Gas phase formic acid dynamics in the atmosphere

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20th Annual CMAS conference

November 2020

Gas phase formic acid in the atmosphere

Introduction

- **Influence SOA formation and aqueous phase chemistry**
- **Tracers of air mass history**
- **Influence indirect radiative forcing**
- **Main contributor of free acidity in rain, fog, and dew**

Sources: Galloway et al., 1982; Jacob, 1986; Khare et al., 1999; Le Breton et al., 2012; Millet et al., 2015; Nah, Guo, et al., 2018; Paulot et al., 2011; Surratt et al., 2007; Souza, 1999; Yu, 2000

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Introduction

Sources

- **Primary anthropogenic emissions (vehicle, etc.)**
- **Primary biogenic emissions (vegetation, etc.)**
- **Secondary photooxidation reactions (isoprene/ monoterpene)**
- **Aqueous phase reactions**

Sinks

- **Wet/ dry deposition**
- **Reaction with OH**

Sources: Chebbi et al., 1996; Hu et al., 2016; Khare et al., 1999; Millet et al., 2015; Paulot et al., 2011; Pye et al., 2013; Surratt et al., 2007

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Objective

- Models underestimate gas phase formic acid concentrations
  - Poorly understood dynamics
    - Incomplete chemistry
    - Underestimated emissions and sinks
- The objective is to have a better understanding of the dynamics of formic acid formation

Sources: Alwe et al., 2019 ;Bannan et al., 2017; Brütsch et al., 2017; Cady-Pereira et al., 2014; Graedel et al., 1988; Kesselmeier et al., 1997; Kesselmeier et al., 1998 ; Khare et al., 1999; Le Breton et al., 2012; Link et al., 2020; Millet et al., 2015; Paulot et al., 2011; Stavrakou et al., 2012

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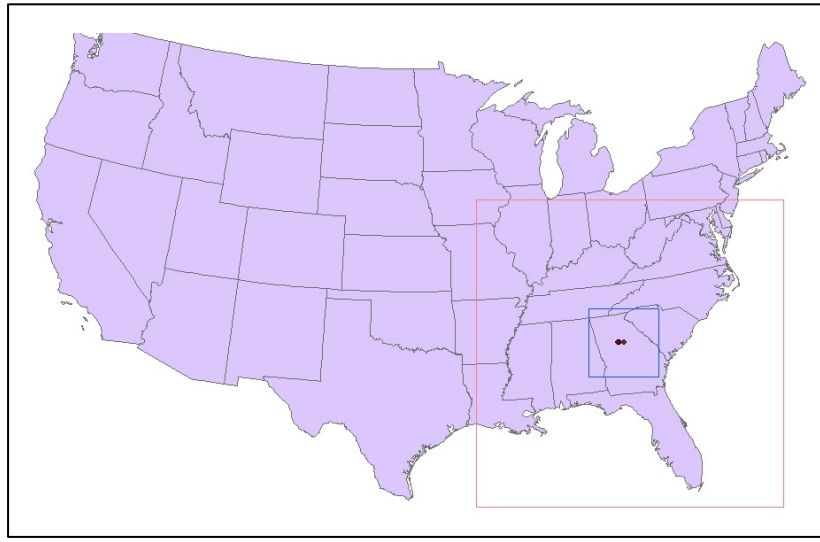
Method

- **Meteorology**: WRF v3.8.1
- **Emissions**: 2014 EPA emissions platform
- **CTM**: CMAQ v5.2
  - Gas-phase chemistry mechanism Carbon Bond 6 (CB6) and AERO6 aerosol module.
  - 36 km resolution outer domain with two nested domains at resolutions of 12 km and 4 km, with 34 vertical layers.
  - Initial conditions and boundary conditions for the outer domain followed Millet et al. (2015)
  - BEIS in-line
  - August 30 to October 6, 2016



