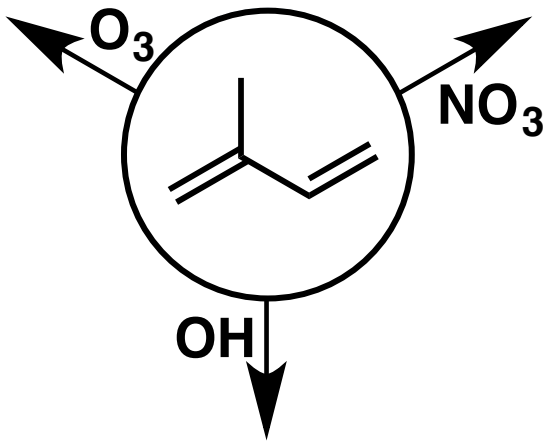




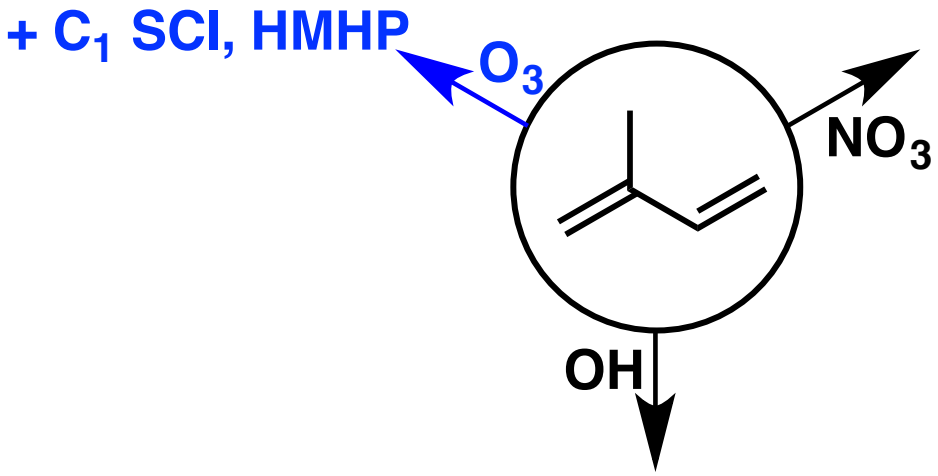
Getting isoprene right <u>matters</u>

K. Travis *et al.*, Atmos. Chem. Phys., 2016; Y. Liu *et al.*, PNAS, 2016;

Updating the Mechanism

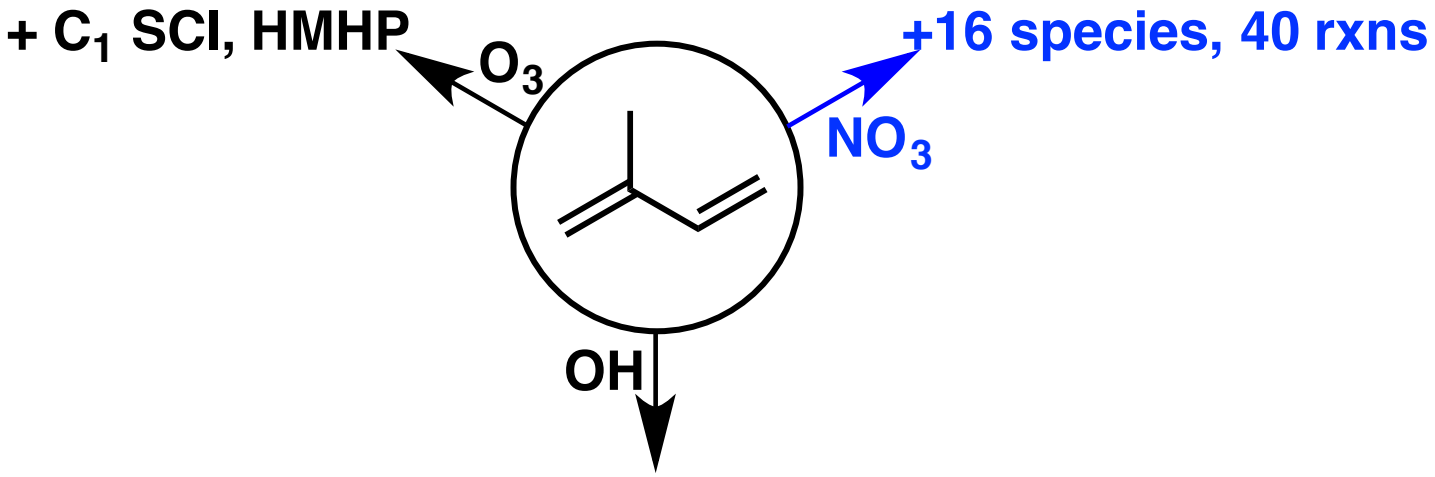


Updating the Mechanism



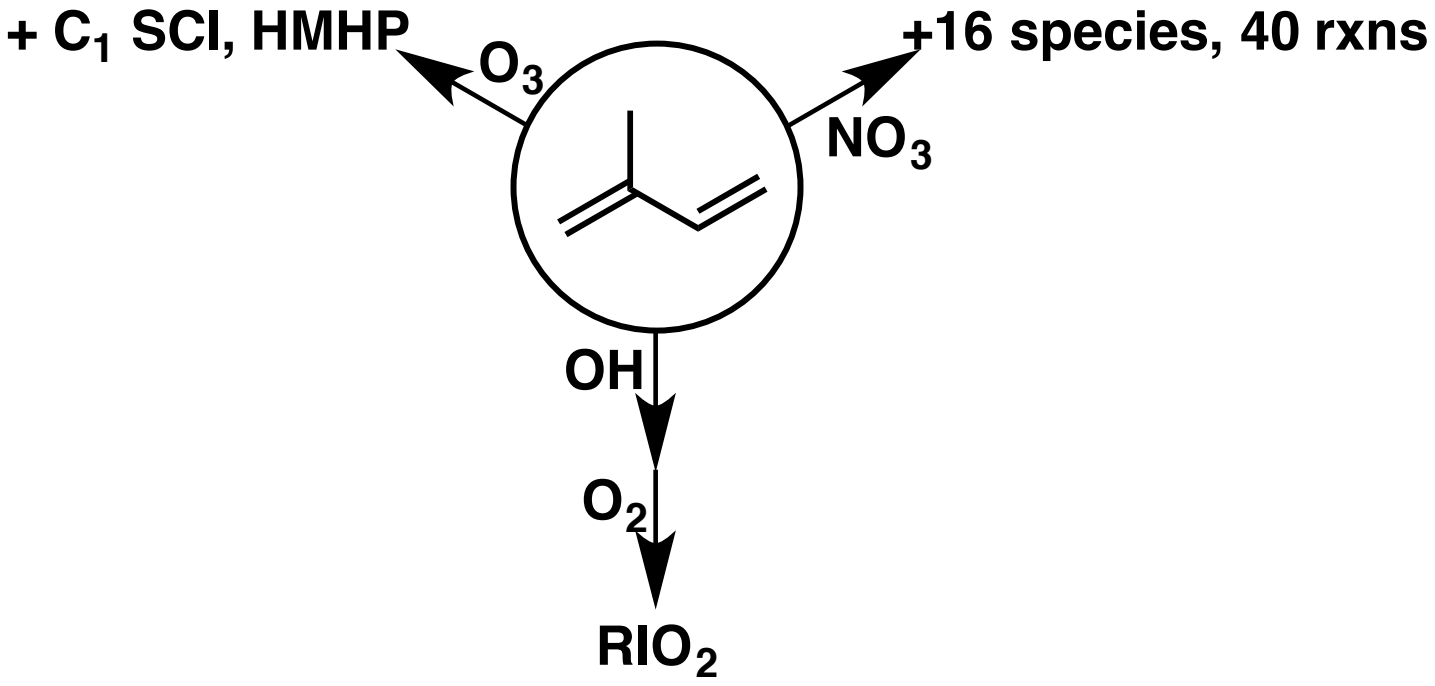
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017;

Updating the Mechanism



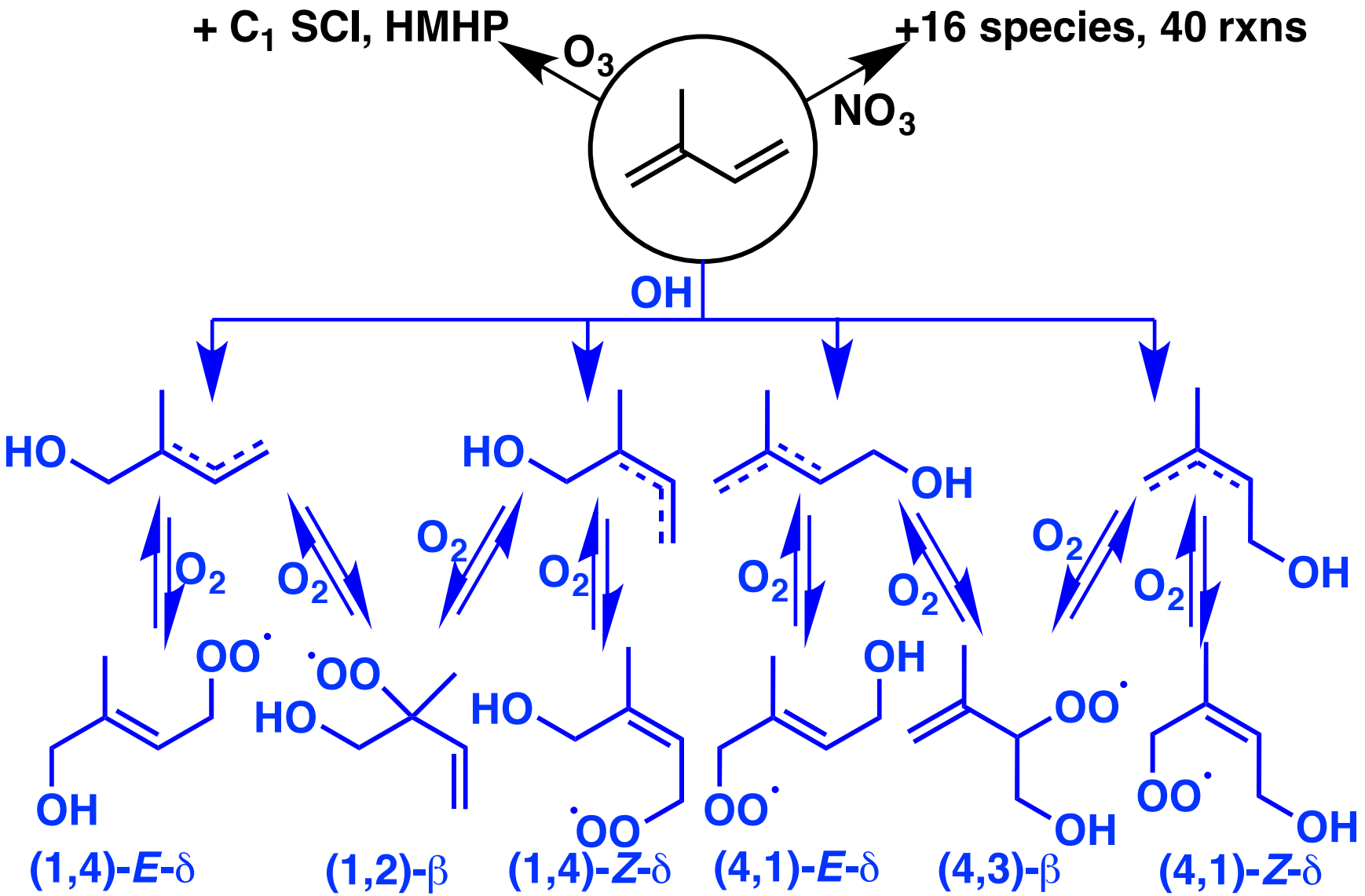
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; **R. Schwantes *et al.*, J. Phys. Chem. A, 2016**

Updating the Mechanism



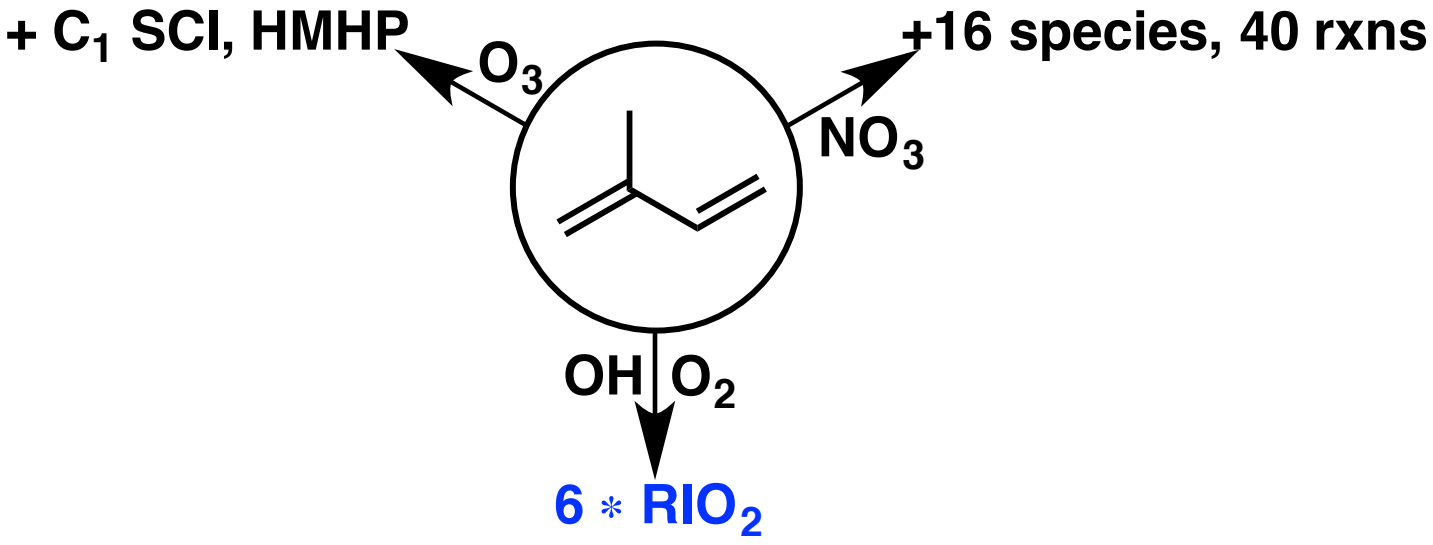
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; R. Schwantes *et al.*, J. Phys. Chem. A, 2016

