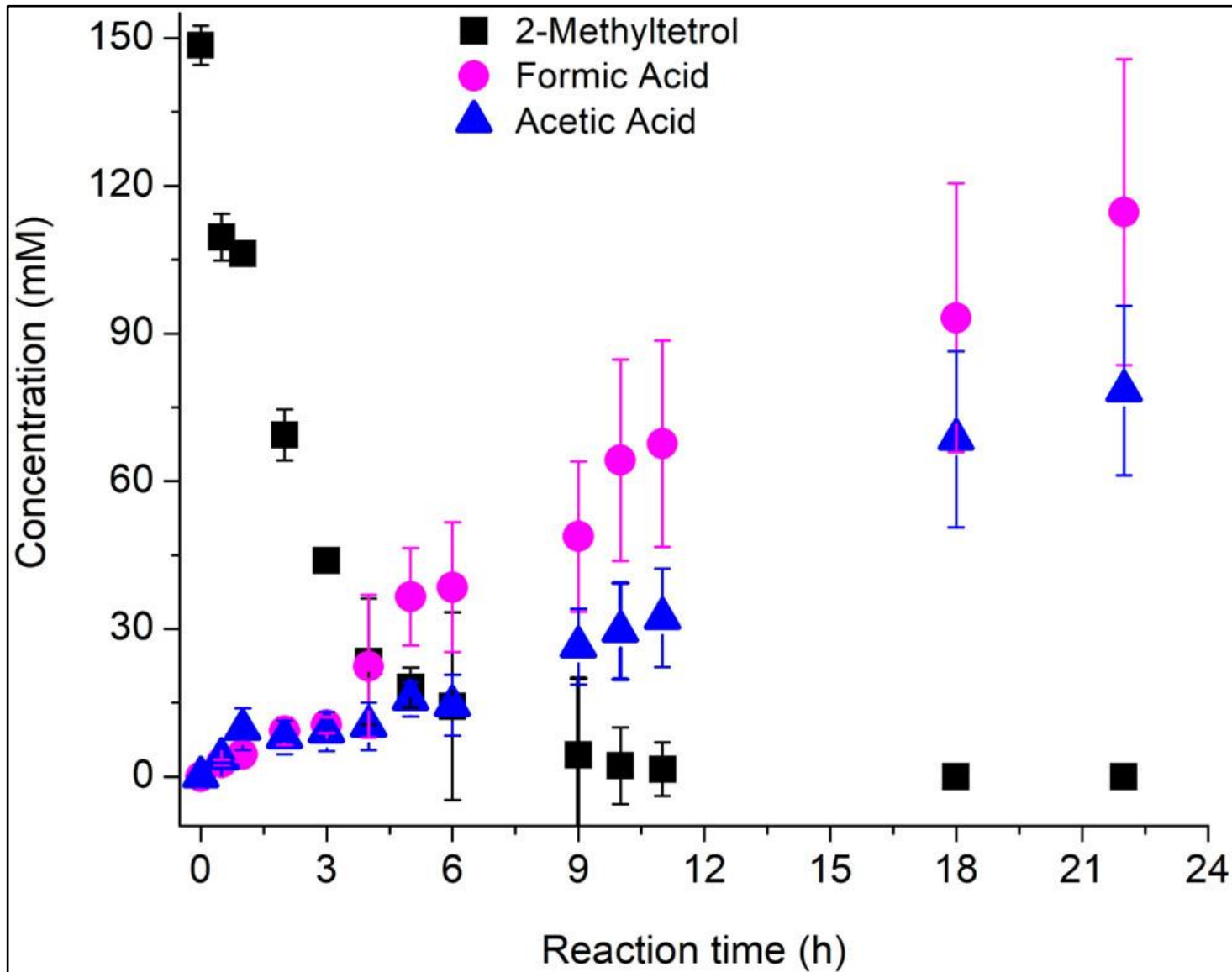


Lab studies support aqueous-phase formation pathway

Concentrations of 2-methyltetrol (precursor) and product acids



← Aqueous phase reaction of 2-methyltetrol at pH 2

2-methyltetrol: aqueous-phase product of isoprene epoxydiols