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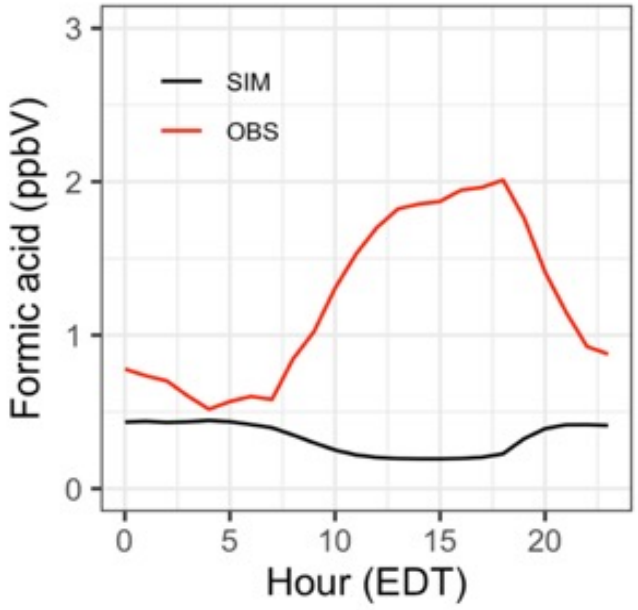
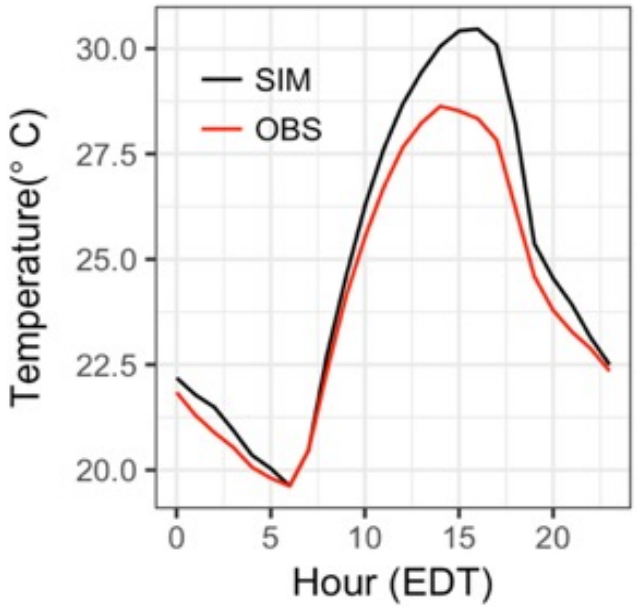
Benchmark simulation of formic acid





- Simulated formic acid underestimated throughout the day, with a pronounced bias during the afternoon.
- Observed formic acid and the observed temperature got to the peak value at similar time.
- Observed formic acid rapid increased in the morning and had a sharp decrease after 6 pm.

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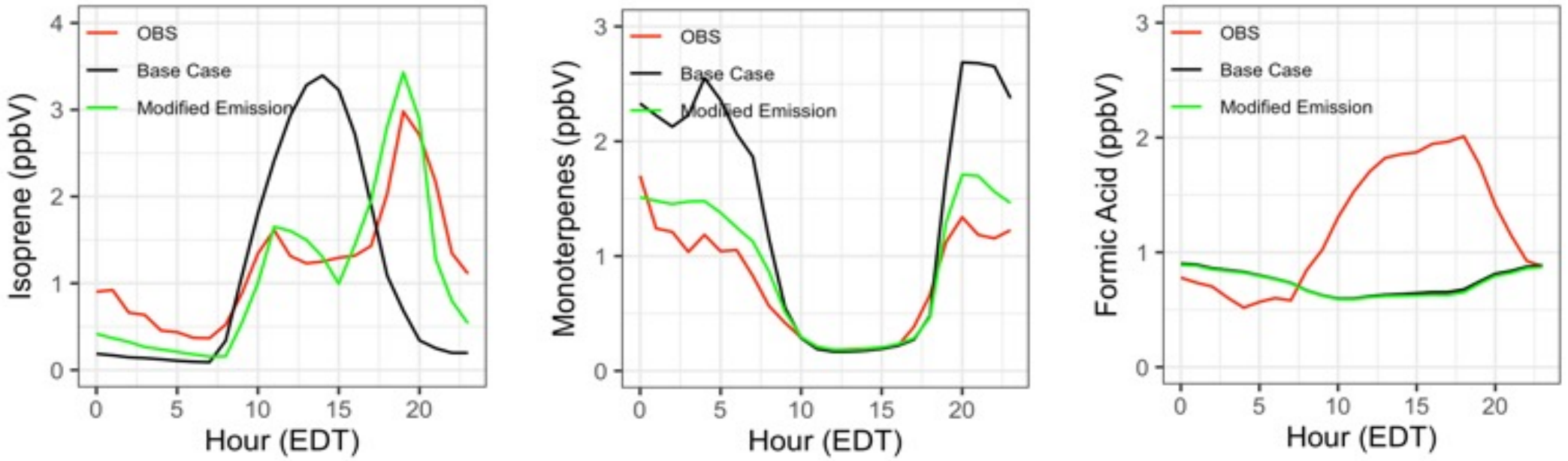
Formic acid precursors concentrations