Updating the Mechanism



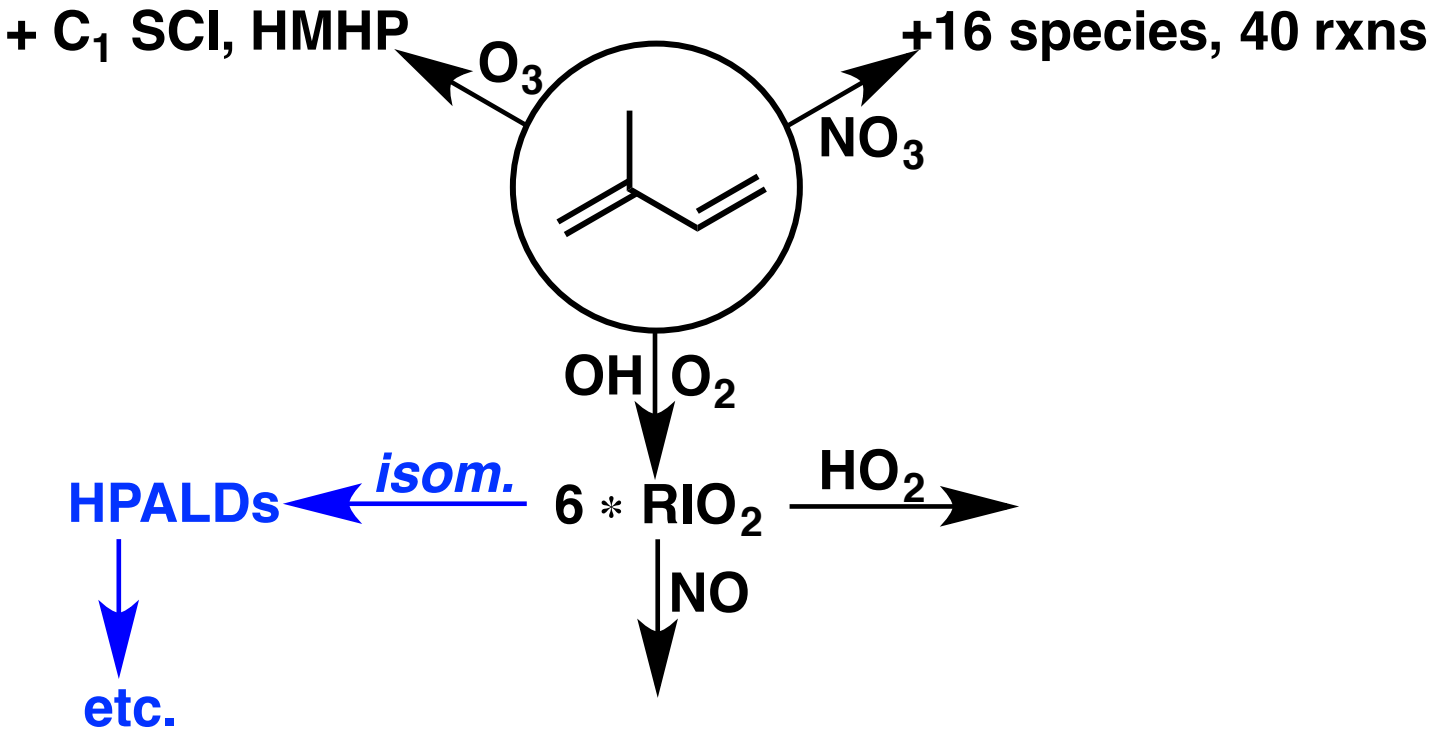
A. Teng *et al.*, in prep, 2017; J. Peeters *et al.*, J. Phys. Chem. A, 2014;
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; R. Schwantes *et al.*, J. Phys. Chem. A, 2016

Updating the Mechanism



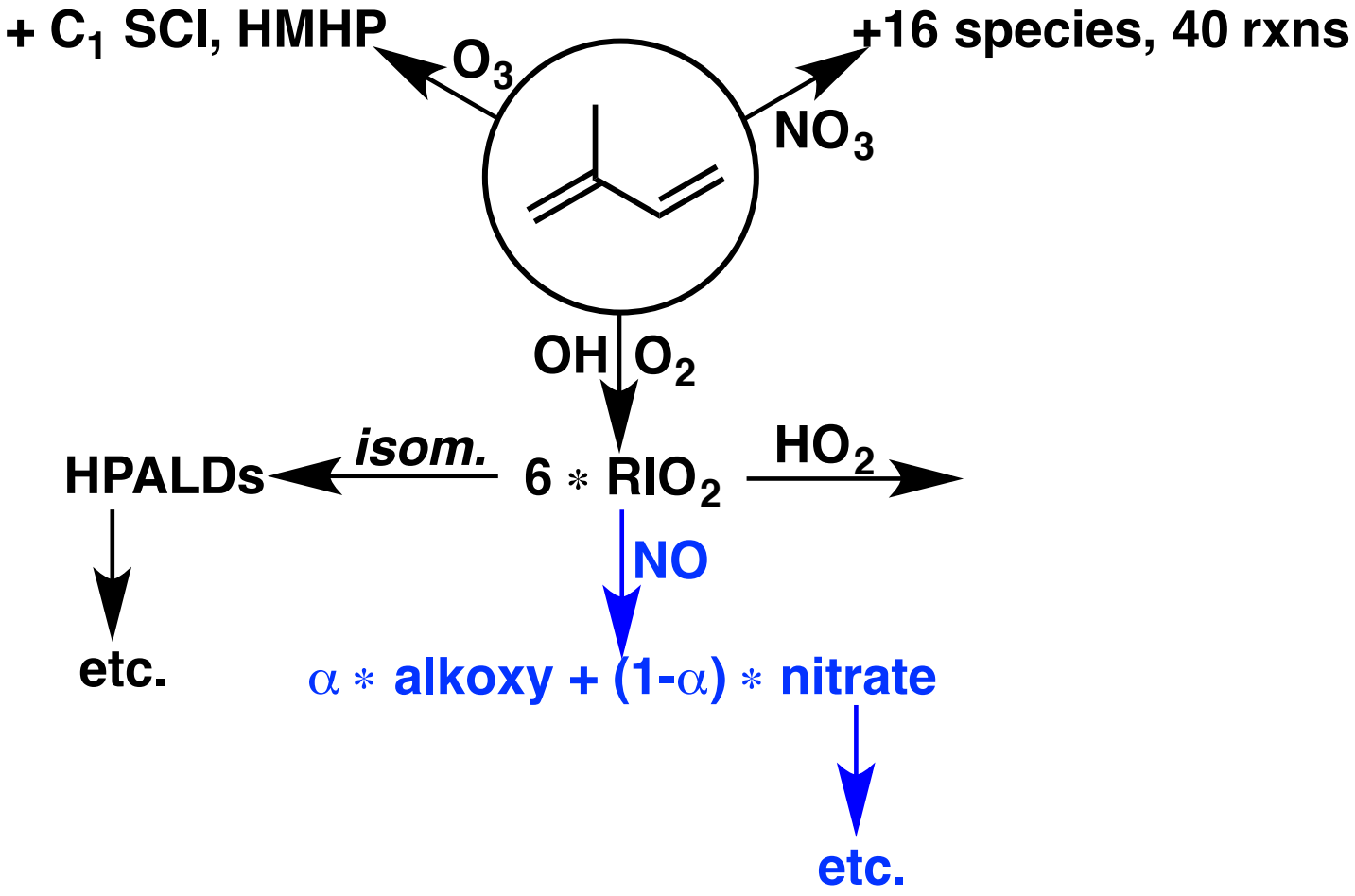
A. Teng *et al.*, in prep, 2017; J. Peeters *et al.*, J. Phys. Chem. A, 2014;
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; R. Schwantes *et al.*, J. Phys. Chem. A, 2016

Updating the Mechanism



A. Teng *et al.*, in prep, 2017; **J. Peeters *et al.*, J. Phys. Chem. A, 2014; J. Crounse *et al.*, Phys. Chem. Chem. Phys., 2011**
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; R. Schwantes *et al.*, J. Phys. Chem. A, 2016

