Intercomparison of Chemical Multiphase Box Models

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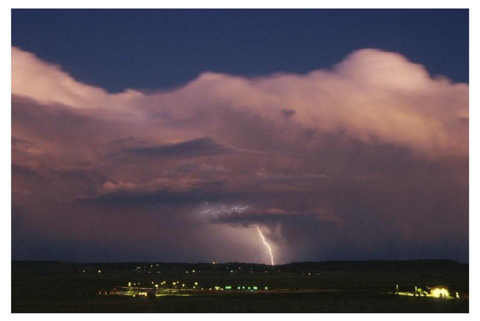
Effects of Clouds on Tropospheric Composition

- Acid rain studies from the 1980s and 1990s identified importance of aqueous-phase chemistry in producing sulfate
- Clouds affect ozone via aqueous chemistry, scattering of radiation, and lightning-NO_x production
- Cloud chemistry can produce more secondary organic aerosols



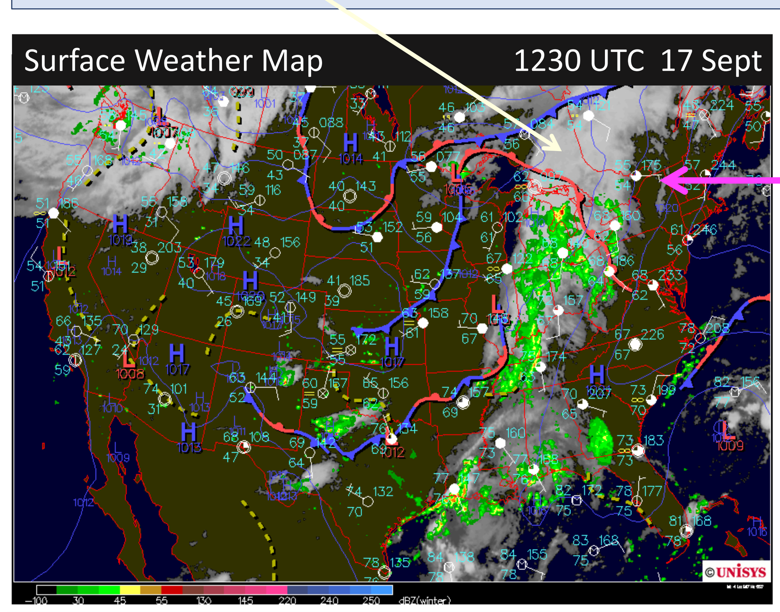
- Three-dimensional chemistry transport models often do not include aqueous-phase chemistry due to lack of complete understanding of the chemistry and the computational burden
- Goal: Evaluate the current state of knowledge in multiphase chemistry box models

Background

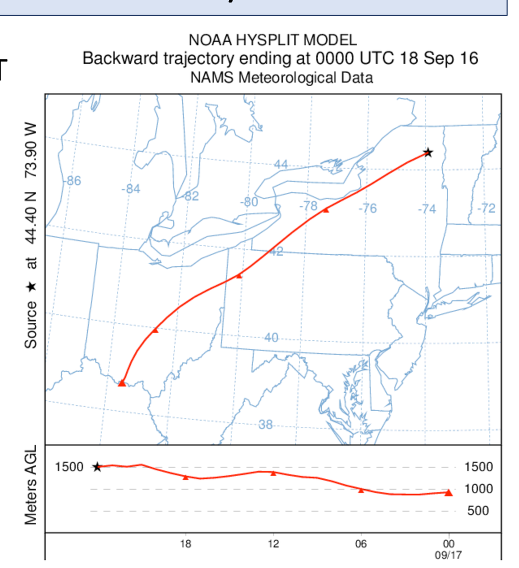
- Intercomparison is being conducted in the context of the Whiteface Mountain Cloud Chemistry Study
- Cloud event of 17-19 September 2016 is being analyzed for its composition by several groups
- In this study we model the first 20 hours of the cloud event using meteorological conditions at Whiteface Mountain

Meteorology of the Case Simulated

Clouds associated with warm front and warm sector storms/clouds



Clouds were stratiform in nature



Air from Ohio River Valley

- Initial concentrations are from a WRF-Chem simulation of 16-19 September 2016 continental United States
- Photolysis rates from TUV v5.3 for WFM in September, for clear sky with some aerosols
- CCN composed of SO_4, NH_4, Organic Carbon
- Cloud drops set to 10 μm radius