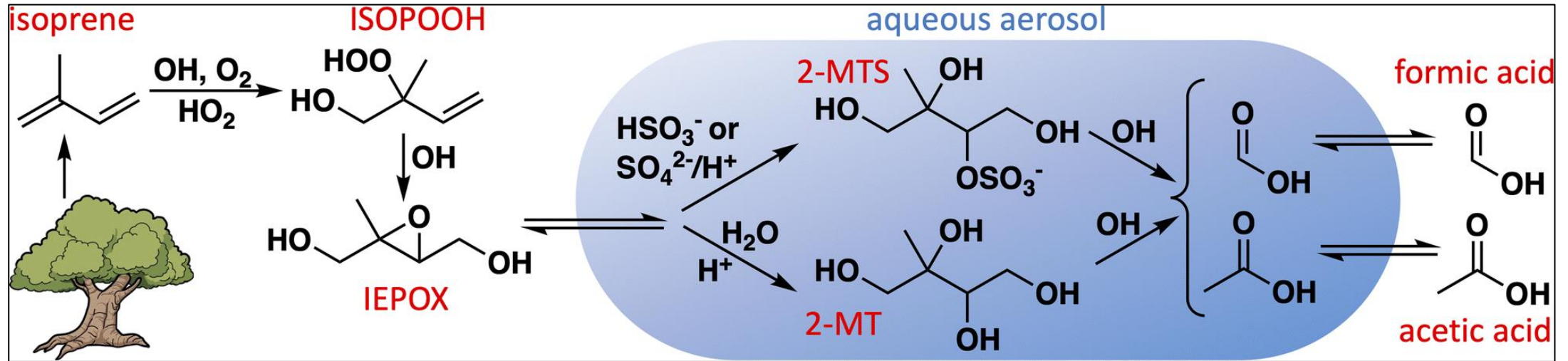
Supports formation of volatile acids that partition to gas phase

Greater yields of formic acid than acetic acid

Experiments in **bulk media**, so extrapolate to aqueous aerosol

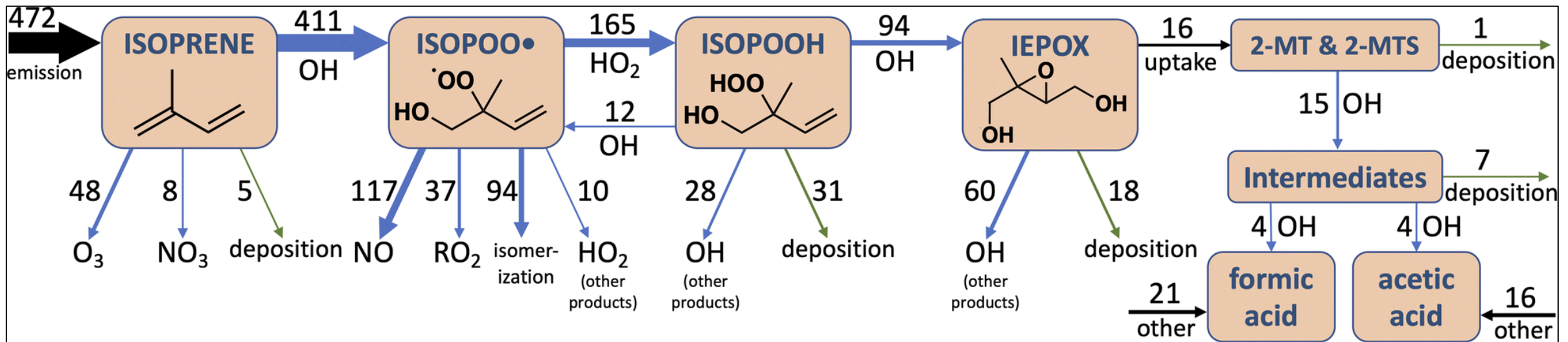
[Cope et al., 2021]