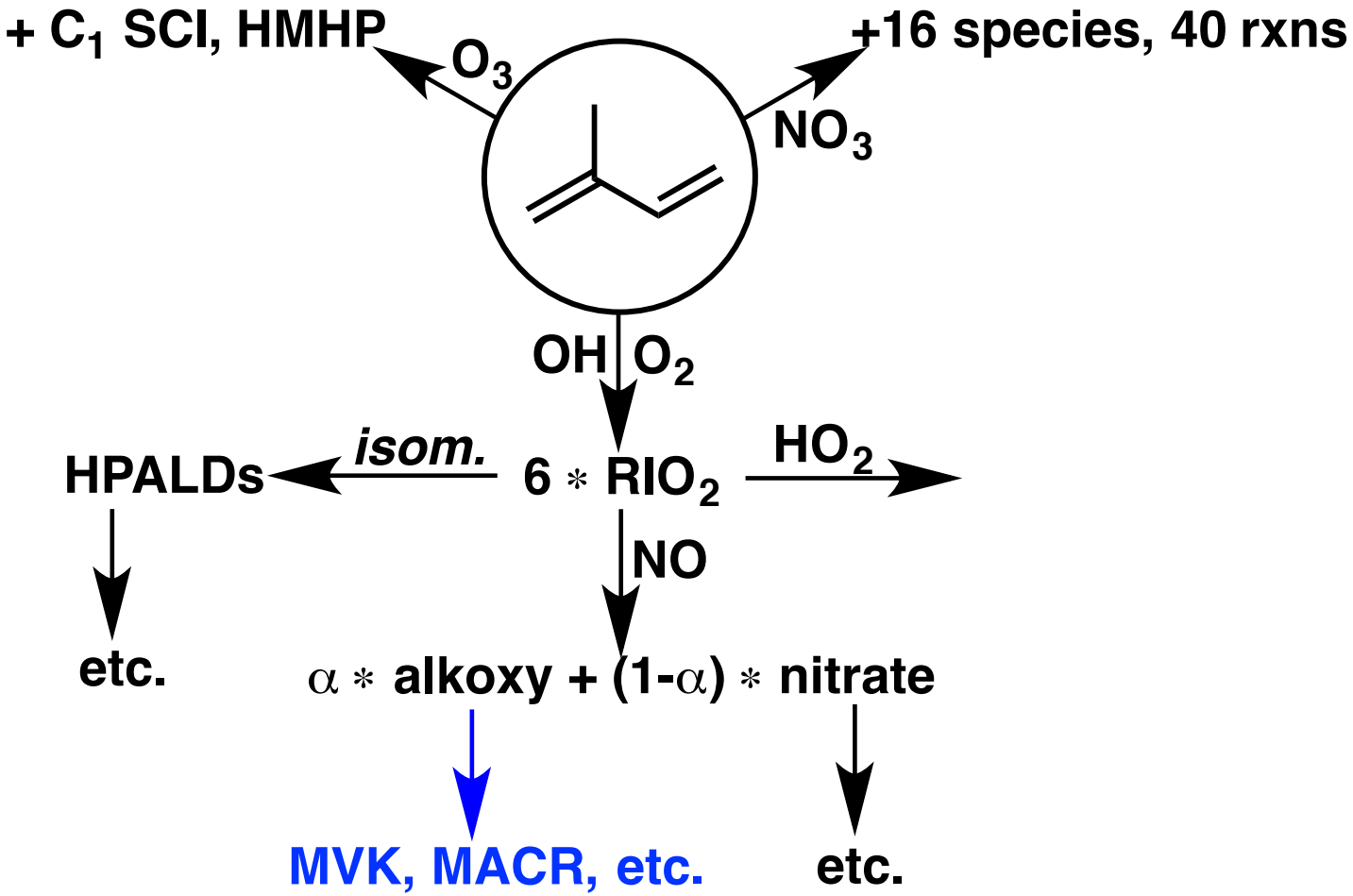
Updating the Mechanism



A. Teng *et al.*, Atmos. Chem. Phys., 2015; L. Lee *et al.*, J. Phys. Chem. A, 2014;

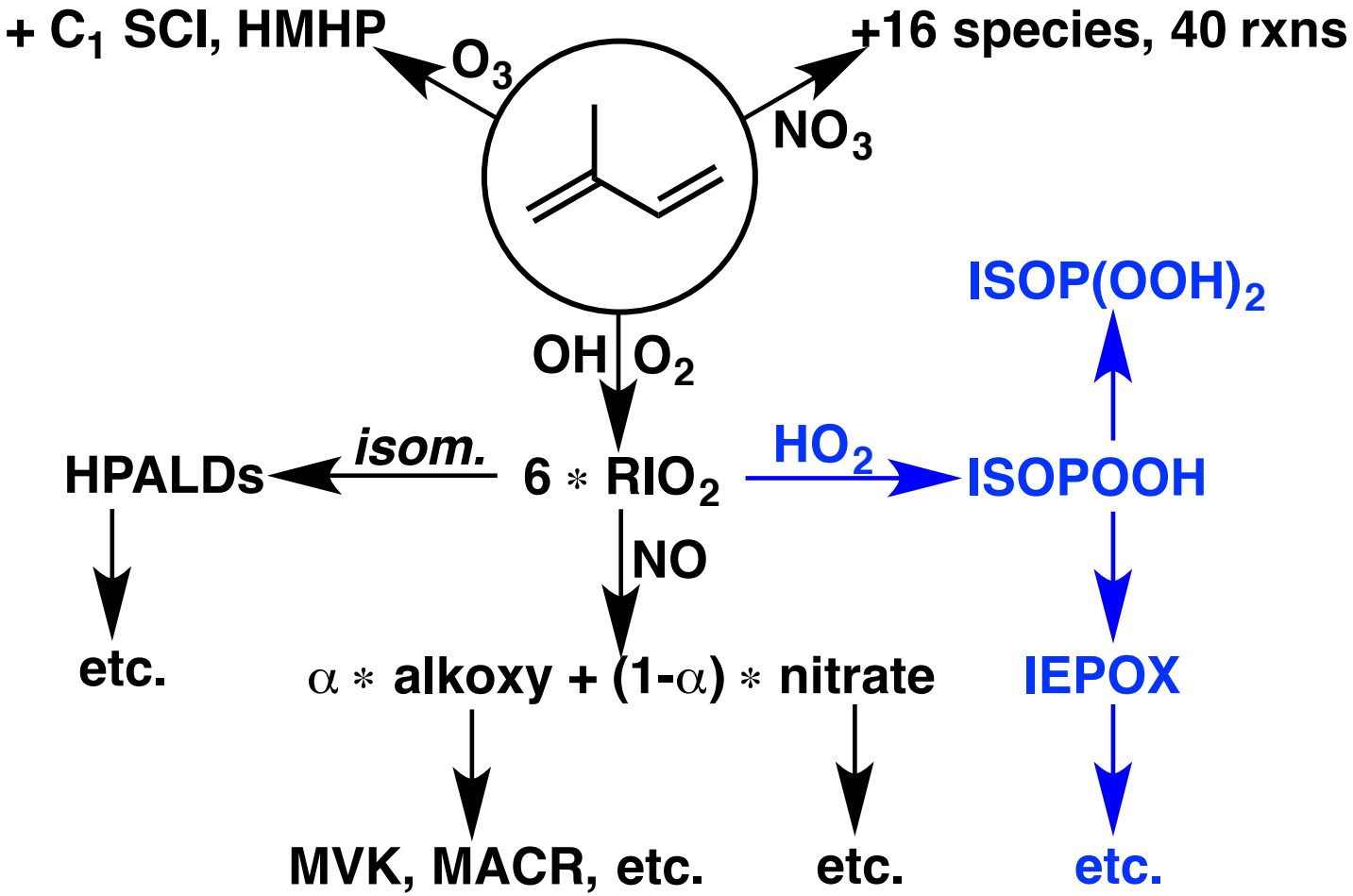
A. Teng *et al.*, in prep, 2017; J. Peeters *et al.*, J. Phys. Chem. A, 2014; J. Crounse *et al.*, Phys. Chem. Chem. Phys., 2011
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; R. Schwantes *et al.*, J. Phys. Chem. A, 2016

Updating the Mechanism



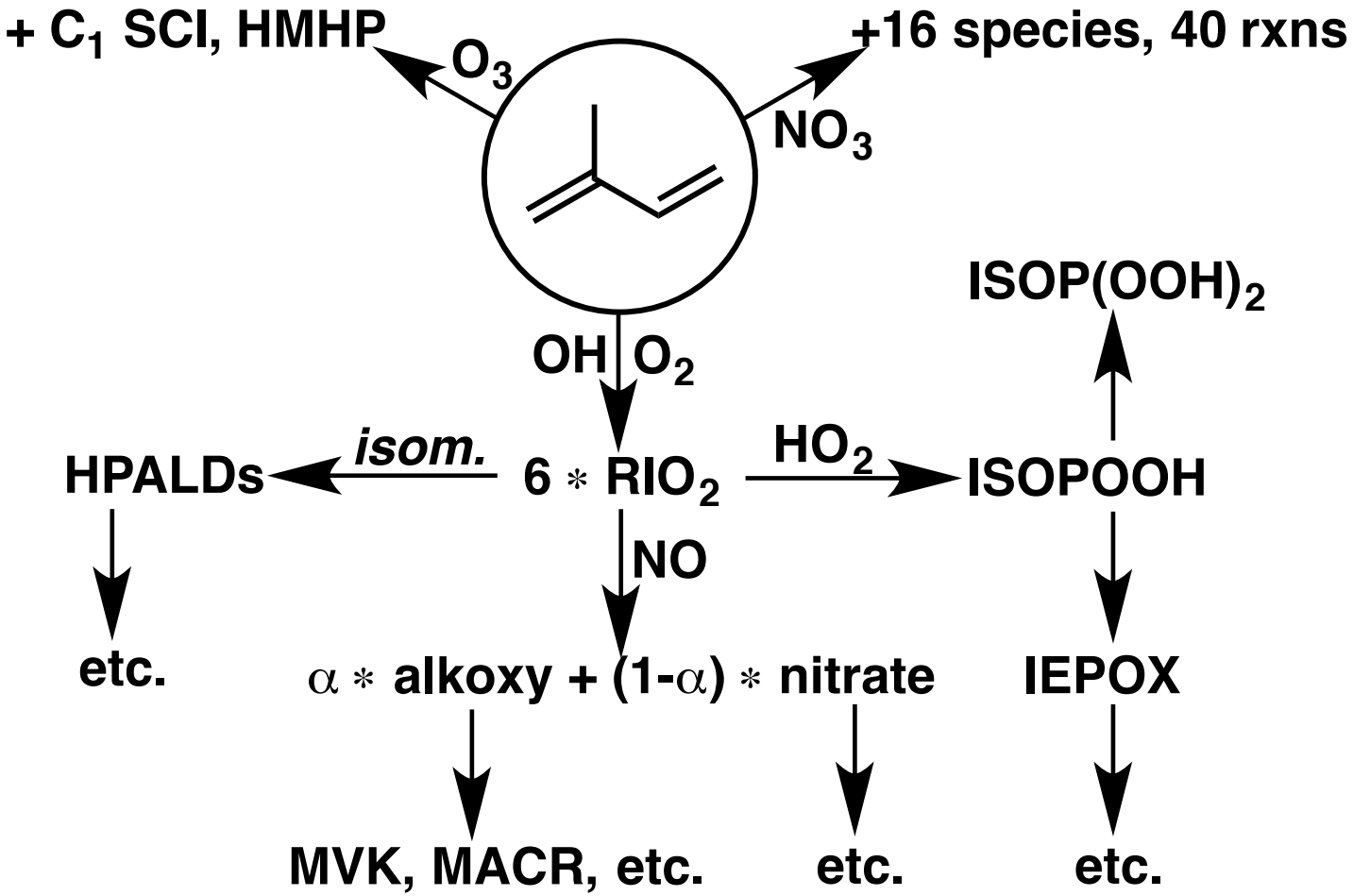
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2015;
A. Teng *et al.*, Atmos. Chem. Phys., 2015; L. Lee *et al.*, J. Phys. Chem. A, 2014**; E. Praske *et al.*, J. Phys. Chem. A, 2015**
A. Teng *et al.*, in prep, 2017; J. Peeters *et al.*, J. Phys. Chem. A, 2014; J. Crounse *et al.*, Phys. Chem. Chem. Phys., 2011
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; R. Schwantes *et al.*, J. Phys. Chem. A, 2016

Updating the Mechanism



J. St. Clair *et al.*, J. Phys. Chem. A, 2015;
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2015; **K. Bates *et al.*, J Phys. Chem. A, 2016; K. Bates *et al.*, J Phys. Chem. A, 2014**
A. Teng *et al.*, Atmos. Chem. Phys., 2015; L. Lee *et al.*, J. Phys. Chem. A, 2014; E. Praske *et al.*, J. Phys. Chem. A, 2015
A. Teng *et al.*, in prep, 2017; J. Peeters *et al.*, J. Phys. Chem. A, 2014; J. Crounse *et al.*, Phys. Chem. Chem. Phys., 2011
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; R. Schwantes *et al.*, J. Phys. Chem. A, 2016

Updating the Mechanism



J. St. Clair *et al.*, J. Phys. Chem. A, 2015; **T. Nguyen *et al.*, PNAS, 2014**
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2015; K. Bates *et al.*, J Phys. Chem. A, 2016; K. Bates *et al.*, J Phys. Chem. A, 2014
A. Teng *et al.*, Atmos. Chem. Phys., 2015; L. Lee *et al.*, J. Phys. Chem. A, 2014; E. Praske *et al.*, J. Phys. Chem. A, 2015
A. Teng *et al.*, in prep, 2017; J. Peeters *et al.*, J. Phys. Chem. A, 2014; J. Crounse *et al.*, Phys. Chem. Chem. Phys., 2011
T. Nguyen *et al.*, Phys. Chem. Chem. Phys., 2016; H. Allen *et al.*, in prep, 2017; R. Schwantes *et al.*, J. Phys. Chem. A, 2016

Updating the Mechanism

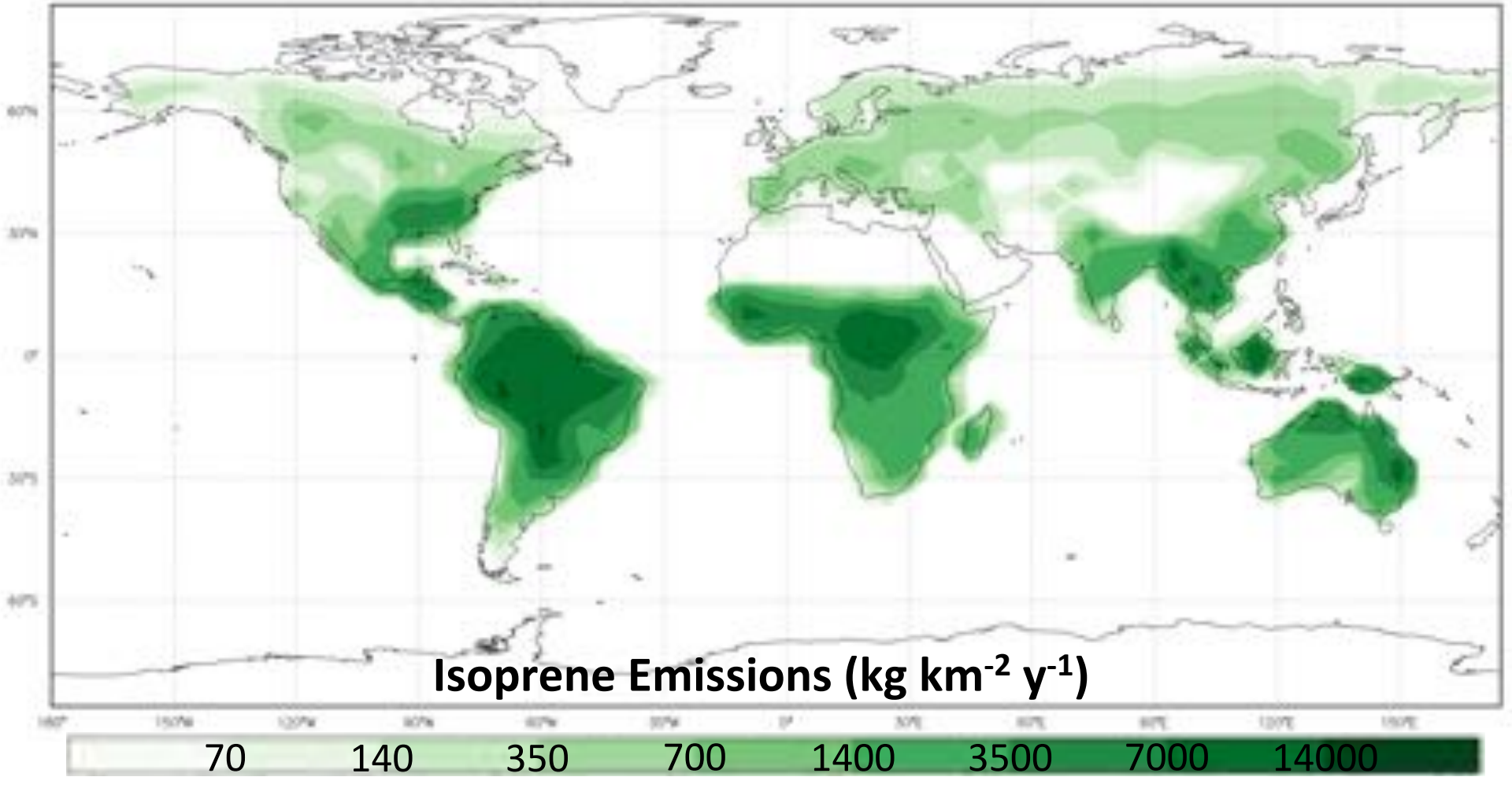
Rules:

1. Retain carbon & radical parity
2. Keep products with >1% overall yield from isoprene
3. Separate isomers if they have different chemistry
4. Defer to nearest analog, then to MCM

