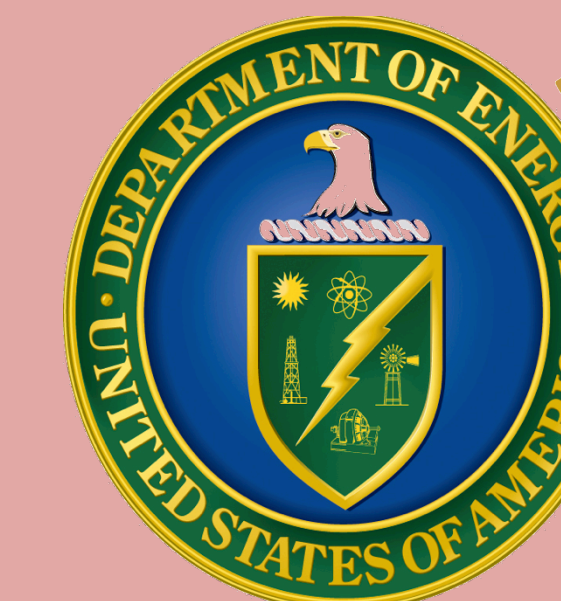




Recent Revisions to Isoprene Photochemistry Based on Caltech Chamber and Field Data

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Background

Since the introduction of the new isoprene scheme to GEOS-Chem,¹⁻⁷ chamber studies conducted at Caltech and data from field studies have allowed us to expand and revise our knowledge of the isoprene oxidation mechanisms. These revisions, including new species, adjusted reaction and deposition rates, and updated product yields, have been successively compiled into an updated GEOS-Chem isoprene mechanism. Simulations run with these revisions, detailed below, show **that even slight adjustments to the oxidative chemistry of isoprene can have profound effects on the budgets of such archetypal tropospheric species as OH, O₃, NO, and secondary organic aerosol (SOA) precursors such as IEPOX.**

1. MVK Oxidation⁸

Recently published results elucidate the OH oxidation mechanism of methyl vinyl ketone (MVK), itself a first-generation product of isoprene oxidation. These mechanistic modifications (Figure 1), along with changes to acyl peroxy radical + HO₂ product yields and MVK-hydroxy-hydroperoxide photolysis rates, were incorporated into GEOS-Chem to investigate their effects on oxidant budgets (Figure 2). Oxidant recycling in the new MVK mechanism resulted in **non-negligible increases in OH mixing ratios over remote forested regions.**