Heterogeneous mechanism already tested in GEOS-Chem



2-MT: 2-methyltetrols; 2-MTS: sulfate esters of 2-MT

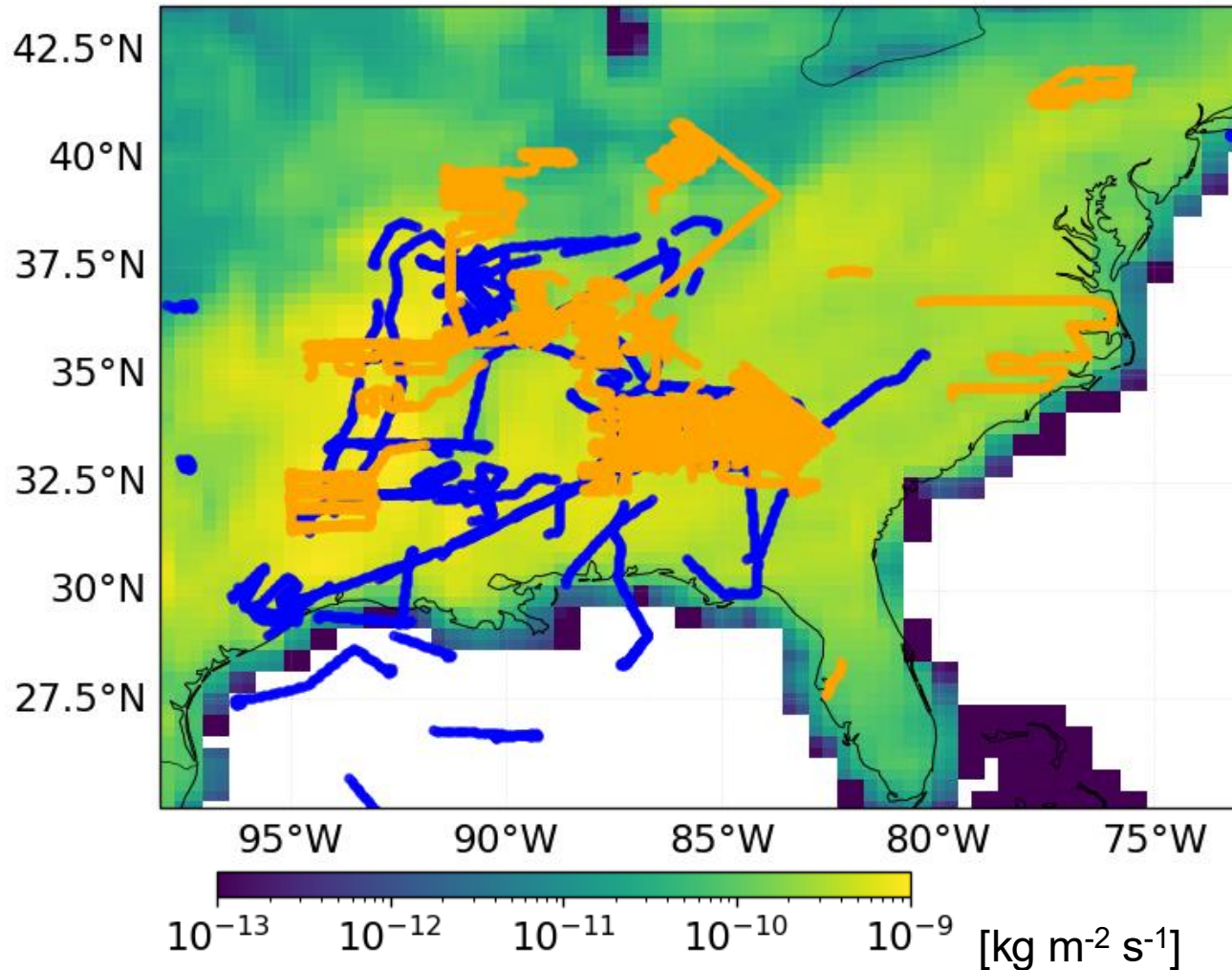
Annual carbon fluxes in Tg C from GEOS-Chem updated with the aqueous-phase mechanism



[Bates et al., 2023]

Constrain mechanism with aircraft observations in the SE US

Boundary layer flight tracks and average MEGAN isoprene emissions for Jun-Sep 2013



Flight tracks below 2 km:

— SENEX (Jun-Jul 2013)

— SEAC⁴RS (Aug-Sep 2013)

Relevant measurements:

SENEX:

HCOOH

isoprene

total organic aerosol (OA)

SEAC⁴RS:

ISOPOOH

IEPOX

isoprene

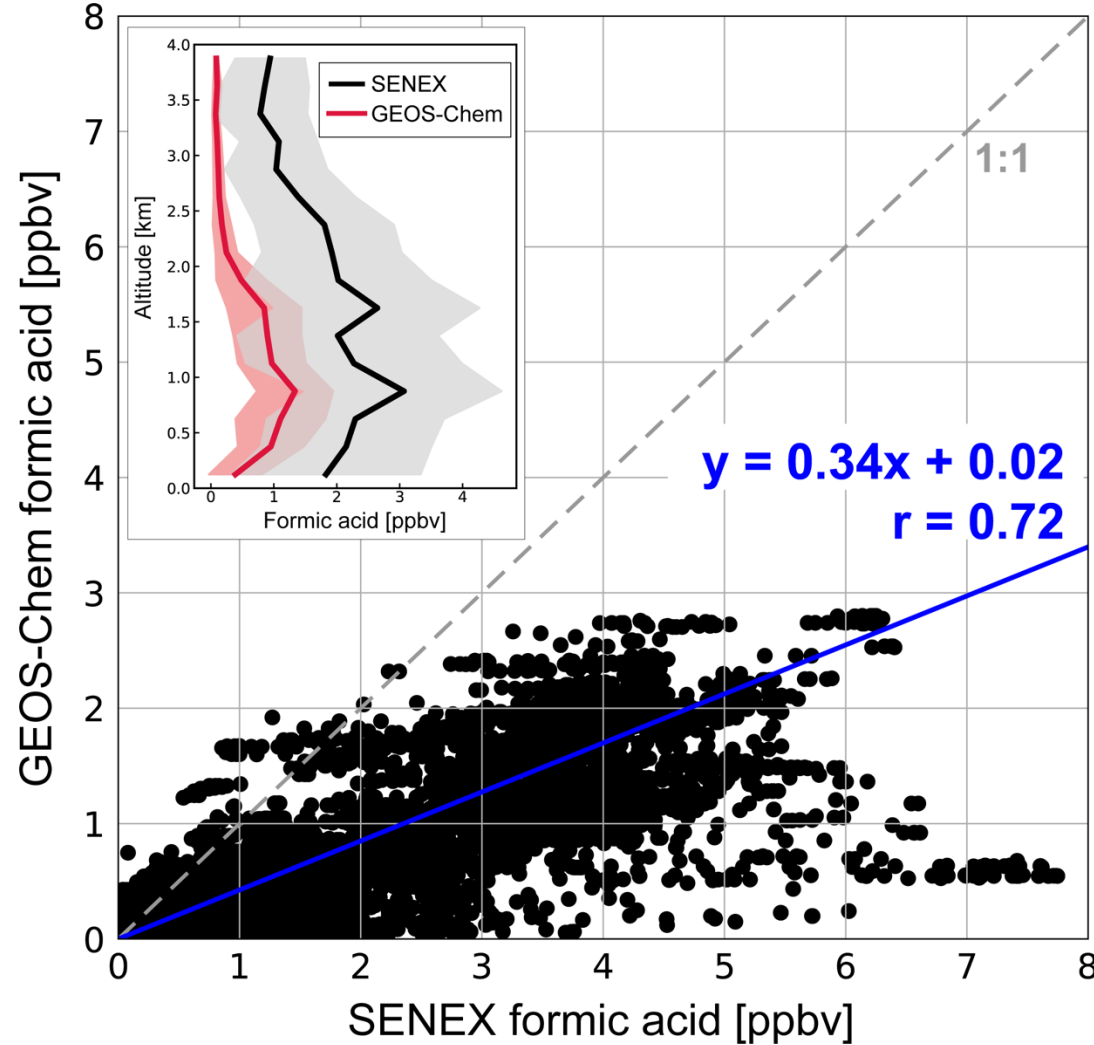
total OA

Evaluate model without and with additional secondary sources of formic and acetic acids