Final tally: + 50 stable species, + 22 radical species

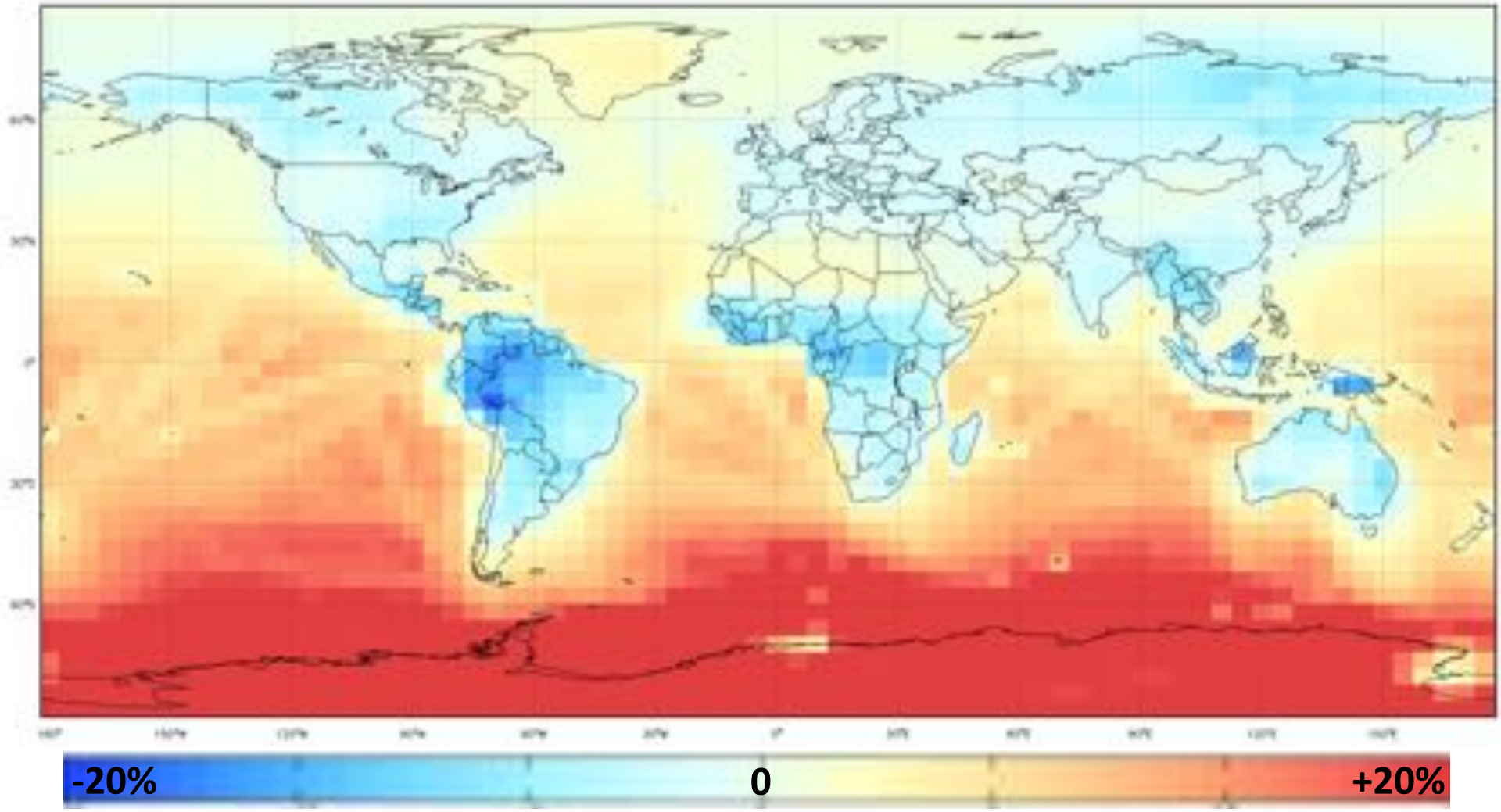
Running the Model

- v. 10-01
- 4˚x5˚ grid
- 1.5-year spinup
- GEOS-FP meteorology
- annual average over 2014



Running the Model: Δ NO_x

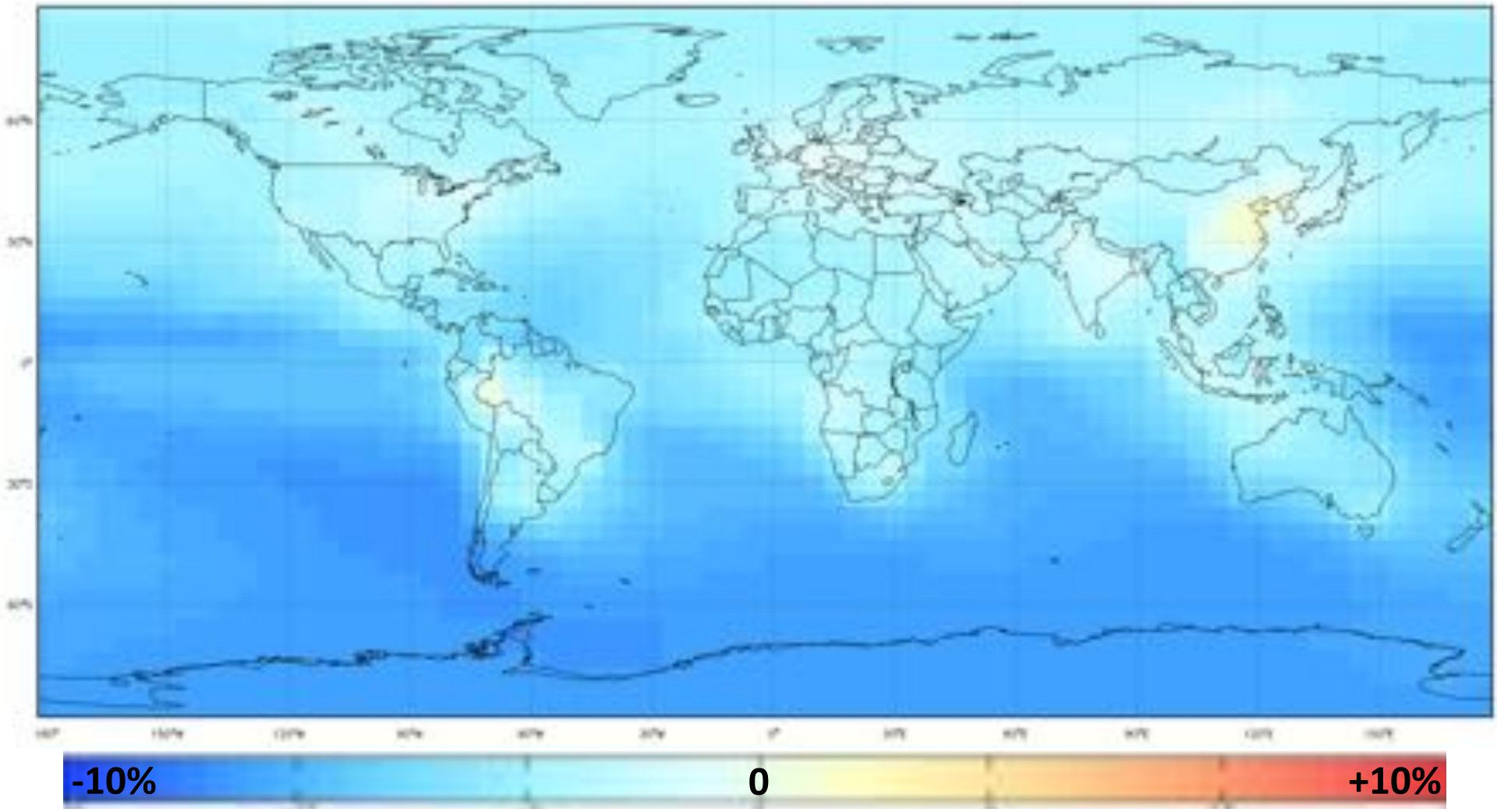
% change in [NO] at surface from old to new isoprene mechanism, 2014



Overall: Production ↓ 0.9%, Loading ↓ 1.4% (1km), 2.6% (atm)

Running the Model: ΔO_3

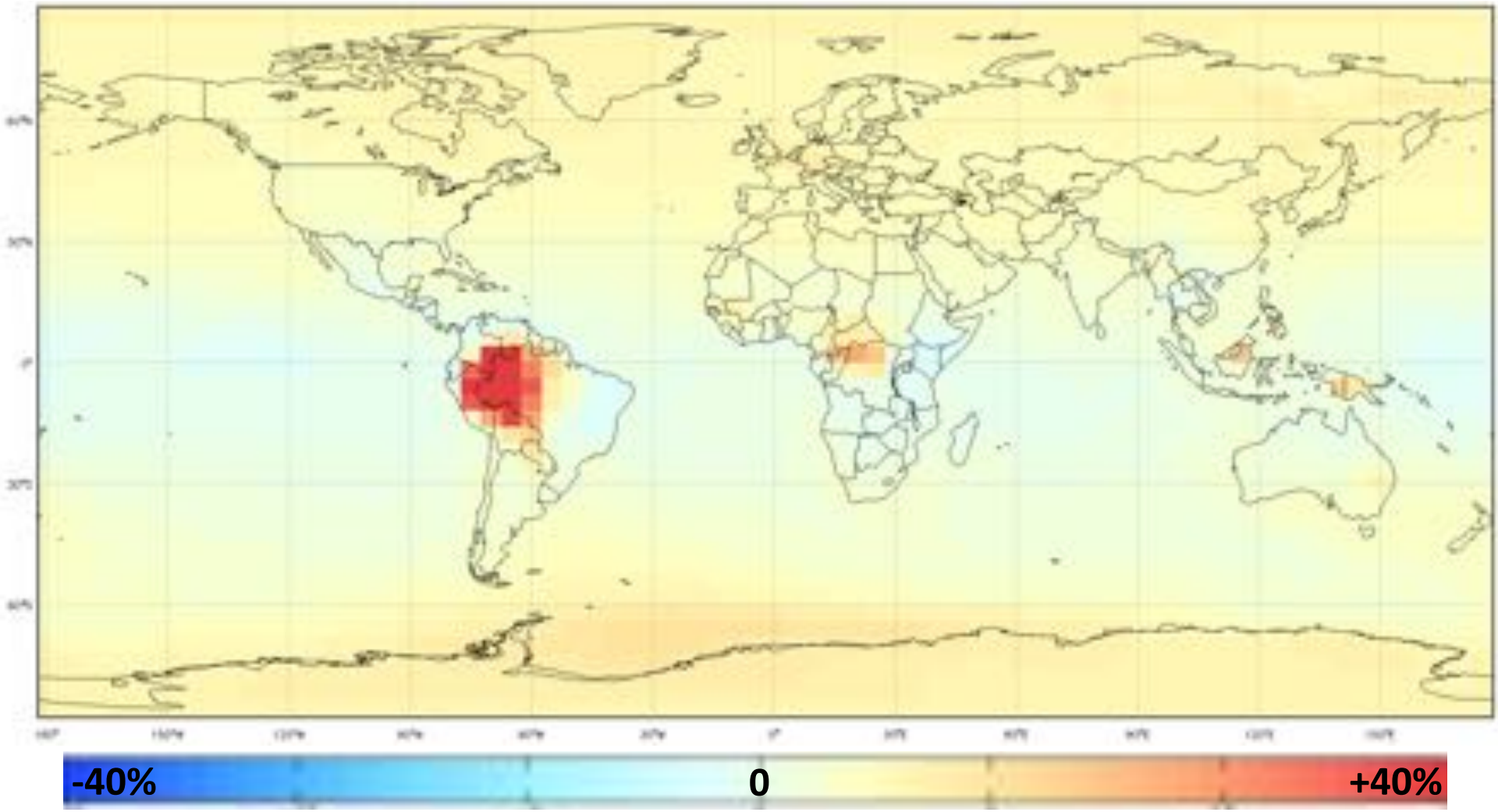
% change in $[O_3]$ at surface from old to new isoprene mechanism, 2014



Overall: Production ↓ 2.3%, Loading ↓ 4.1% (1km), 7.2% (atm)