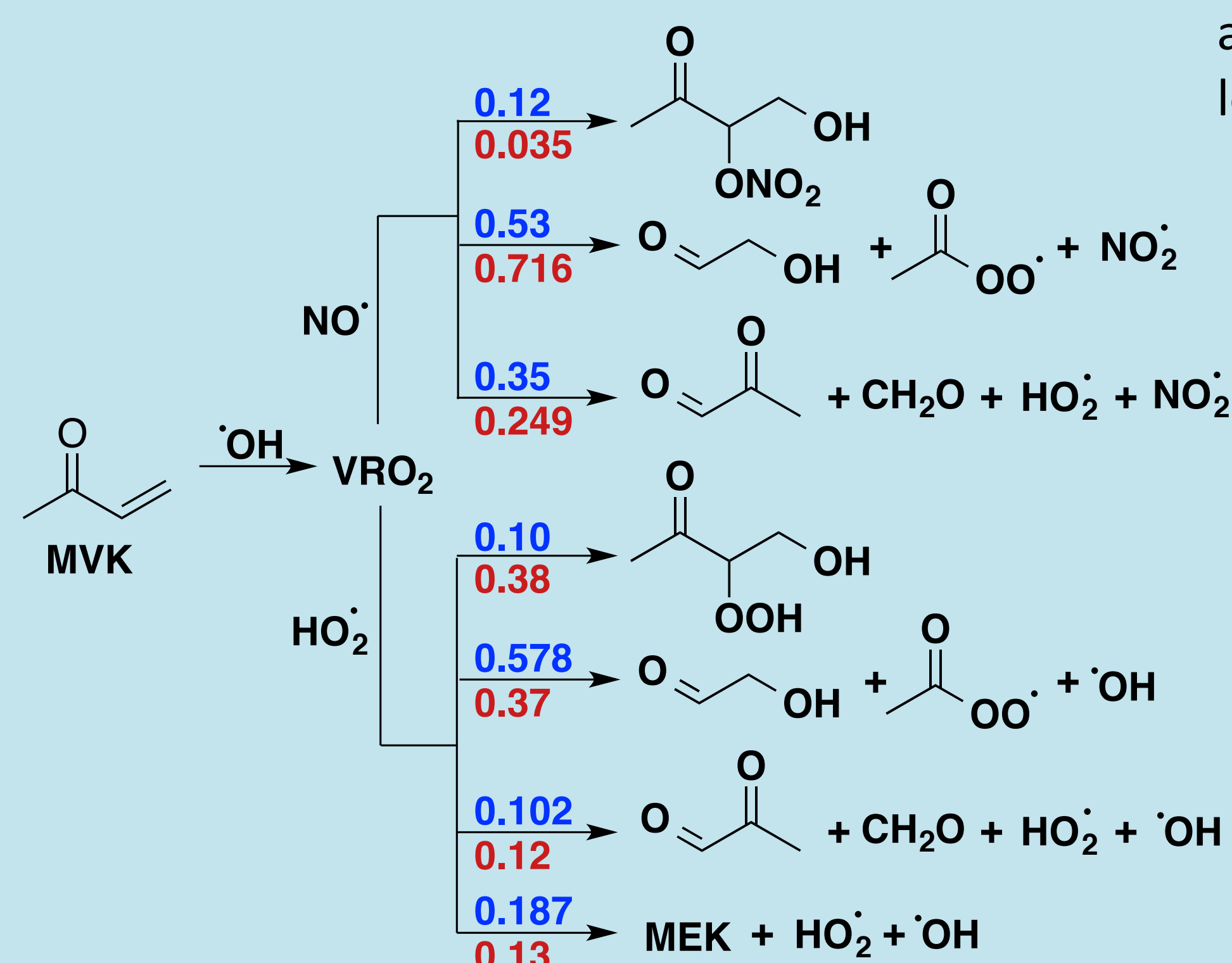


Figure 1: Old and updated MVK oxidation product yields

3. Dry Deposition¹⁰

Fluxes and dry deposition velocities for 16 trace gases were measured at the Southern Oxidant and Aerosol Study (SOAS). From these measurements, GEOS-Chem parameterizations of dry deposition (H^*) for select species were adjusted to match observed deposition velocities (Table 2). **GEOS-Chem underpredicts dry deposition velocities for many trace gases;** as a result, the adjustments made in these simulations decreased surface level trace gas concentrations by up to 45% (Figure 5).

| Species | H^* _{old} | H^* _{new} |
|-------------------------------|----------------------|----------------------|
| H ₂ O ₂ | 1.00 E+05 | 5.00 E+07 |
| Isoprene nitrates | 1.70 E+04 | 2.00 E+06 |
| Propanone nitrate | 1.00 E+03 | 5.00 E+05 |
| Hydroxyacetone | 2.90 E+03 | 1.40 E+06 |
| Glycolaldehyde | 4.10 E+04 | 2.00 E+07 |
| MACR/MVK nitrates | 1.70 E+04 | 2.00 E+06 |
| ISOPOOH | 1.70 E+06 | 1.70 E+06 |
| IEPOX | 1.30 E+08 | 8.00 E+07 |