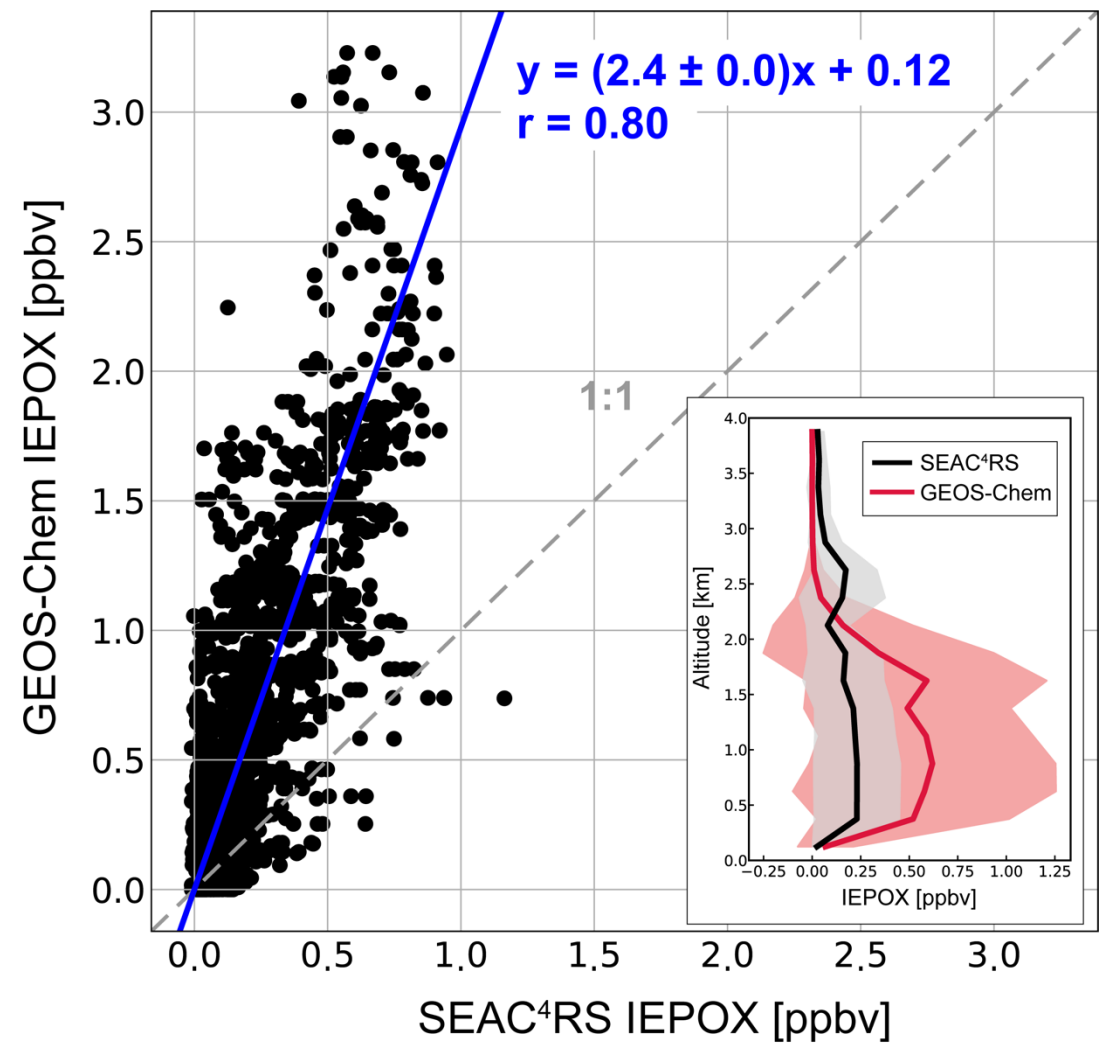
Sample model along flight tracks using GCClassic version 14.5.0 driven with MERRA-2 on $0.25^{\circ} \times 0.3125^{\circ}$ grid