Model Configuration

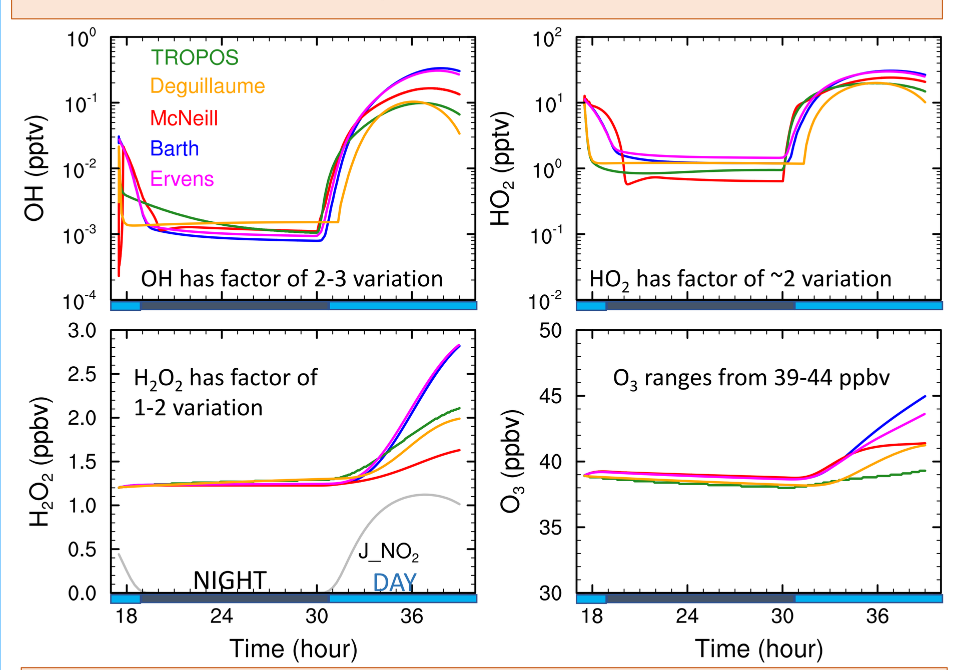
- Location: Whiteface Mountain: z = 1.5 km MSL, 44.4N, 73.9W
- Start/End times: 17:30 LT 17 Sept. / 15:00 LT 18 Sept.
- 30 minutes clear sky, 20 hours cloud, 30 minutes clear sky
- Simulation 1: Clear Sky Only
- Simulation 2: Cloud Water = 0.78 g/kg, pH = 4.5
- Simulation 3: Cloud Water = 0.78 g/kg, pH varies as calculated by model

	Gas chemistry	Aqueous chemistry	Gas-liquid transfer	Reference
TROPOS (Tilgner, Herrmann)	MCMv3.2 13,927 reactions	CAPRAM4.0α 7129 reactions	275 species	Tilgner et al. (2013, J. Atmos. Chem.)
Deguillaume	MCMv3.3.1 2043 reactions	CLEPS 850 reactions	591 species	Mouchel-Vallon et al. (2017, GMD)
McNeill	Isoprene, aromatics, and C1-C3 photochemistry 165 reactions	GAMMA 239 reactions	35 species	McNeill et al. (2012, ES&T)
Barth	Similar to MOZART4 168 reactions	45 reactions	45 species	Li et al. (2017, JGR)
Ervens	Similar to Barth's 168 reactions	Ervens 58 reactions	22 species	Ervens et al. (2014, JGR; 2008, GRL)

Sample of Box Model Results

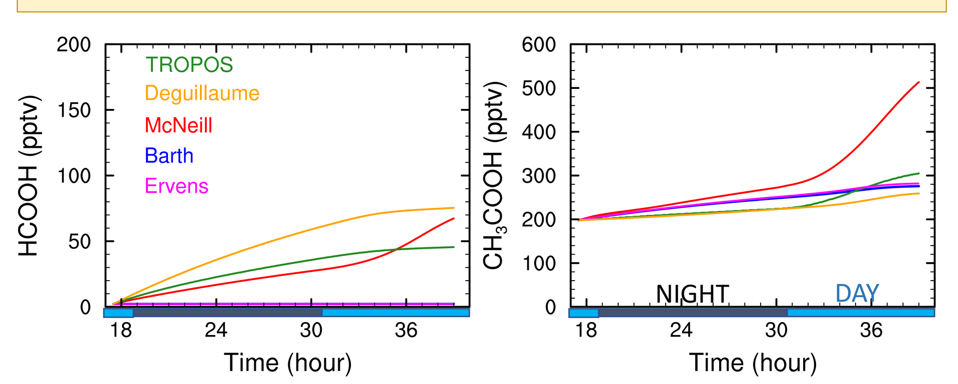
Simulation 1: Clear Sky Only

Gas-phase Oxidants



Variation in clear-sky results needs to be accounted for in interpreting multiphase results