Table 2: Old and revised dry deposition parameters for select species

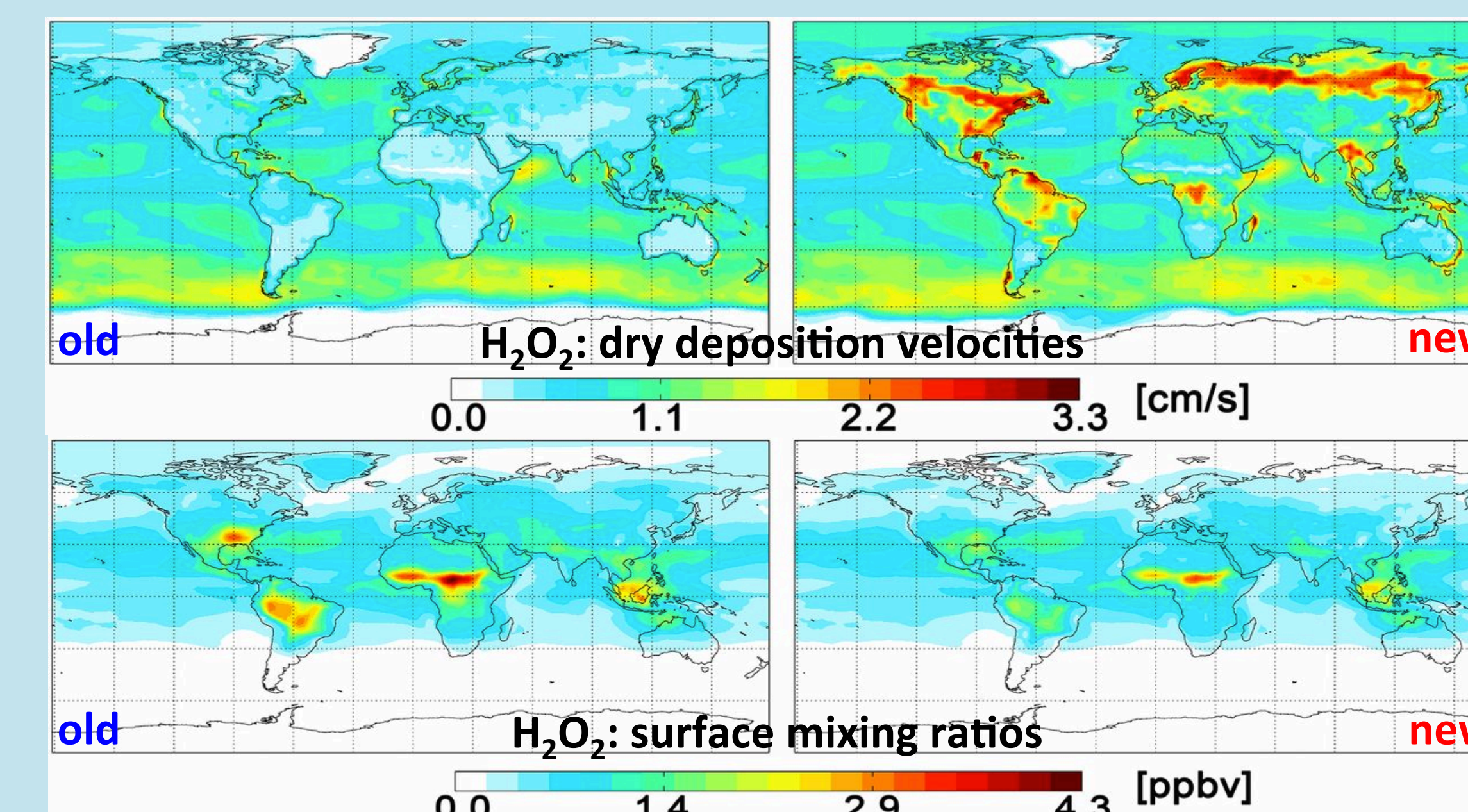


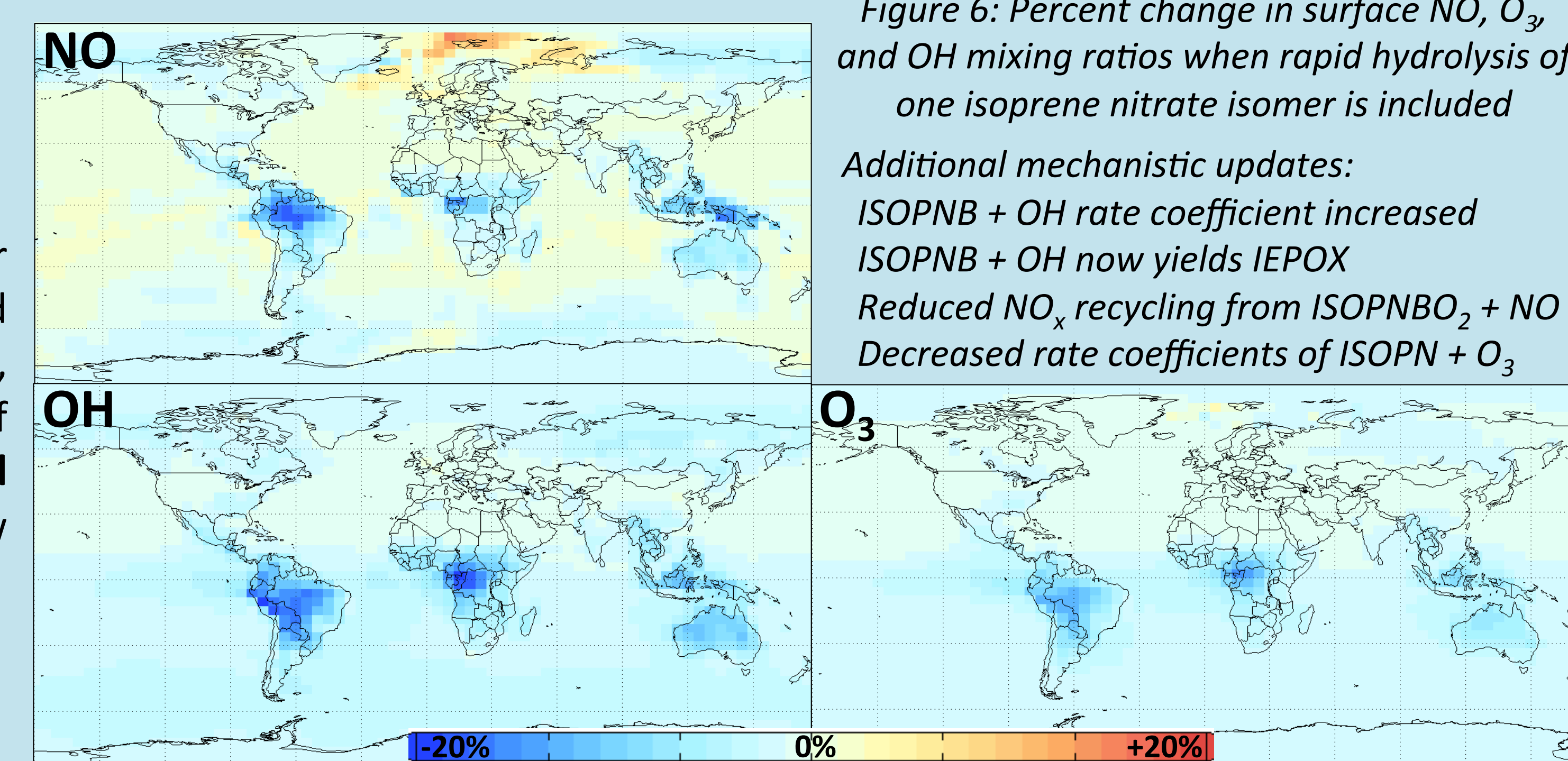
Figure 5: Effects of updated dry deposition parameters for H₂O₂

4. Isoprene Nitrates (ongoing)^{11,*}

Individual isoprene nitrate isomers have recently been synthesized and used in chamber experiments, the results of which have been incorporated into GEOS-Chem (listed below). Additionally, recent field data suggest that certain isomers may react much faster with surfaces than previously thought. We model the extreme case of this reactivity – instantaneous hydrolysis, with 0% NO_x recycling from said isomers – **to put an upper limit on the dramatic effects of this chemistry on NO_x, OH, and O₃ budgets** (Figure 6).

Figure 6: Percent change in surface NO, O₃, and OH mixing ratios when rapid hydrolysis of one isoprene nitrate isomer is included

Additional mechanistic updates:
 ISOPNB + OH rate coefficient increased
 ISOPNB + OH now yields IEPOX
 Reduced NO_x recycling from ISOPNB₂ + NO
 Decreased rate coefficients of ISOPN + O₃



All models use GEOS-Chem v.9-02 with GEOS5 meteorology and the Rosenbrock Rodas-3 KPP solver, with extra tracers and species added. Models are run at 4° × 5° resolution and are initialized with a 1.5 year spinup before a January-December 2012 final simulation (except in Figure 6, which uses 2° × 2.5° resolution for 2013), and unless otherwise stated, figures show mixing ratios or percent changes in the lowest 1 km of the atmosphere.