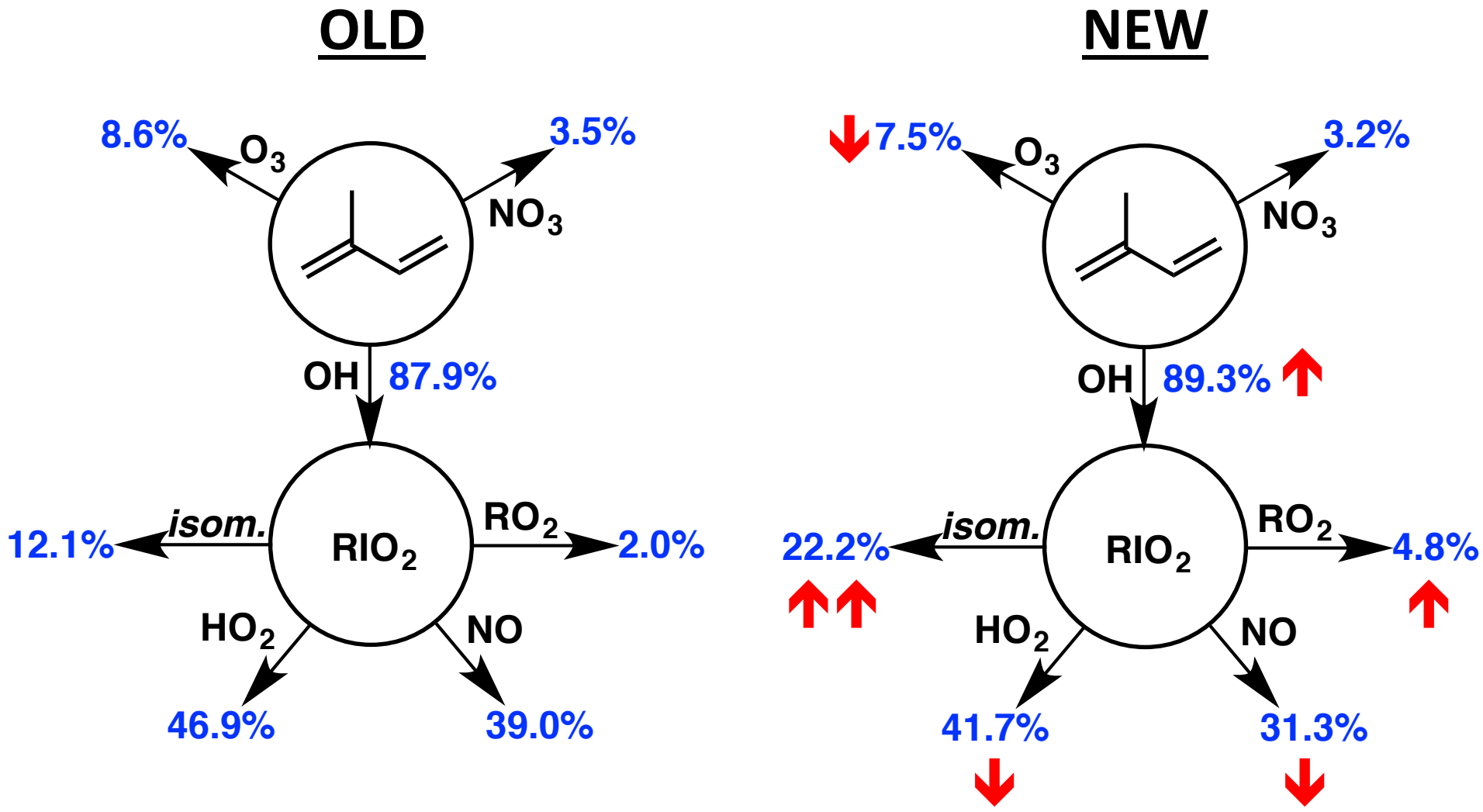
Running the Model: Δ OH

% change in [OH] at surface from old to new isoprene mechanism, 2014

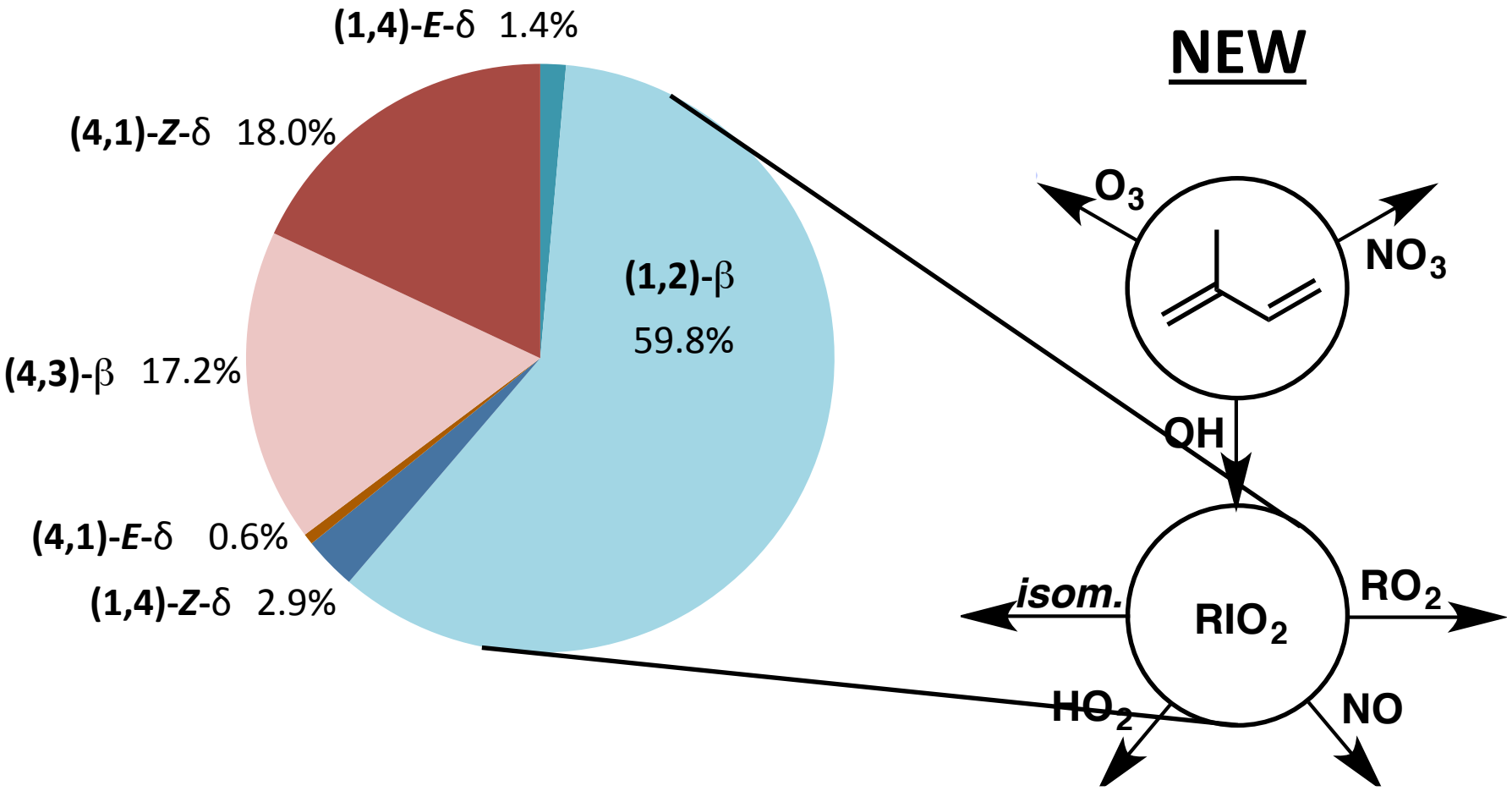


Overall: Loading ↑ 2.7% (1km), ↓ 0.8% (atm)

Running the Model: VOCs



Running the Model: VOCs



Running the Model: MVK/MACR

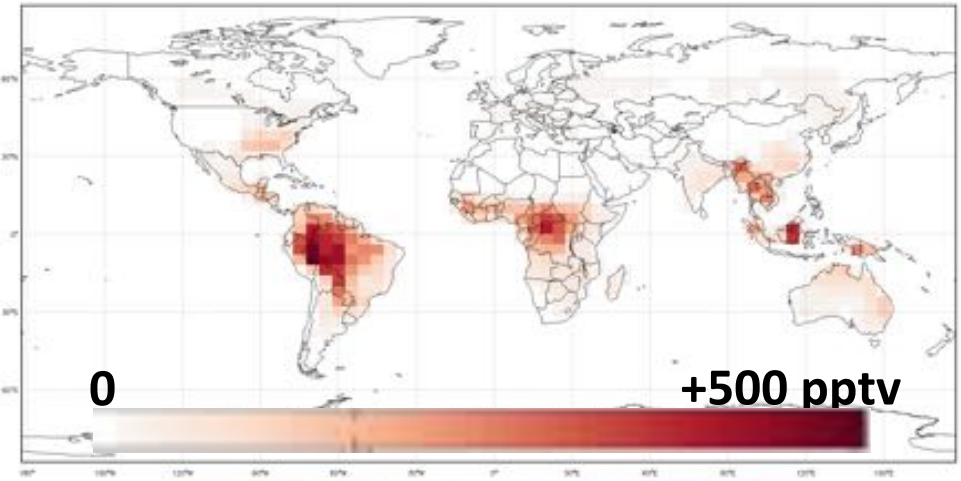
MVK

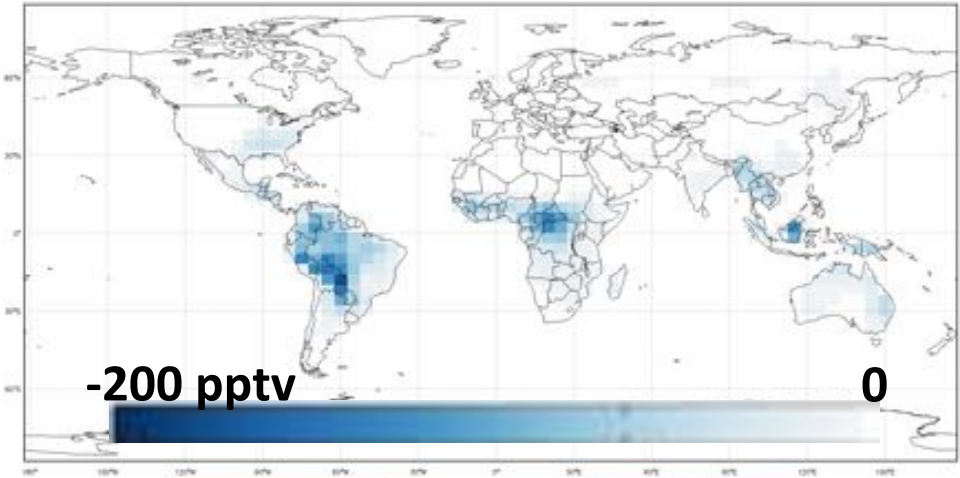
Production: ↑ 42.5%
Atmospheric loading:
Surface: ↑ 43.3%
Total: ↑ 47.4%

Methacrolein

Production: ↓ 23.0%
Atmospheric loading:
Surface: ↓ 25.7%
Total: ↓ 23.5%

Absolute change at surface from old to new isoprene mechanism, 2014

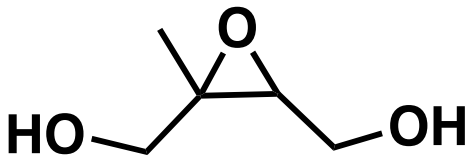




[MVK]/[MACR] ratio nearly doubles from 1.38 to 2.57

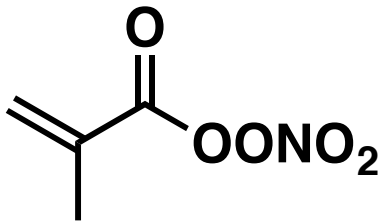
Running the Model: SOA Precursors

IEPOX



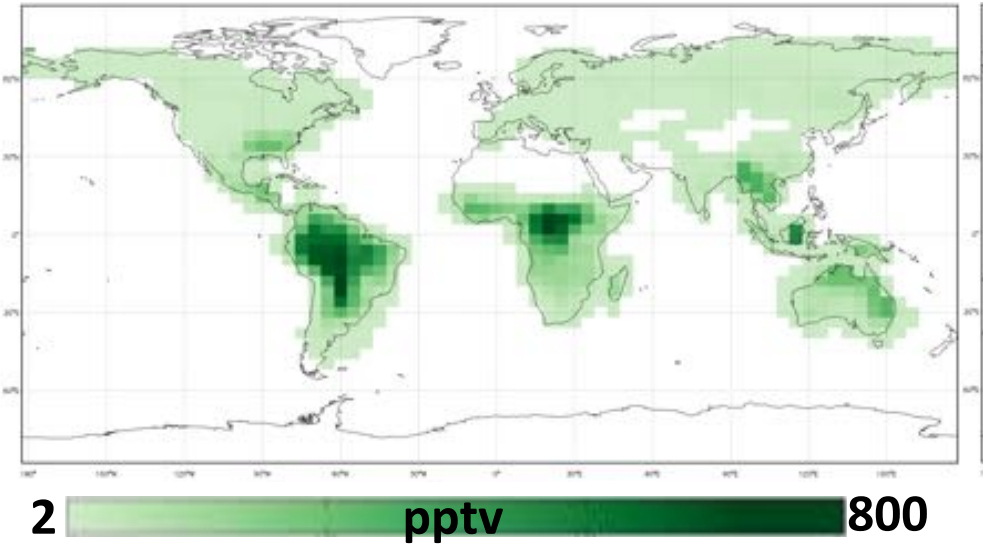
Production: 183 Tg y^{-1} (↓ 19%)

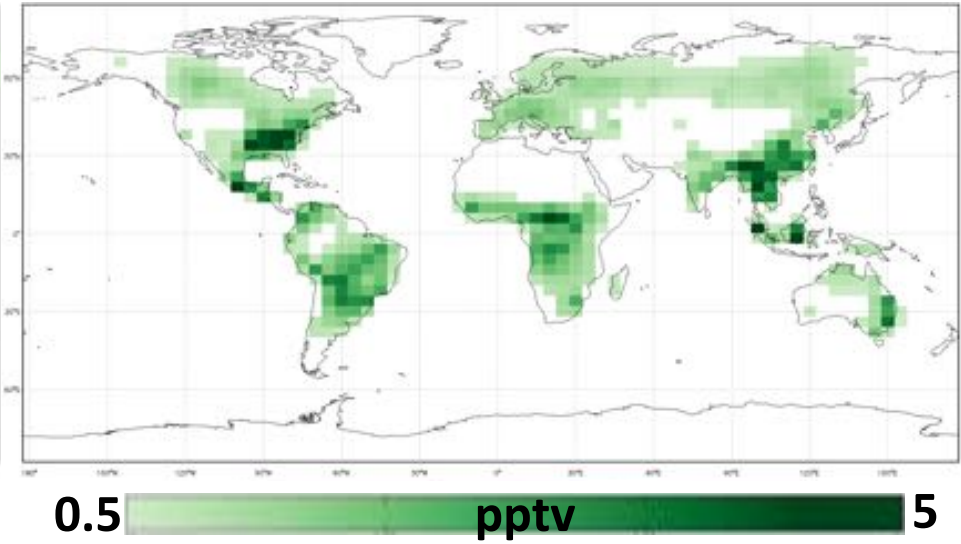
MPAN



Production: 32.7 Tg y^{-1} (↑ 29%)