Evaluate model without mechanistic updates

Evaluation of modelled formic acid



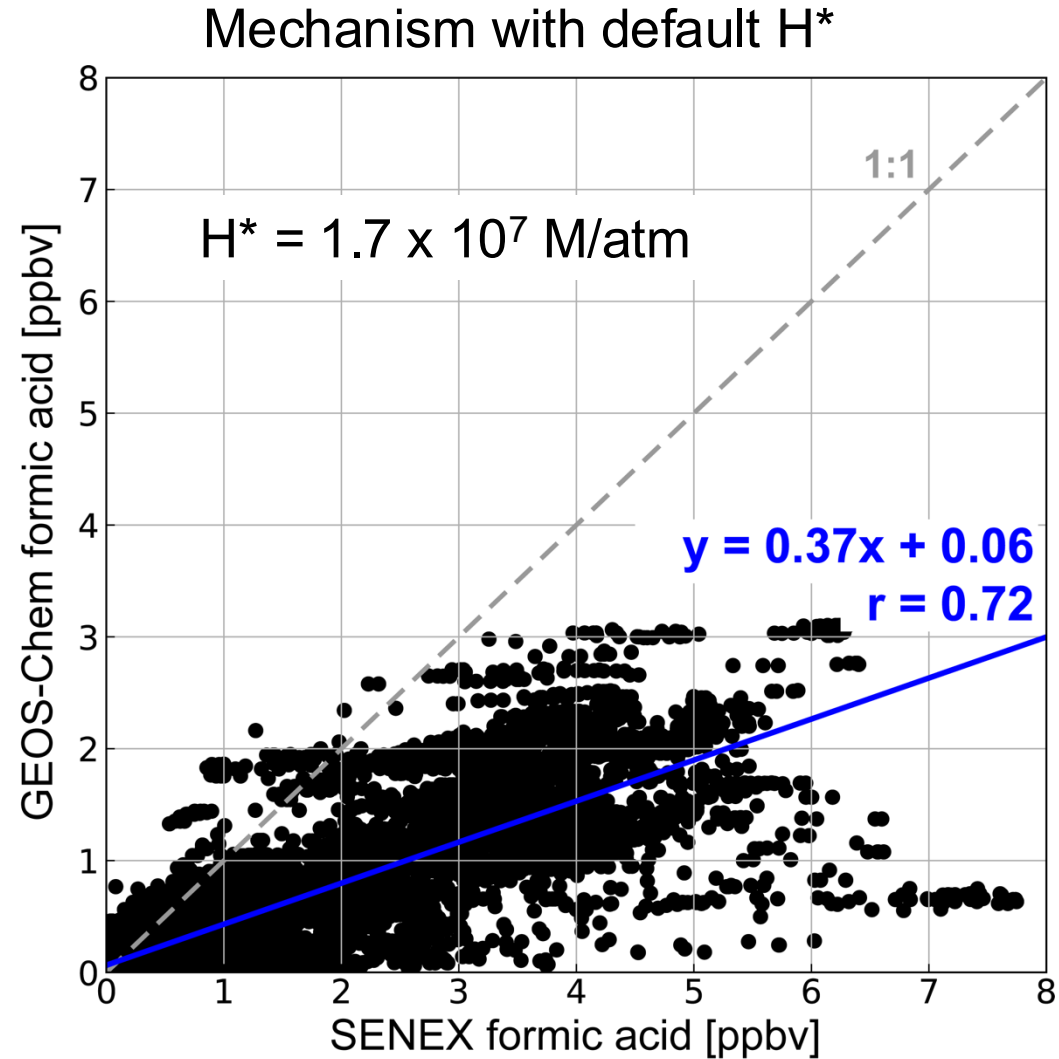
Evaluation of modelled IEPOX



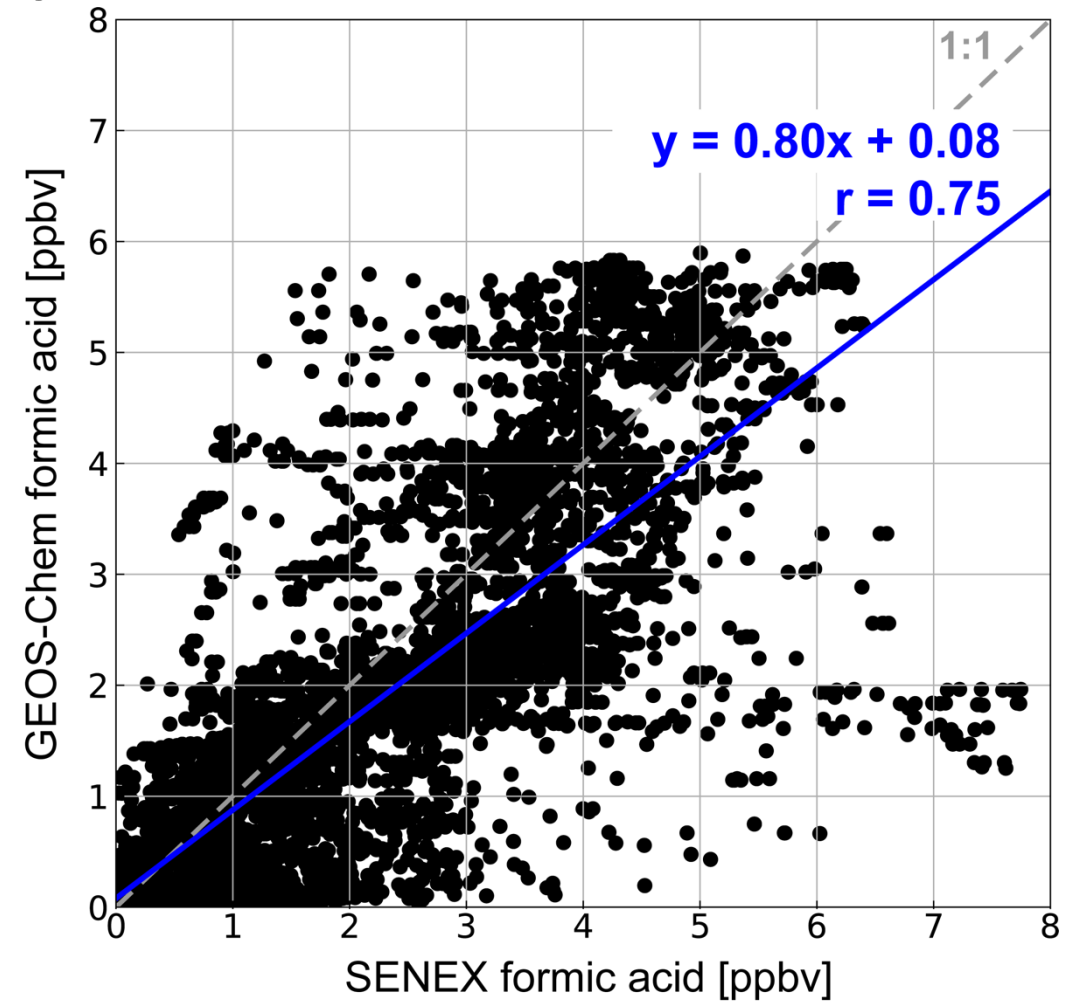
Expected formic acid underestimate (~65%) and gas-phase IEPOX overestimate (>2-fold)