*denotes currently unpublished work

Sources

- Crouse, J. D., et al. Peroxy radical isomerization in the oxidation of isoprene. *Phys. Chem. Chem. Phys.* 2011, 13, 13607-13613.
- Crouse, J. D., et al. Atmospheric fate of methacrolein. 1. Peroxy radical isomerization following addition of OH and O₂. *J. Phys. Chem. A* 2012, 116, 5756-5762.
- Lockwood, A. L., et al. Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry. *Atmos. Chem. Phys.* 2010, 10, 6169-6178.
- Paulot, F., et al. Isoprene photooxidation: new insights into the production of acids and organic nitrates. *Atmos. Chem. Phys.* 2009, 9, 1479-1501.
- Paulot, F., et al. Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science* 2009, 325 (5941), 730-737.
- Peeters, J., et al. HOx radical regeneration in the oxidation of isoprene. *Phys. Chem. Chem. Phys.* 2009, 11, 5935-5939.
- Peeters, J., et al. HOx radical regeneration in isoprene oxidation via peroxy radical isomerisations. 2. Experimental evidence and global impact. *Phys. Chem. Chem. Phys.* 2010, 12, 14227-14235.
- Praske, E., et al. Atmospheric fate of methyl vinyl ketone: peroxy radical reactions with NO and HO₂. *J. Phys. Chem. A* 2014, Article ASAP.
- Bates, K., et al. Gas phase production and loss of isoprene epoxydiols. *J. Phys. Chem. A* 2014, 118 (7), 1237-1246.
- Nguyen, T., et al. Rapid deposition of oxidized biogenic compounds to a temperate forest. *Proc. Nat'l. Acad. Sci.* 2015, 112 (5), E392-E401.
- Lee, L., et al. On rates and mechanisms of OH and O₃ reactions with isoprene-derived hydroxy nitrates. *J. Phys. Chem. A* 2014, 118, 1622-1637.

2. ISOPOOH and IEPOX^{9,*}

New experimental techniques and synthetic standards of isoprene hydroxyhydroperoxides (ISOPOOH or RIP) and isoprene epoxydiols (IEPOX) have allowed us to determine isomer-specific reaction rates and product yields. In GEOS-Chem, ISOPOOH and IEPOX were separated into their dominant isomers (1,2-β, 4,3-β, and δ for ISOPOOH; *cis*- and *trans*-β for IEPOX), and experimentally determined rates and yields of each isomer's reaction with OH were compiled into a new mechanism (Figure 3) to determine **updated global yields of ISOPOOH and IEPOX** (Table 1). Simulations with this new chemistry also show **substantial global production of the newly identified C₄O₃H₈ and C₄O₃H₆ oxidation products** (Figure 4).

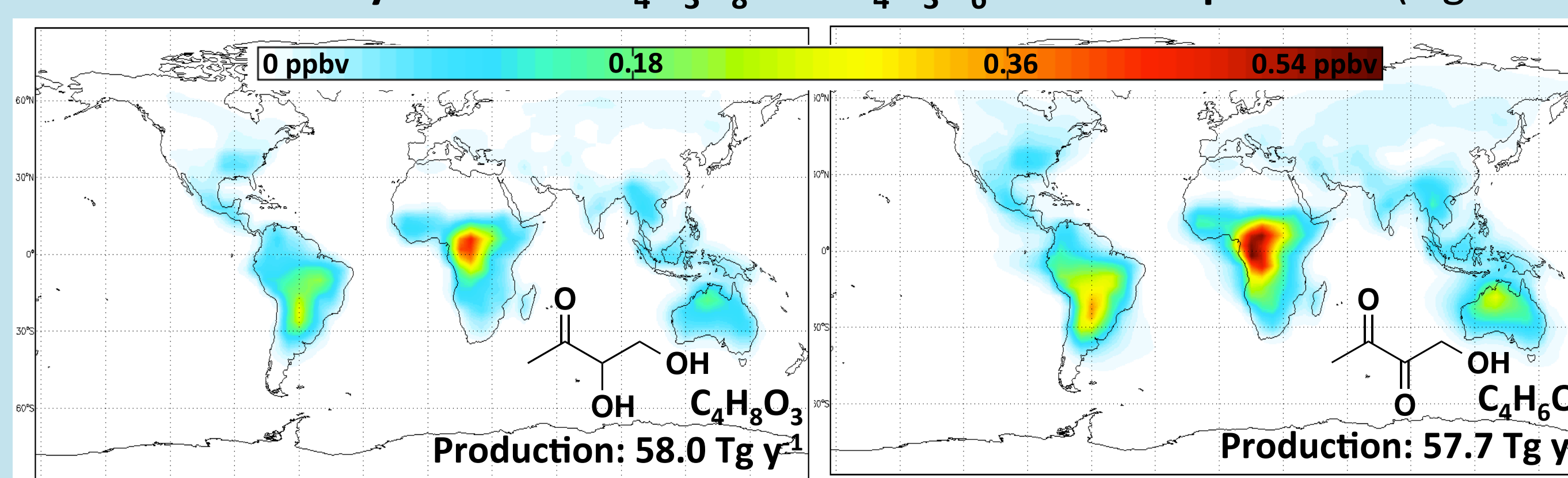


Figure 4: Average annual surface mixing ratios of newly identified IEPOX + OH products

| Mechanism: | Old ⁵ | Standard | New |
|----------------------------|------------------|----------|-------|
| Isoprene emissions (Tg/y): | 515 | 515 | 515 |
| ISOPOOH production (Tg/y): | 253.1 | 329.9 | 355.0 |
| IEPOX production (Tg/y): | 185.1 | 239.4 | 226.0 |