- Modify the emission ratio of the biogenic emissions of isoprene.
- Modify the minimum vertical diffusivity to correct the simulated monoterpenes.
- The simulated formic acid are very close before and after the modifications of precursors.

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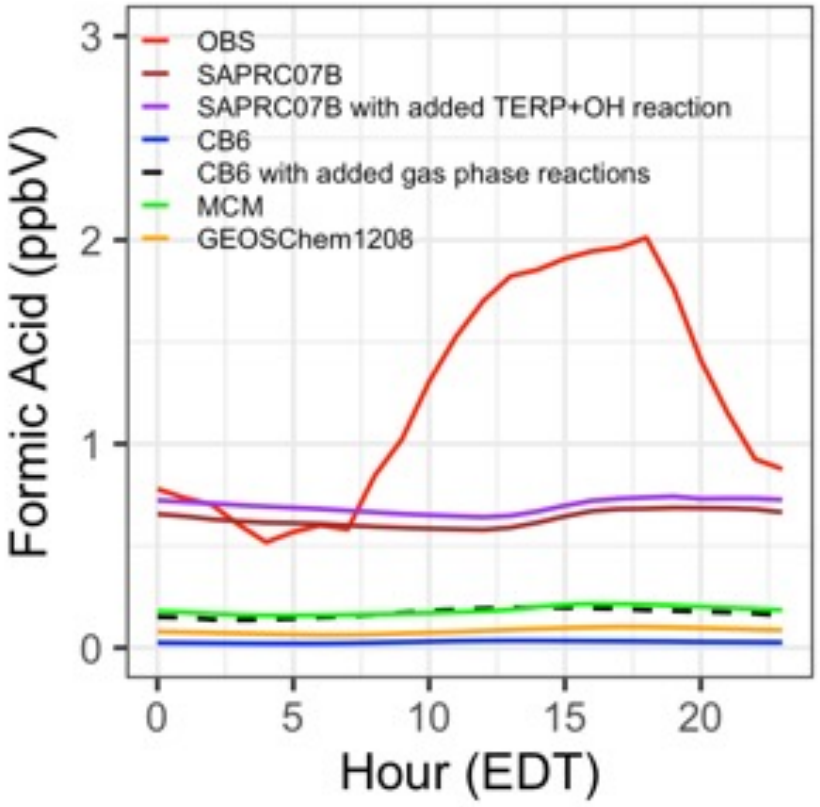
Box Model Simulations



- Model Settings:
  - **Constrain** the primary VOCs and inorganic trace gases using the observations following Kaiser et al., 2016 and Link et al., 2020.
  - **Dilution rate** is 4 day^{-1}.
  - **Dry deposition rate** are set based on Nguyen et al., 2015 and Kaiser et al., 2016
  - **Chemical Mechanisms**: MCM v 3.3.1, GEOS-Chem v 12-08, SAPRC07B, CB6.
  - The simulation ran six days with two days spin-up.