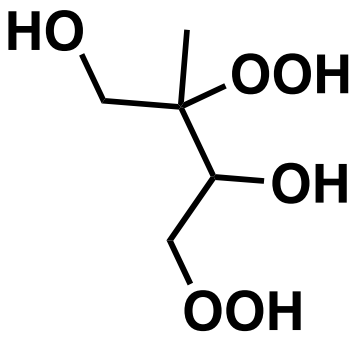
Annual average pptv in lowest 1 km, 2014

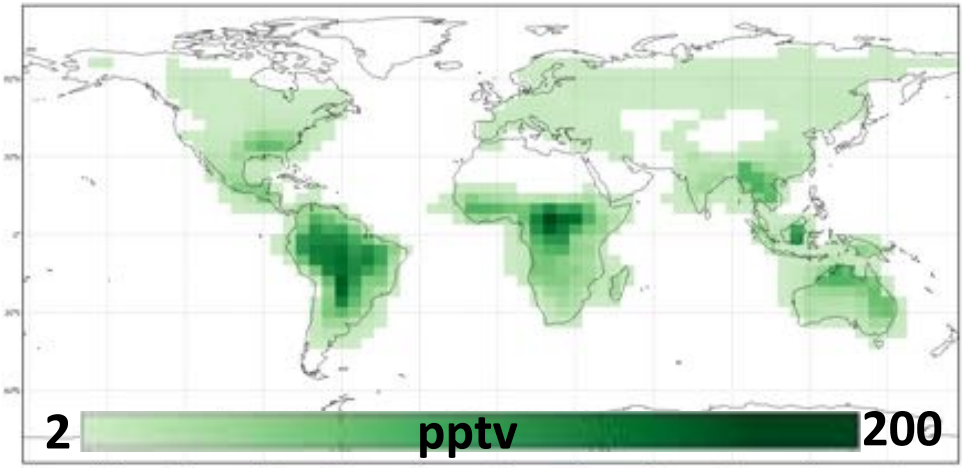


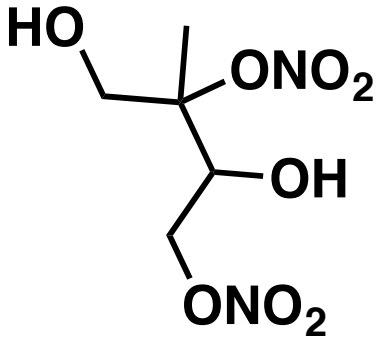


Running the Model: SOA Precursors

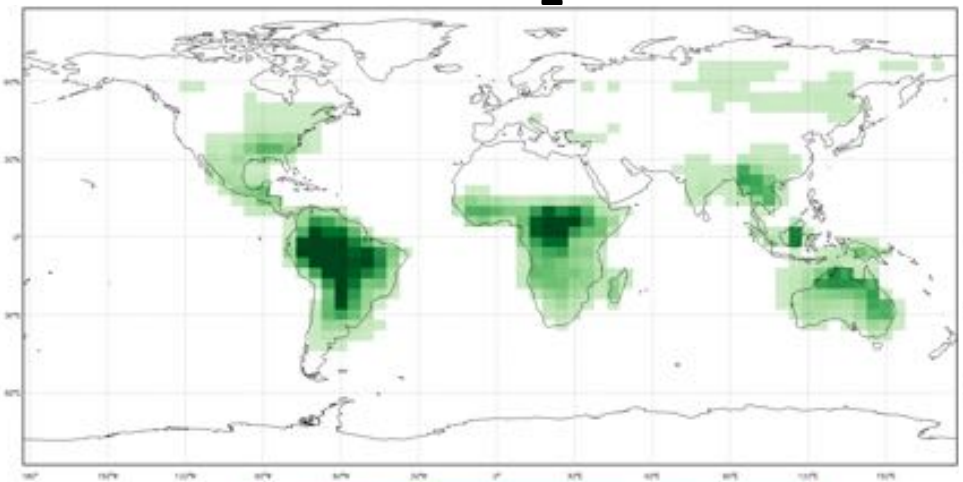
Tetrafunctionals: 44.2 Tg y^{-1}



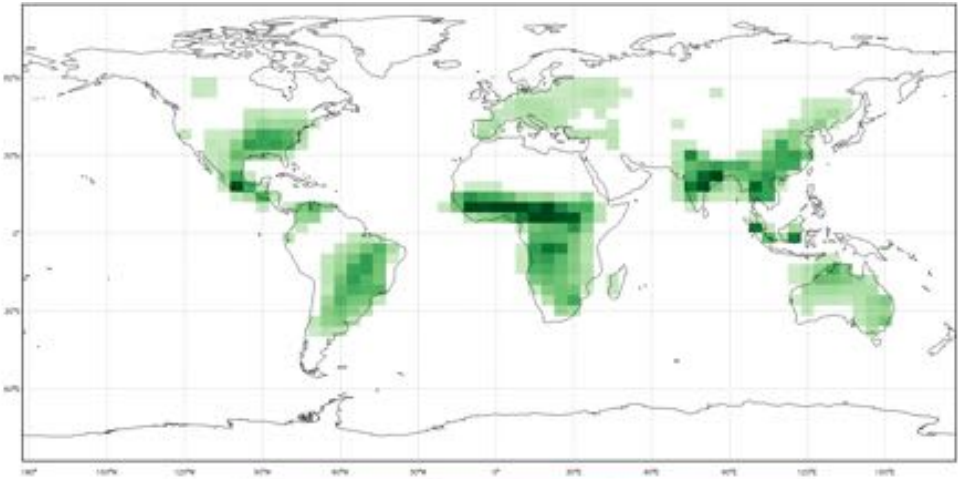




$ISOP(OOH)_2$ (*2)



Dihydroxy-dinitrates (*10)



Annual average pptv in lowest 1 km, 2014

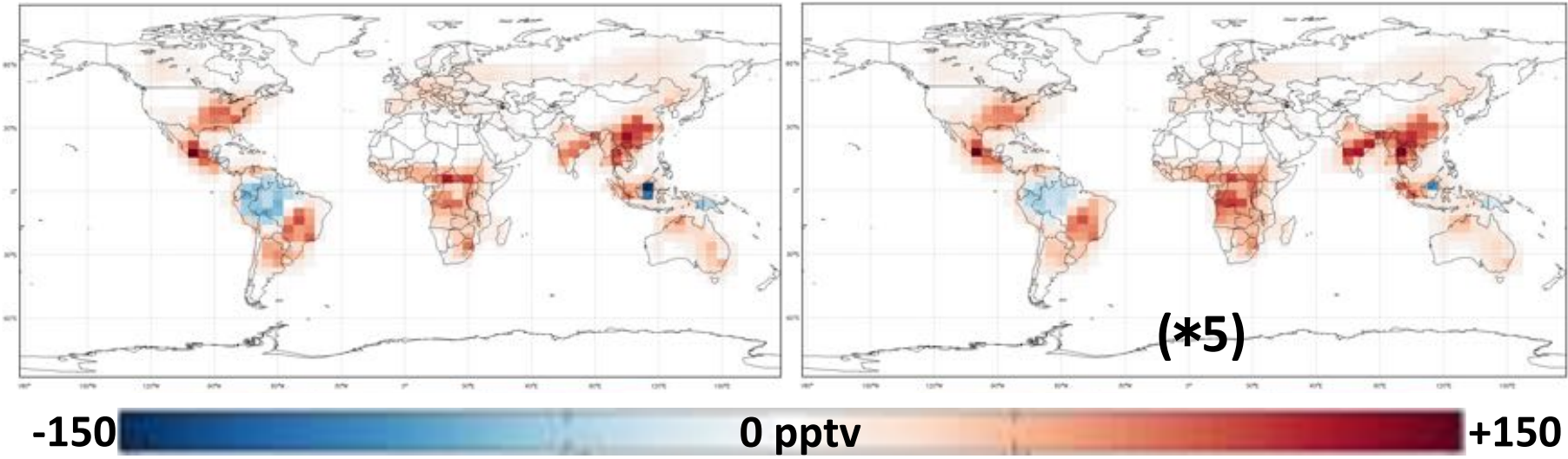
Running the Model: Preindustrial Baseline

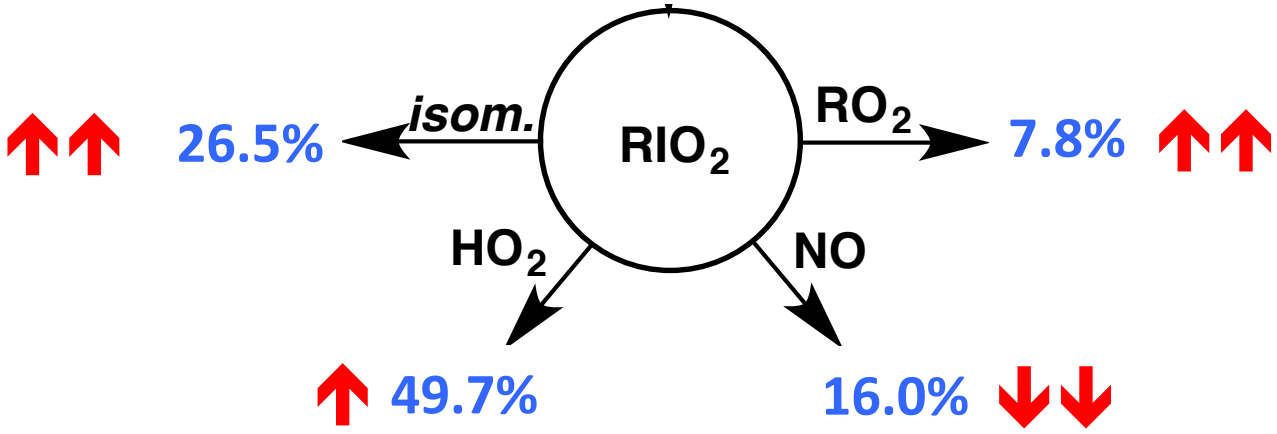
pptv change at surface when anthropogenic emissions removed, 2014

IEPOX: ↑ 35%

$ISOP(OOH)_2$: ↑ 42%

Absolute





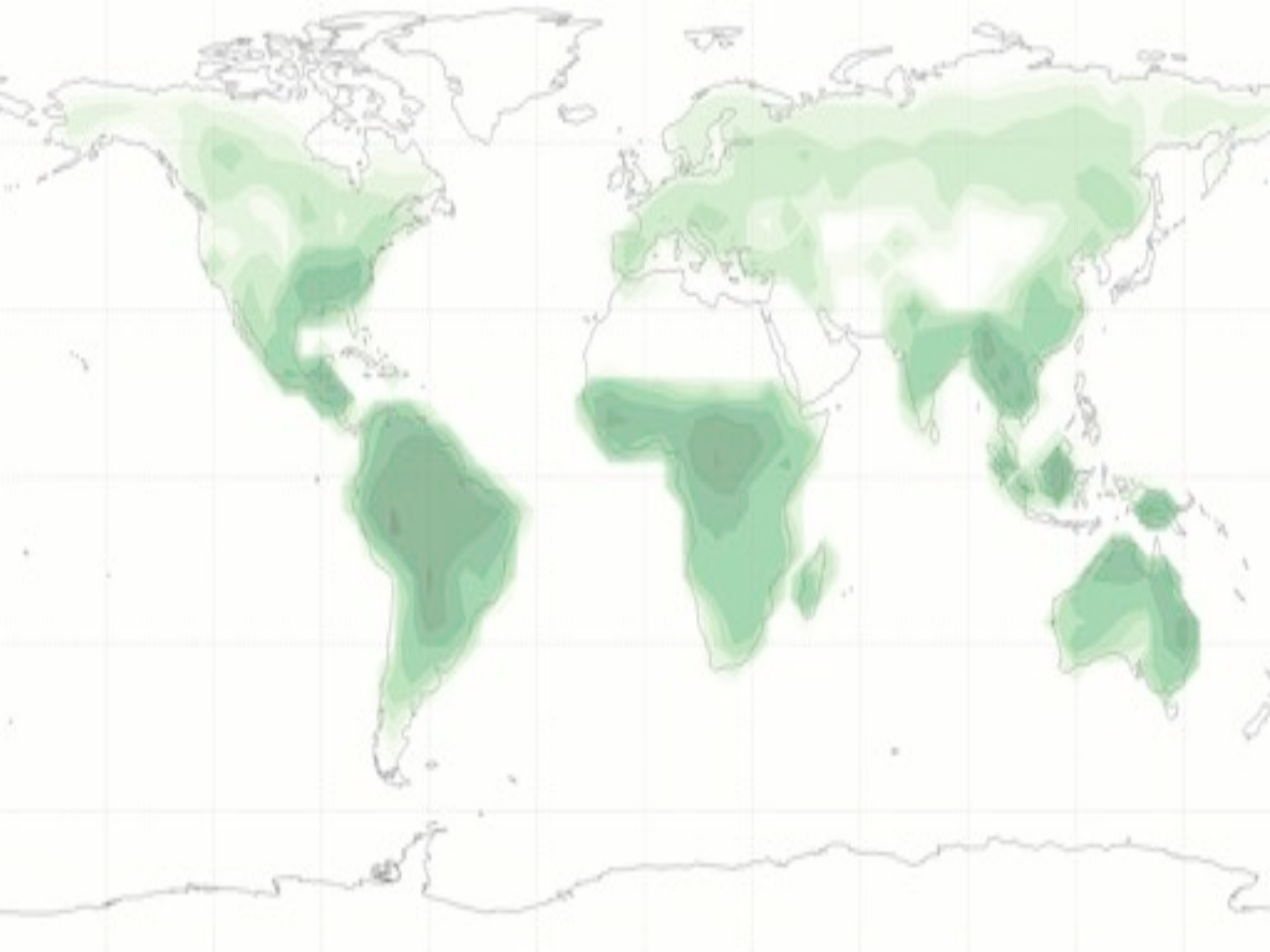
Takeaways

Outcomes of the new model:

- [NO]: ↓ over forests, ↑ over oceans
- Oxidants: ↓ [O_3]; ↑ [OH] in BL, ↓ overall
- VOCs: ↑ isomerization fraction; ↑ MVK/MACR ratio; better representation of SOA-forming molecules
- Sensitivity: $\partial[O_3]/\partial NO$ and $\partial[O_3]/\partial Isop$ skew positive

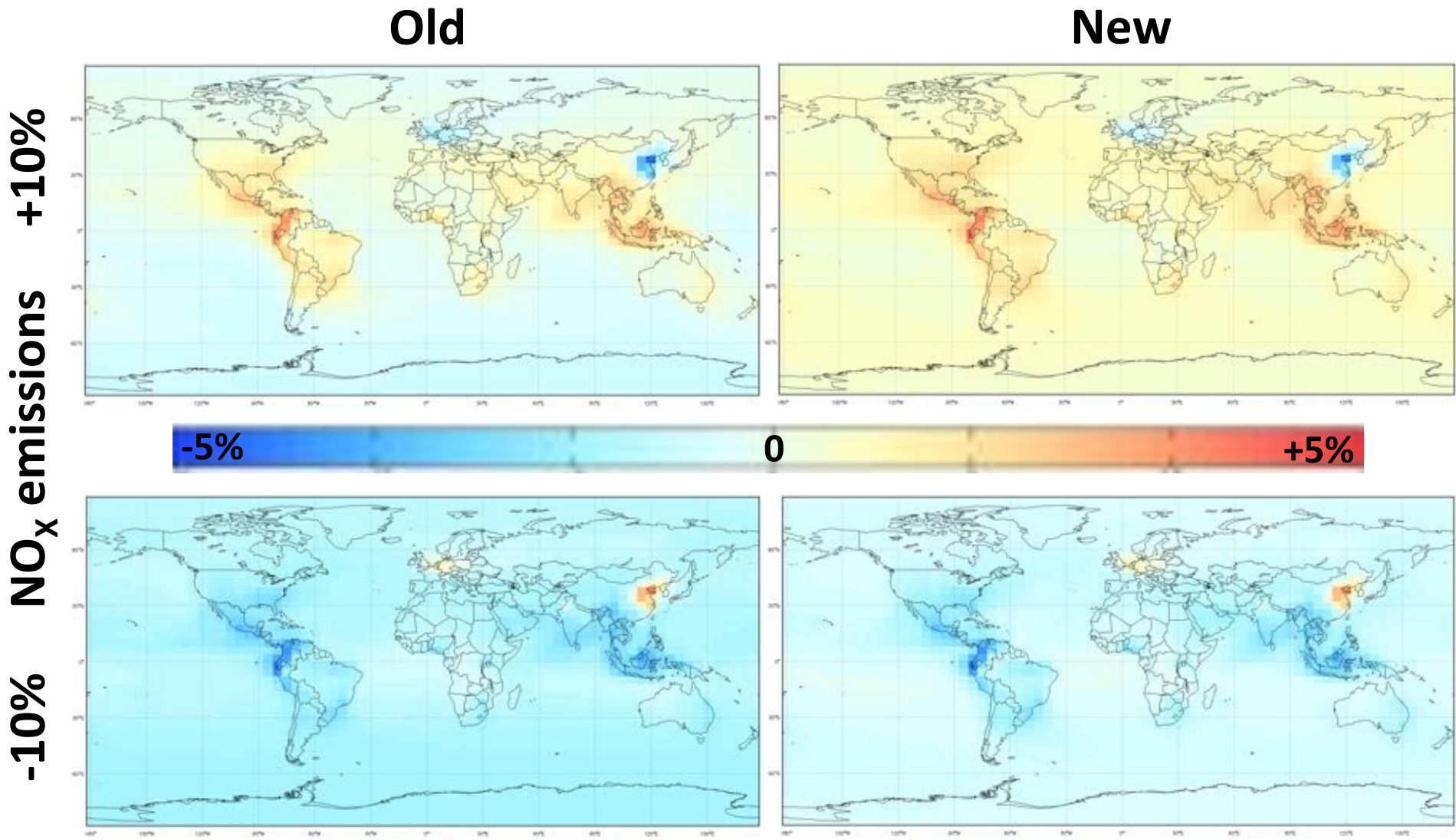
Next Steps:

- Trim the mechanism
- Compare to observations
- Investigate NO_X emissions
- Investigate diurnal and seasonal cycles



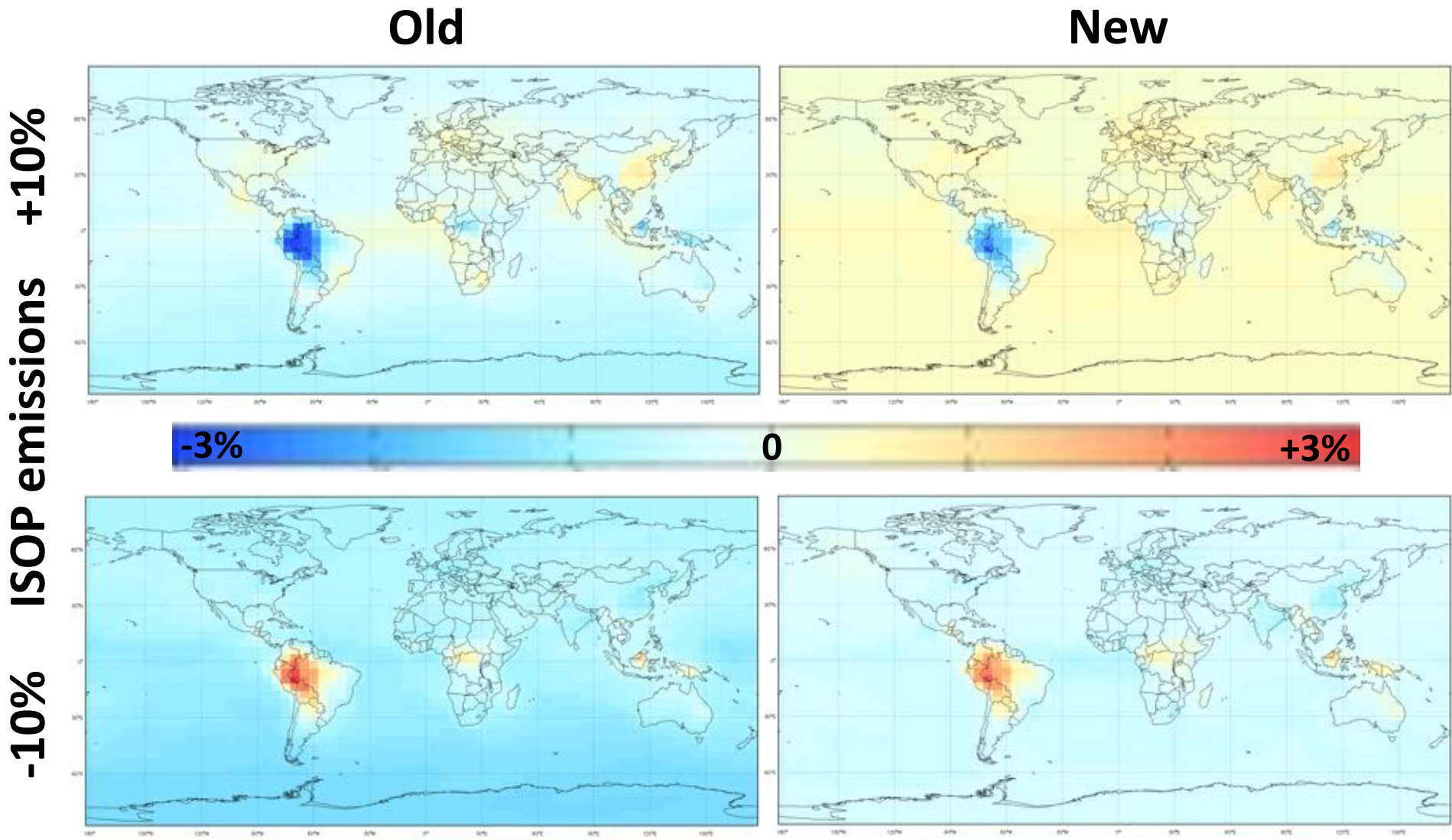
Running the Model: NO_X Sensitivity

% change in $[O_3]$ at surface with 10% change in NO_X emissions, 2014



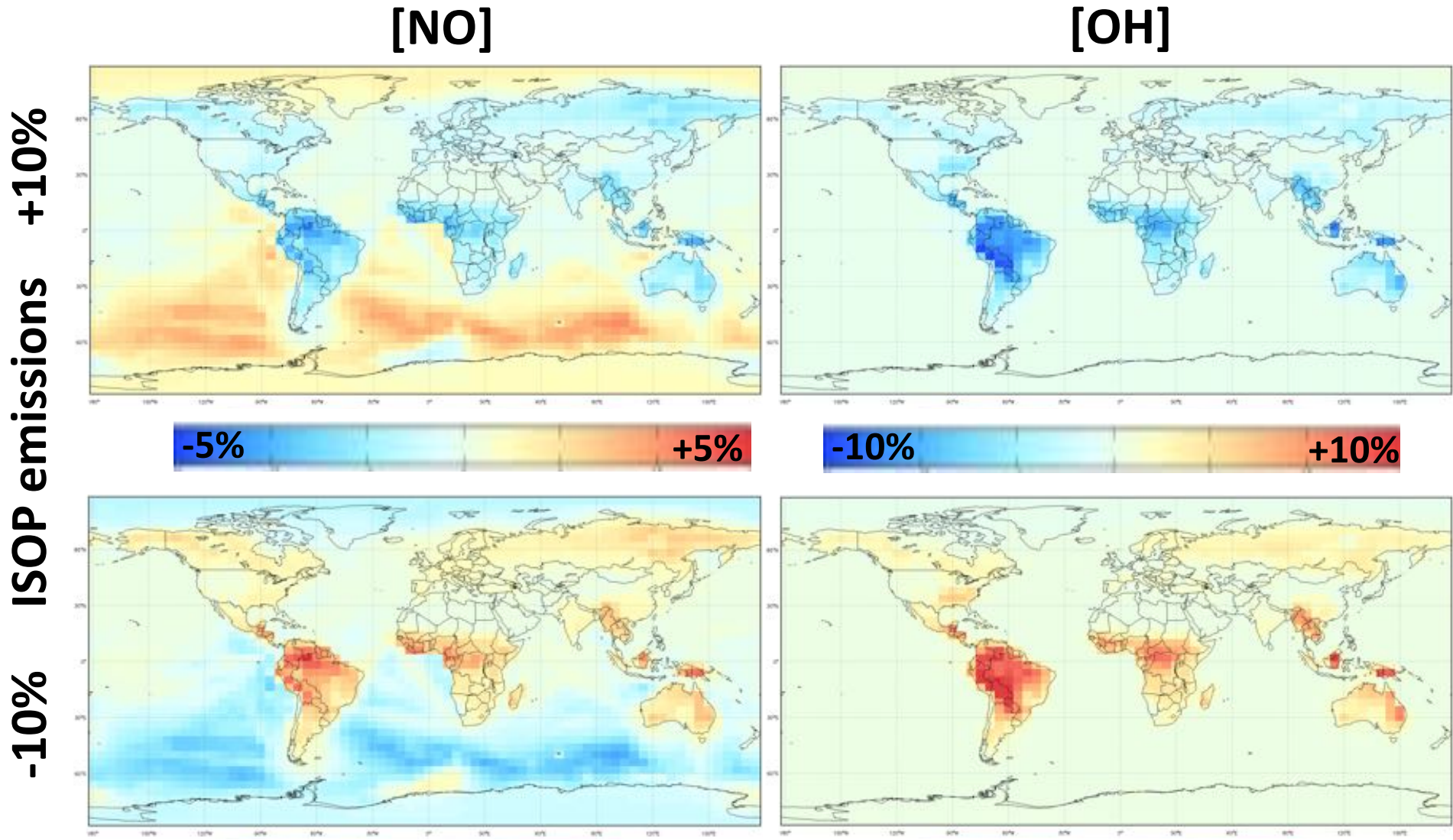
Running the Model: Isoprene Sensitivity

% change in $[O_3]$ at surface with 10% change in isoprene emission, 2014



Running the Model: Isoprene Sensitivity

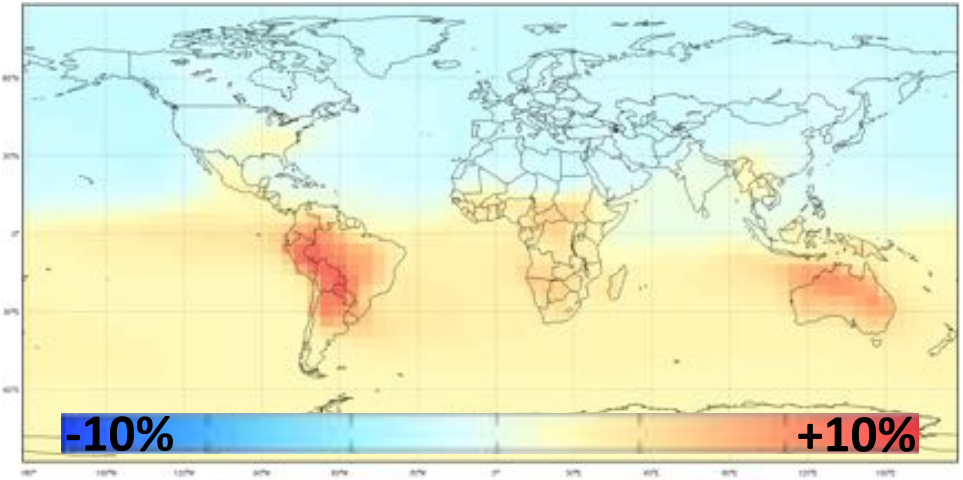
% change at surface with 10% change in isoprene emission, 2014