Table 1: Annual production of ISOPOOH and IEPOX in old and revised mechanisms

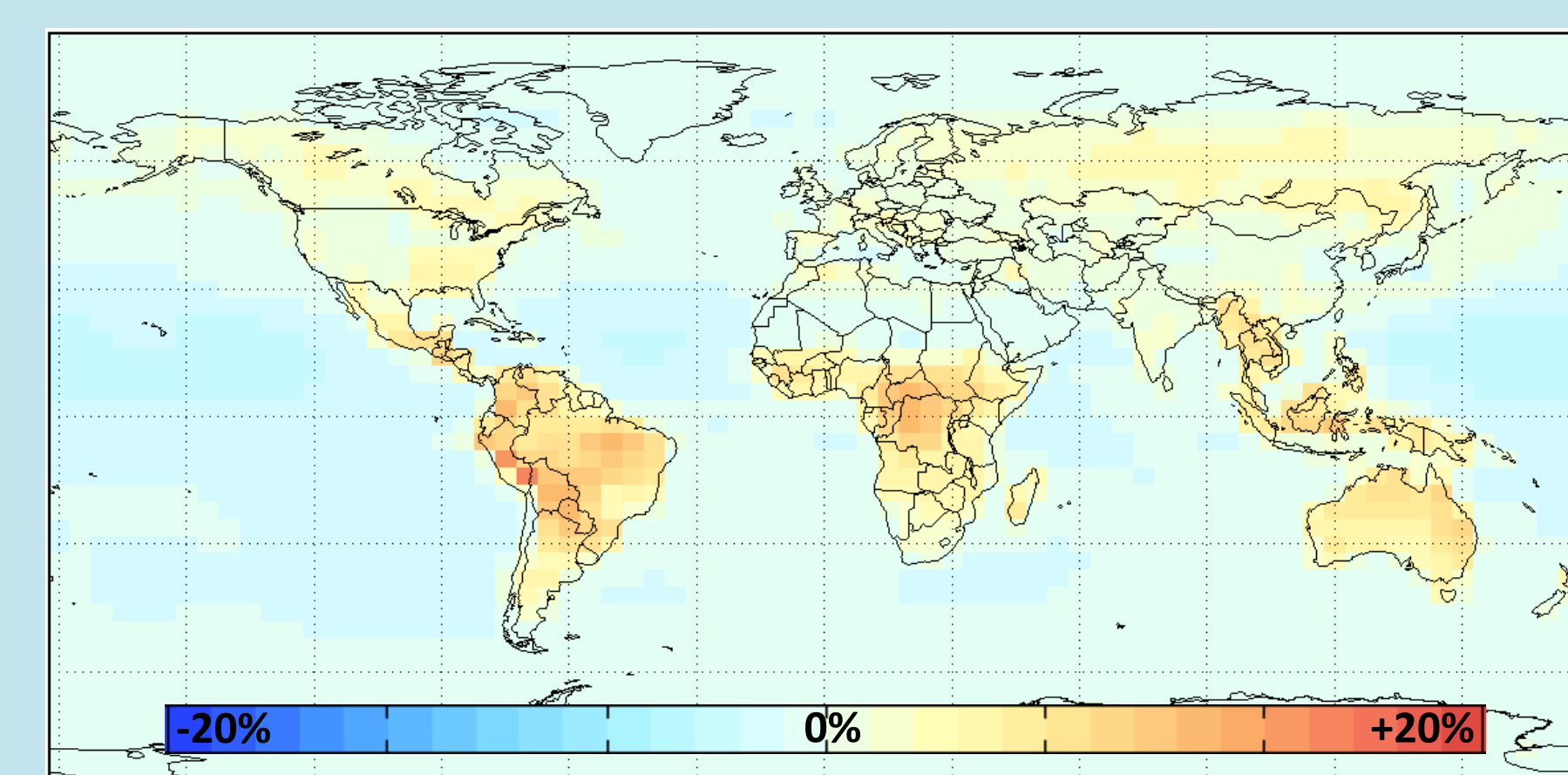


Figure 2: Change in average annual surface OH concentrations between the new and old MVK oxidation mechanisms