Supports implementation of process that consumes IEPOX to generate small acids

Model with IEPOX heterogeneous formation mechanism



Agreement achieved with 300-fold increase in H^*

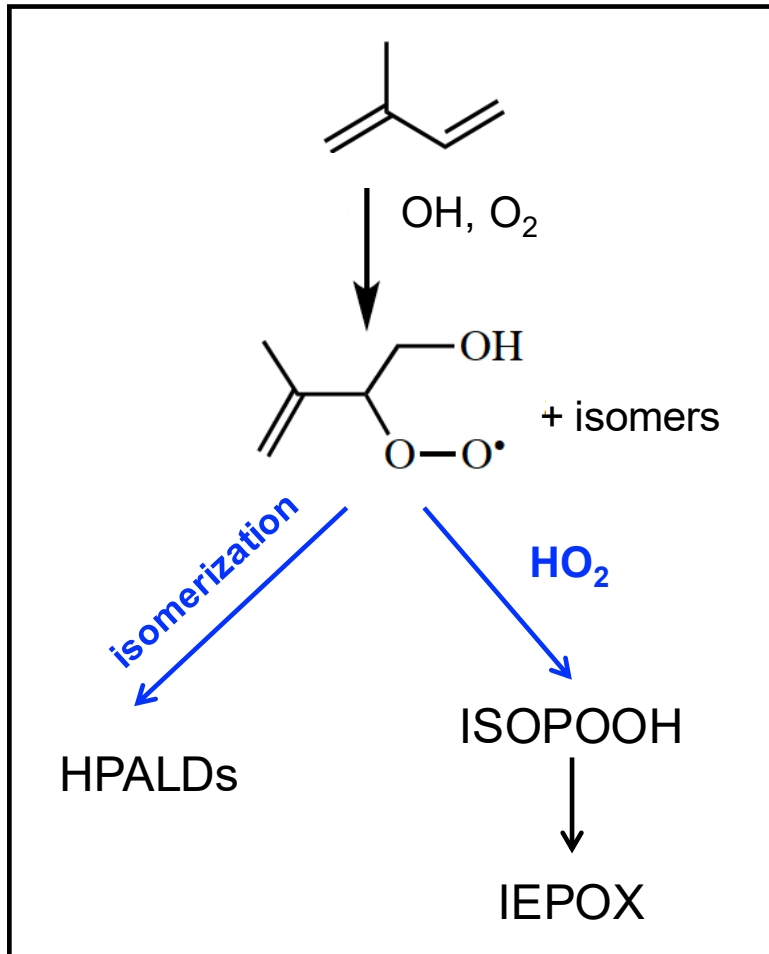


Also test HCHO cloud processing forming HCOOH, but it slightly decreases formic acid abundance

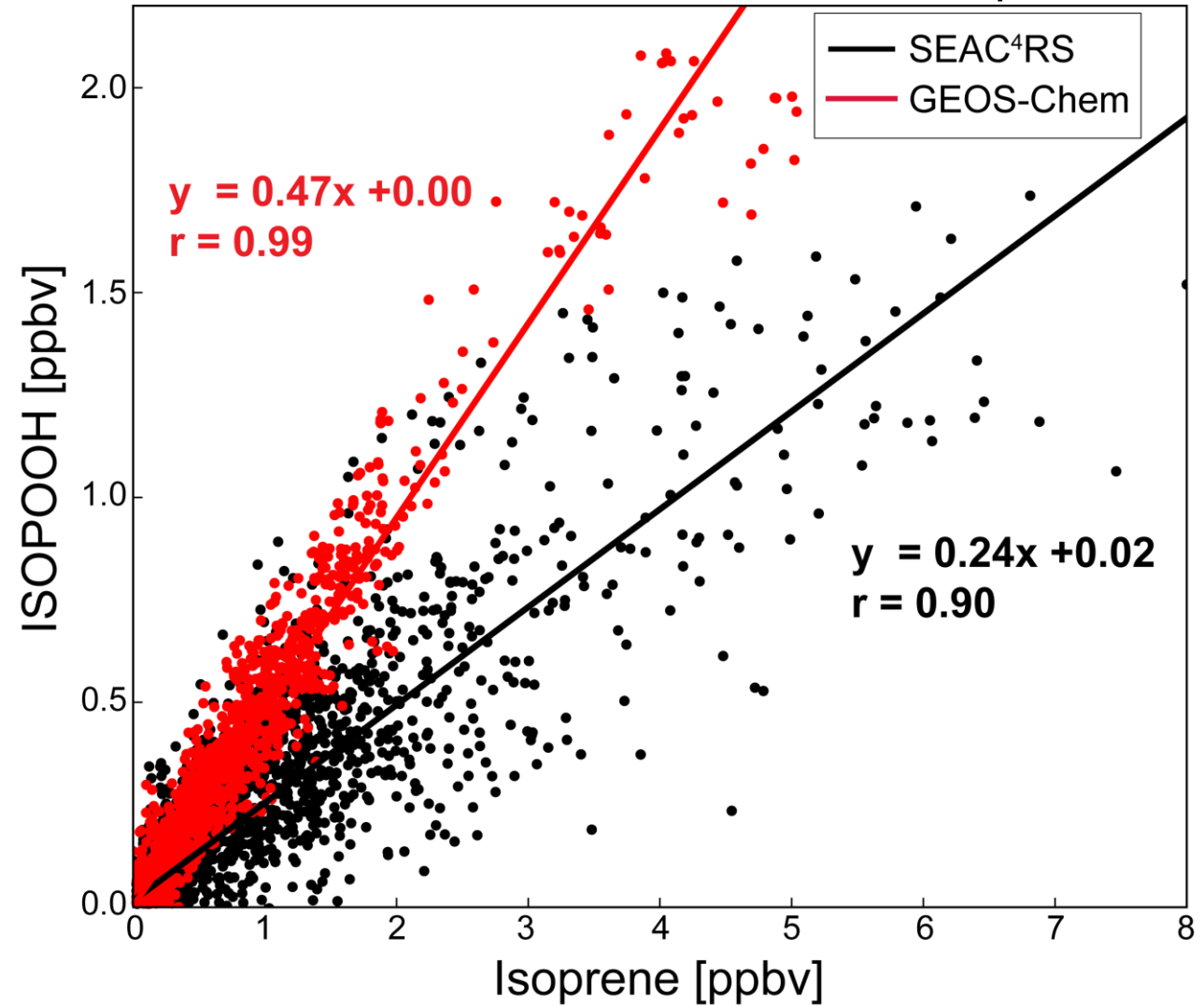
Despite increase in H^* , more than 2-fold model overestimate in IEPOX persists