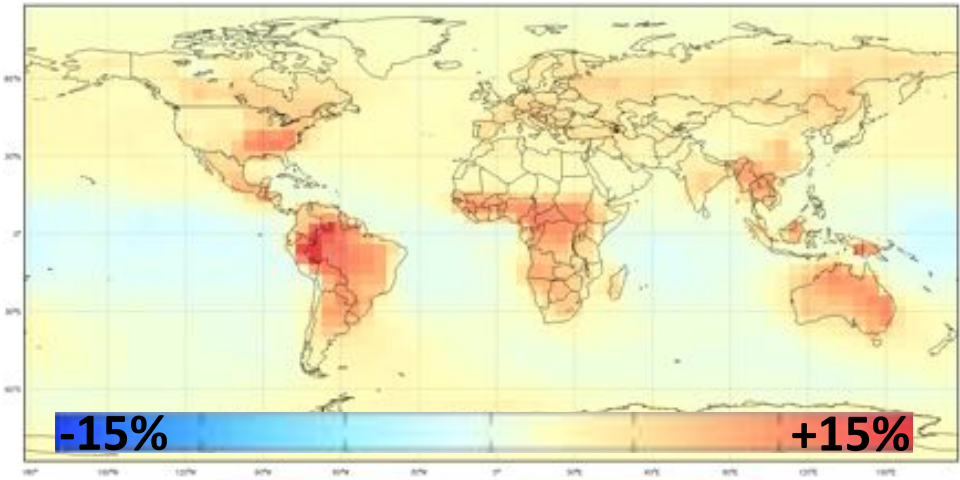
Running the Model: Small Molecules

% change in ppbv at surface from old to new isoprene mechanism, 2014

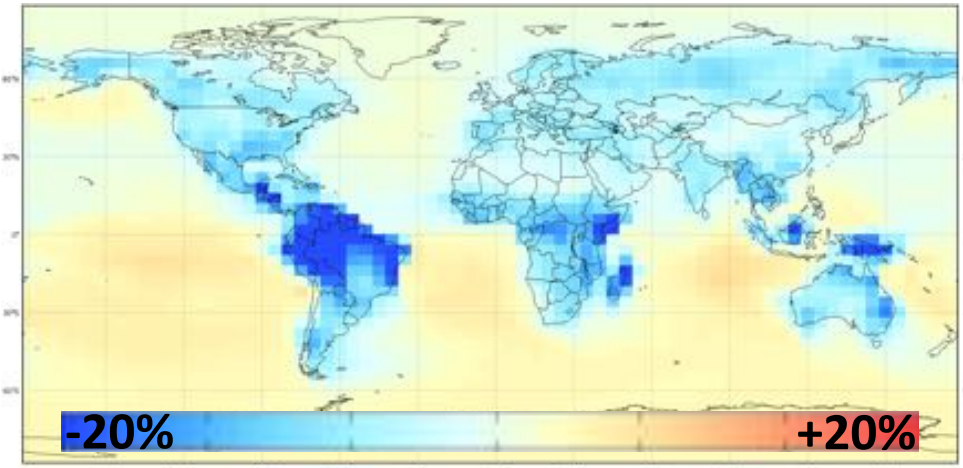
CO: prod ↓ 0.7%, loading ↑ 1.2%



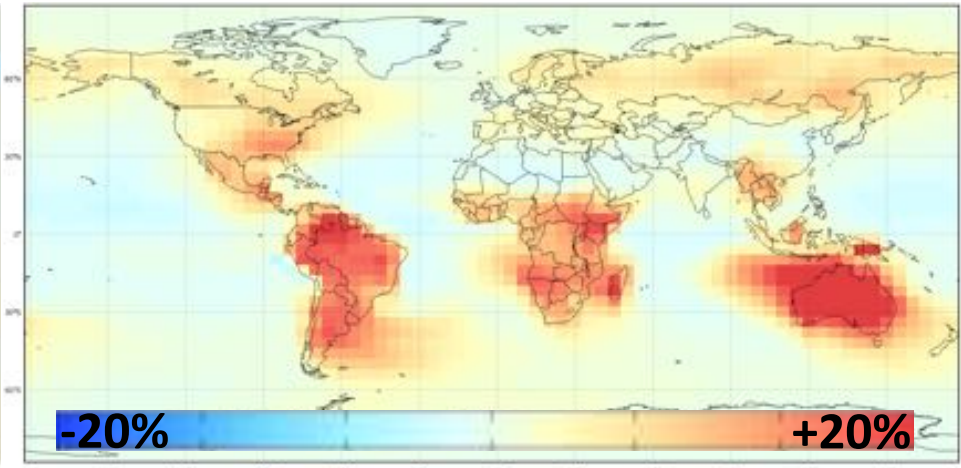
HCHO: prod ↓ 1.1%, loading ↑ 3.9%



Formic: prod ↓ 16%, loading ↑ 1.1%

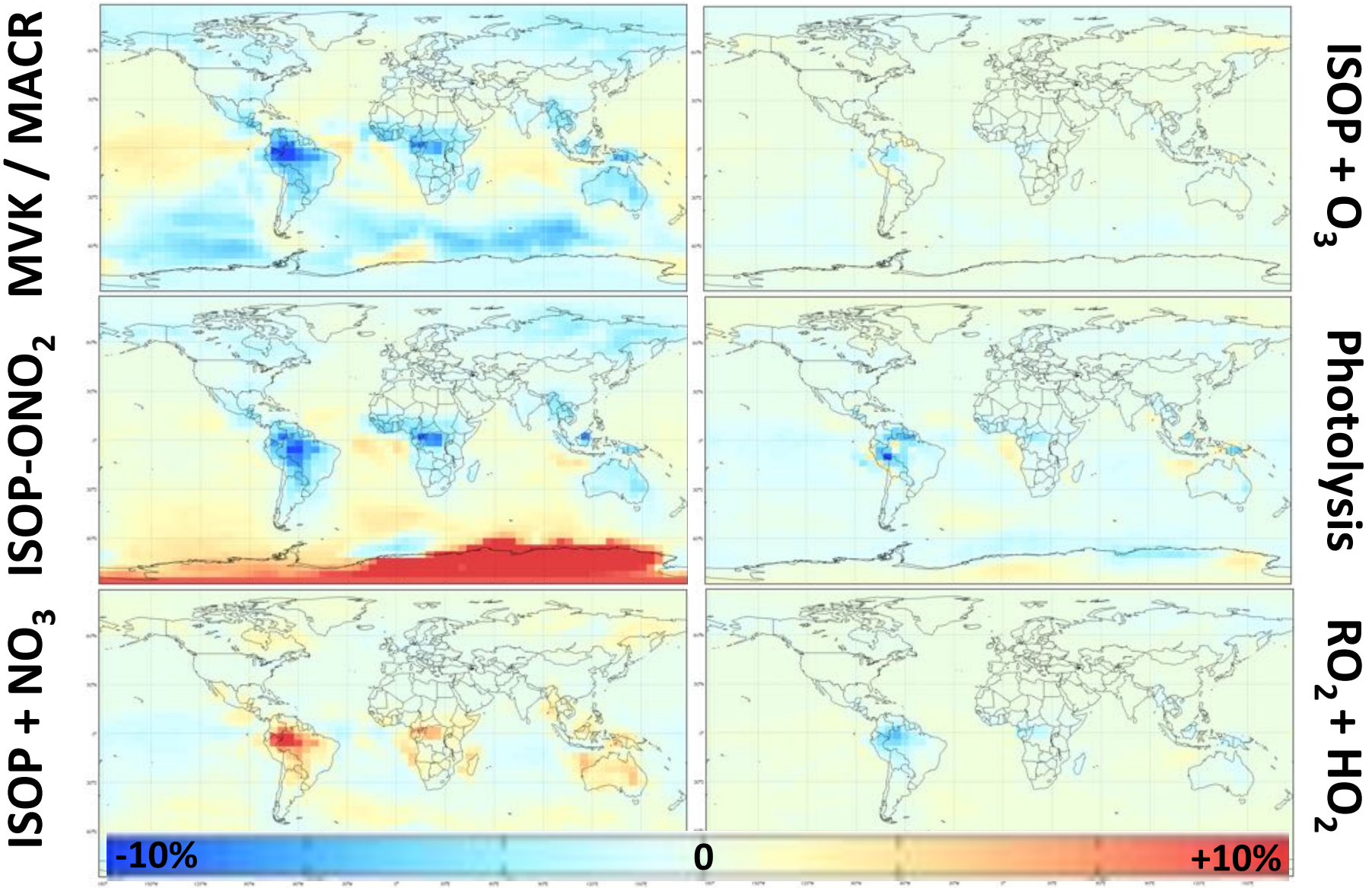


Acetic: prod ↓ 14%, loading ↑ 4.5%



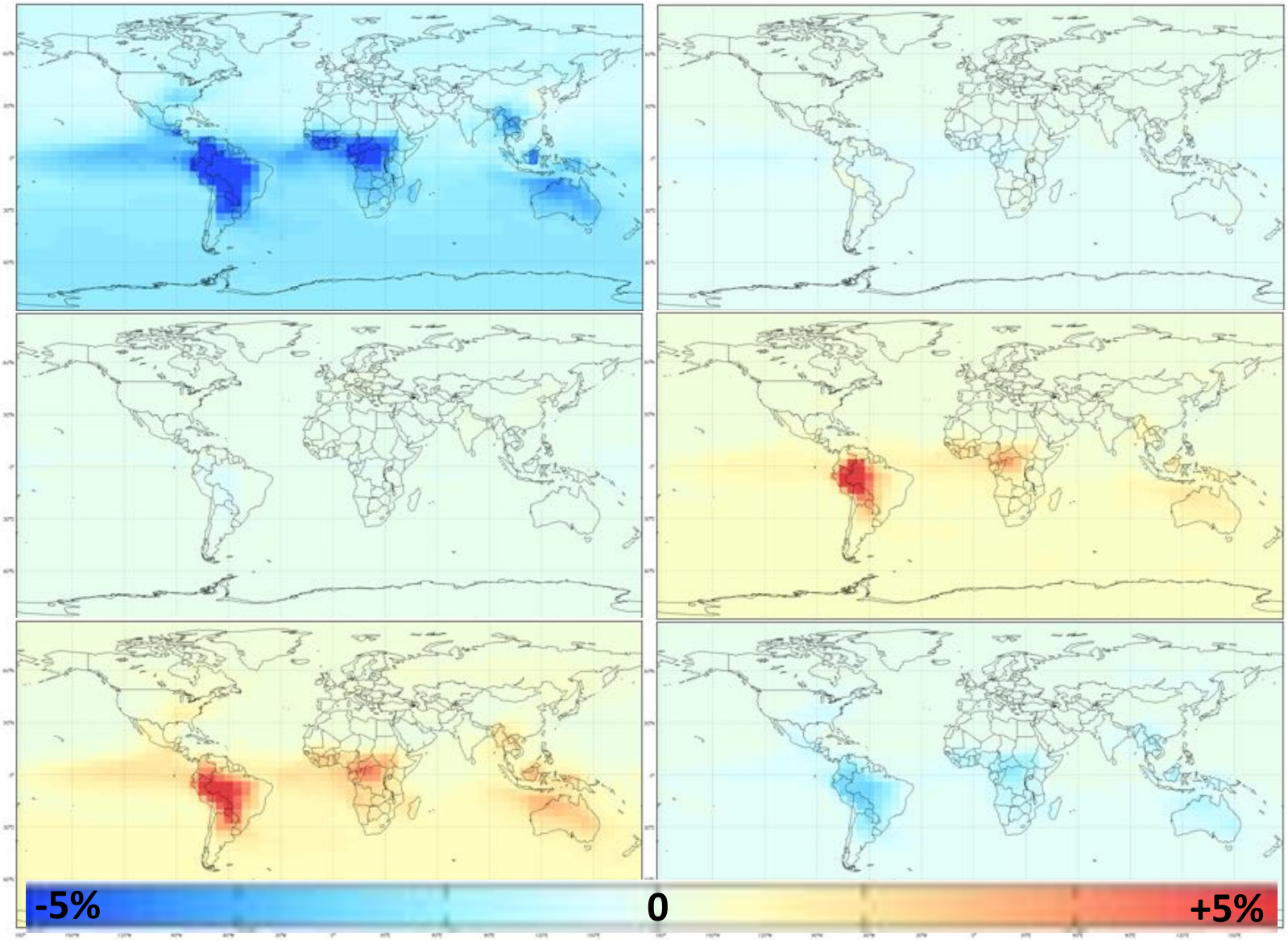
Running the Model: Δ NO_x

% change in [NO] at surface from specific sub-mechanisms, 2014



Running the Model: ΔO_3

% change in $[O_3]$ at surface from specific sub-mechanisms, 2014



Running the Model: Δ OH

% change in [OH] at surface from specific sub-mechanisms, 2014