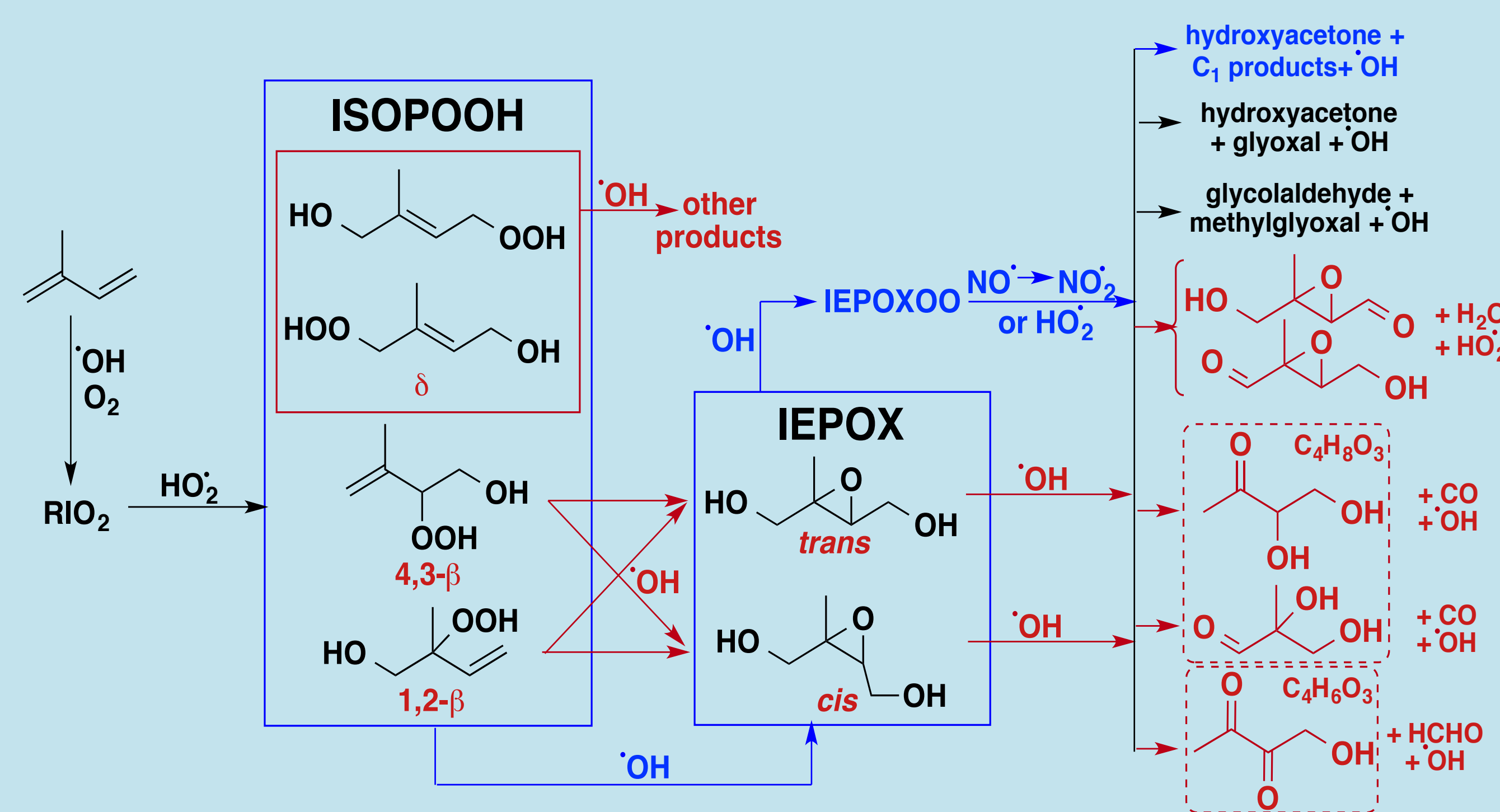


Figure 3: Old and updated ISOPOOH and IEPOX oxidation mechanism