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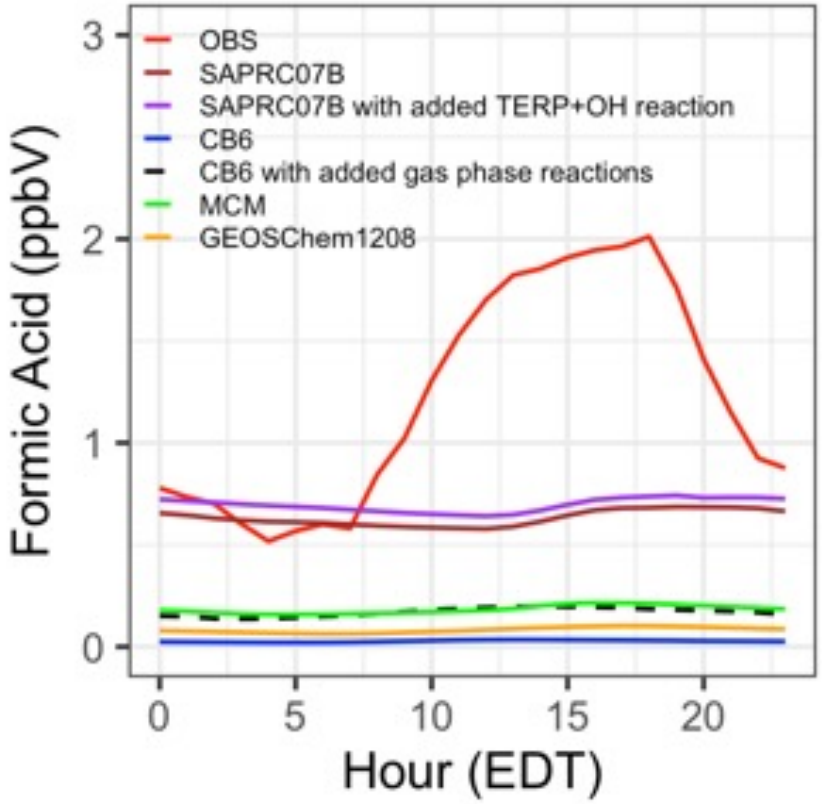
Box Model Simulations



- ISOP+O3->0.204 FACD
- ISPD+O3->0.686 FACD
- GLYD + OH->0.18 FACD (Depends on Temperature)
- TERP + OH -> 0.155 FACD
- TERP + O3 -> 0.075 FACD

***ISPD**:Isoprene product (lumped methacrolein, methyl vinyl ketone, etc.); **ISOP**: Isoprene; **FACD**: Formic acid; **TERP**: Monoterpenes; **GLYD**: Glycoaldehyde*

Reactions from Aschmann et al., 1996; Butkovskaya et al., 2006; Carter, 2010; Millet et al., 2015; Nguyen et al., 2016; Paulot et al., 2011