Assess model ISOPOOH as precursor to IEPOX

Isomerization vs HO₂ pathway



Observed vs modelled ISOPOOH:isoprene



Scatterplot suggests model overpredicts ISOPOOH pathway, but increasing isomerization reaction rate increases OH, decreasing isoprene and maintaining a model slope of ~0.47

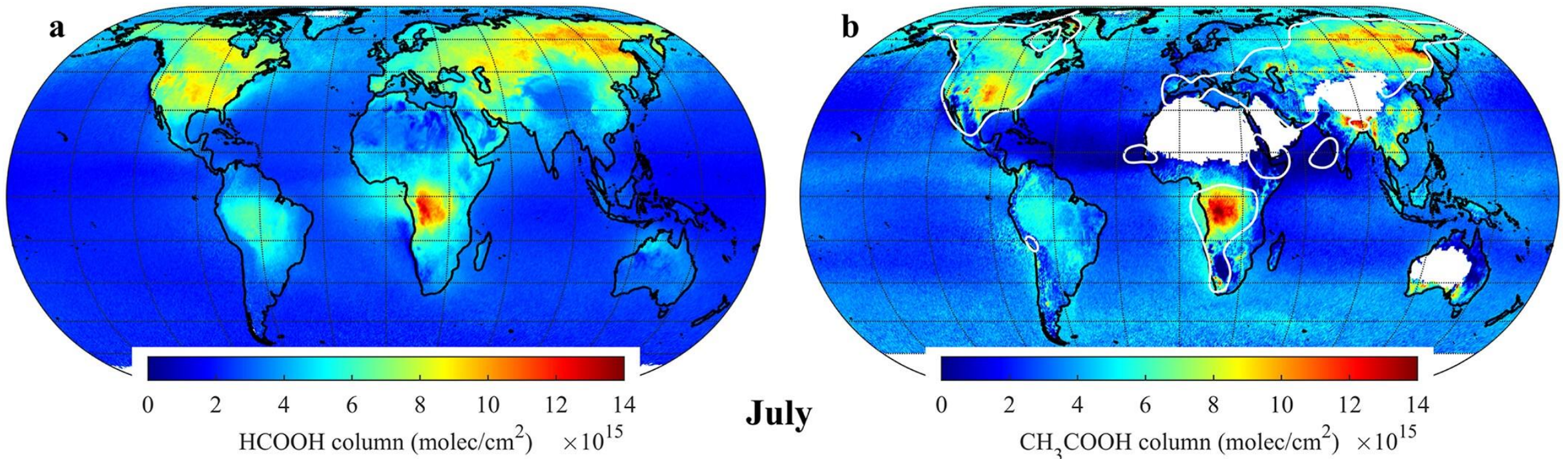
Summary and Ongoing Work

Match formic acid observations by scaling IEPOX H*, but IEPOX overestimate remains

Isomerization pathway fine-tuning needed. Also consider increasing IEPOX deposition H*

Eventually extend model runs to globe to test against satellite (IASI) observations of formic acid and acetic acid where isoprene is dominant source

IASI multiyear monthly means of formic acid (left) and acetic acid (right) in July



[Franco et al., 2020]