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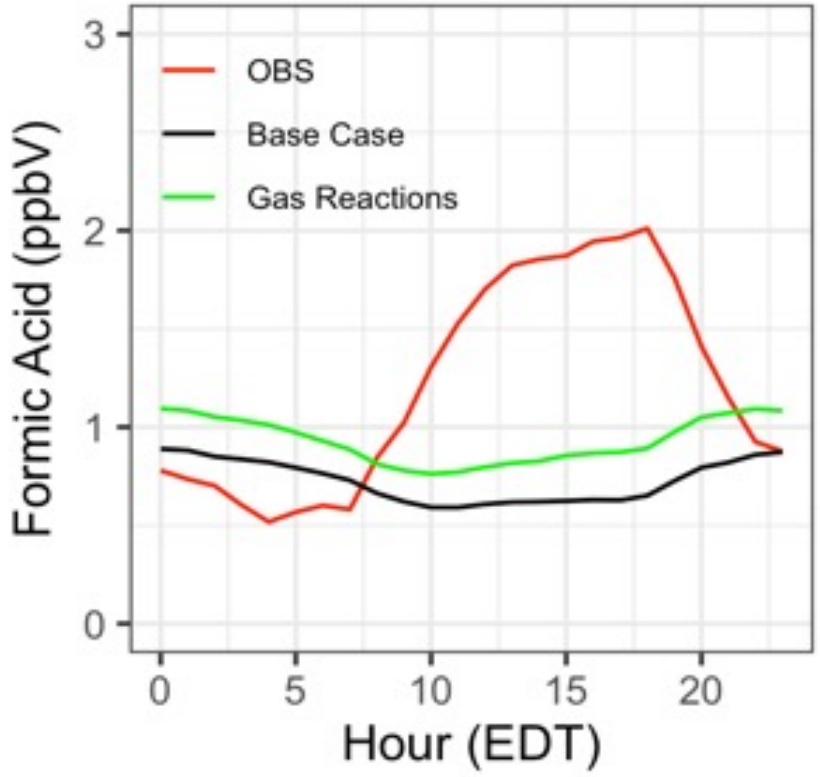
Added missing gas phase photooxidation reactions



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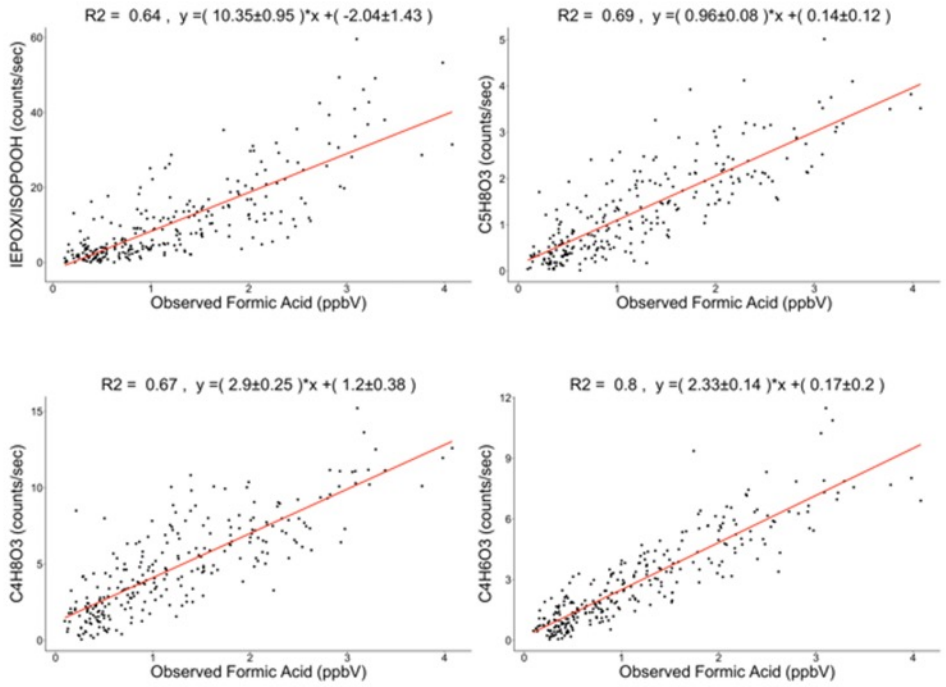
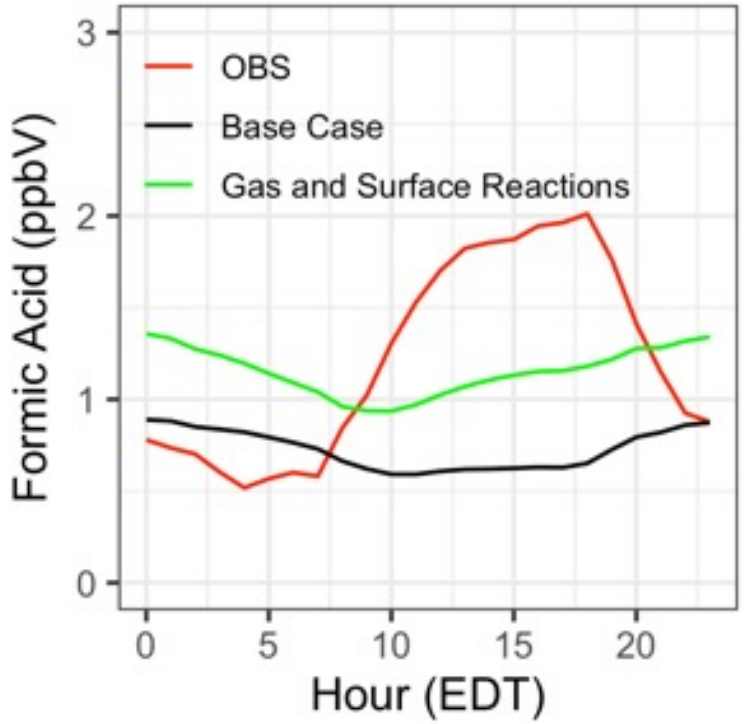
Potential surface reaction between IEPOX and OH





- Observed oxidized VOCs all strongly correlated with the observed formic acid concentration.
- After adding this potential surface reaction, the simulations could not capture the trend of the observations and was biased high at night and low during the day.

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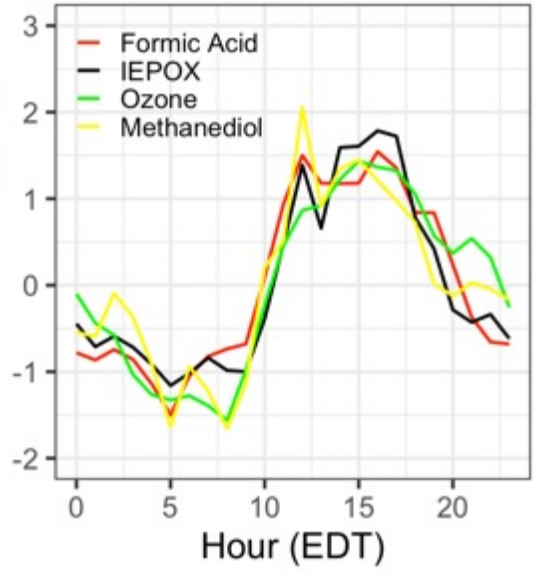
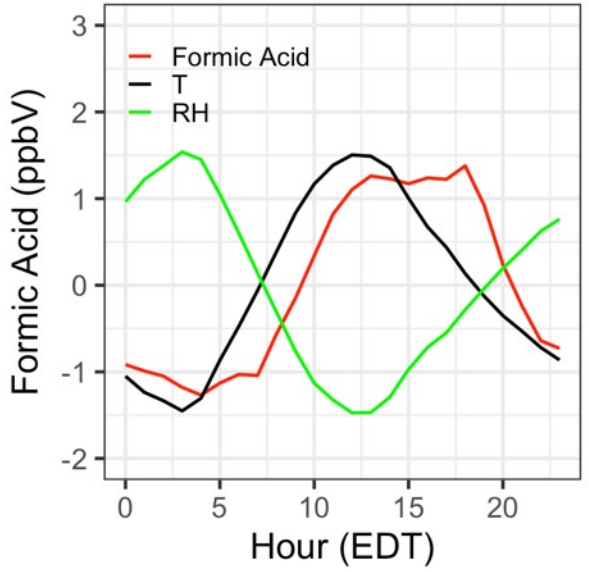
Bidirectional deposition-emission





- FACD began increasing earlier than ozone, methanediol and IEPOX.
- Observed FACD and temperature start increasing at a similar time.
- Observed FACD is anticorrelation with RH.
- Missing direct emission at daytime and potential reservoir formed at night.

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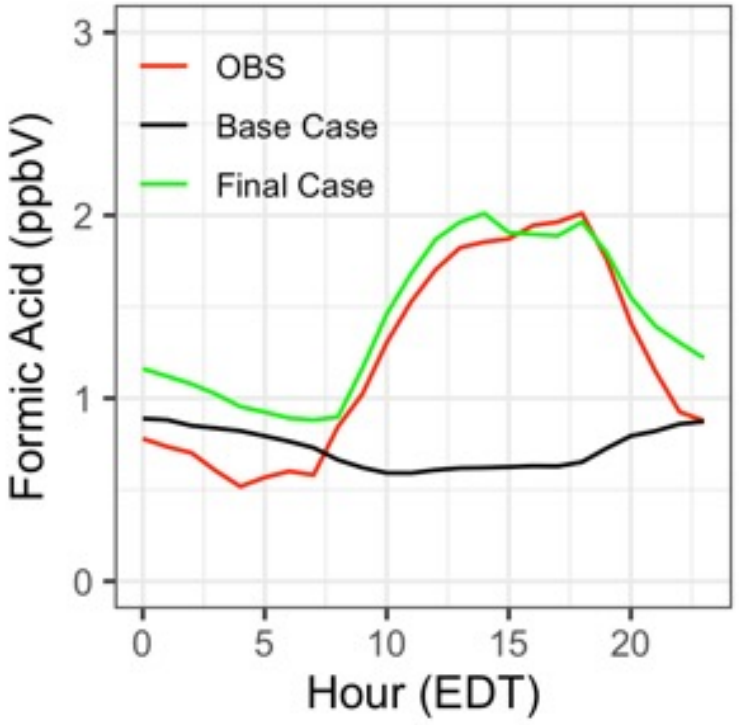
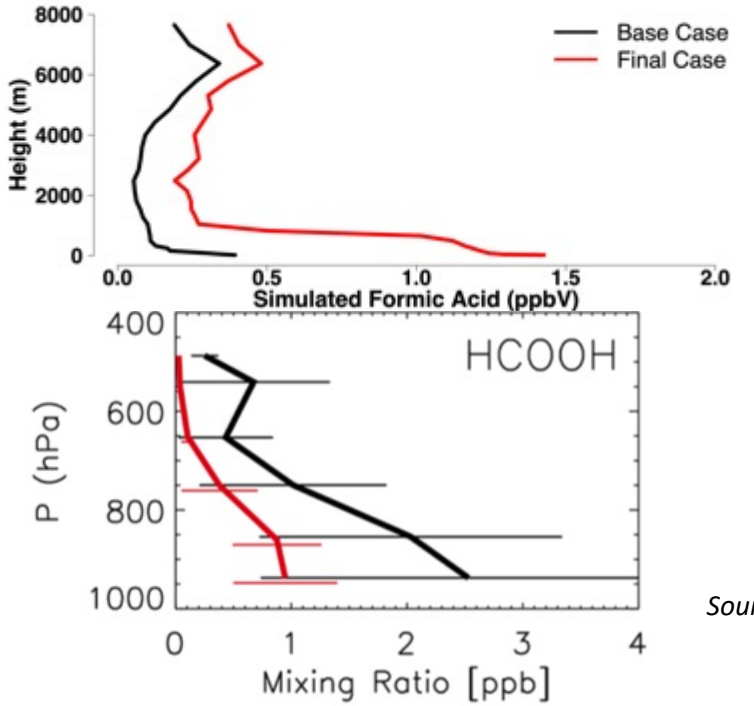
Effects of bidirectional deposition-emissions





Source: Millet et al., 2015

- Increased the formic acid emission at daytime (~20 times).
- Increased the dry deposition rate at night.
- Simulated formic acid showed better agreement with observations.
- Vertical profile is similar to the observations over the Southeast (black line in right bottom figure).

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Conclusion

- Summary of modifications:
  - Added missing gas phase chemical reactions
  - Potential IEPOX+OH surface reaction
  - Increased biogenic emission of formic acid
  - Changed the deposition rate

- Bidirectional deposition-emission and potential dew formation could capture the diurnal trend of the observed formic acid well while additional chemical reactions and potential IEPOX-OH surface reaction have little impact.