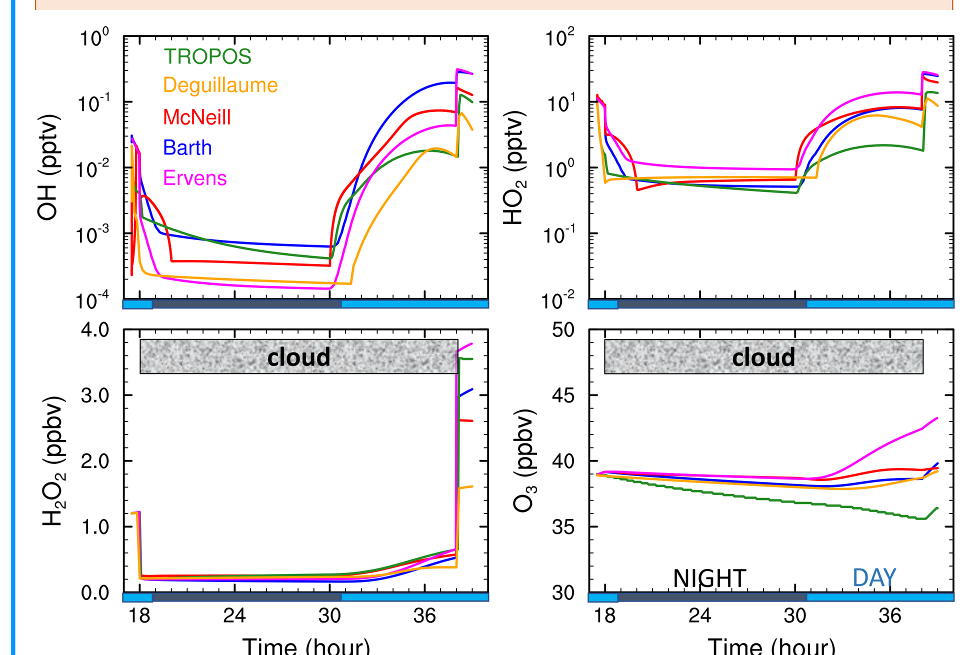
Gas-phase Organic Acids



- Gas-phase HCOOH production is 50-70 pptv in three models; it does not occur in the MOZART4 gas-phase mechanism
- CH_3COOH production is ~100 pptv for all mechanisms except McNeill who predict larger production of CH_3COOH in gas phase

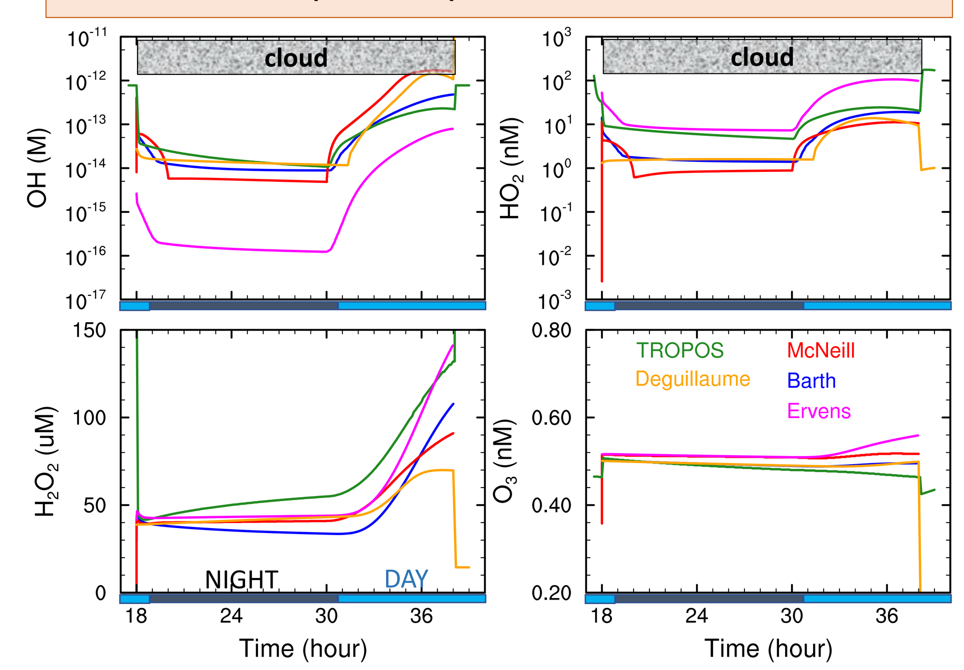
Simulation 2: Set LWC = 0.78 g/kg, Set pH = 4.5

Gas-phase Oxidants



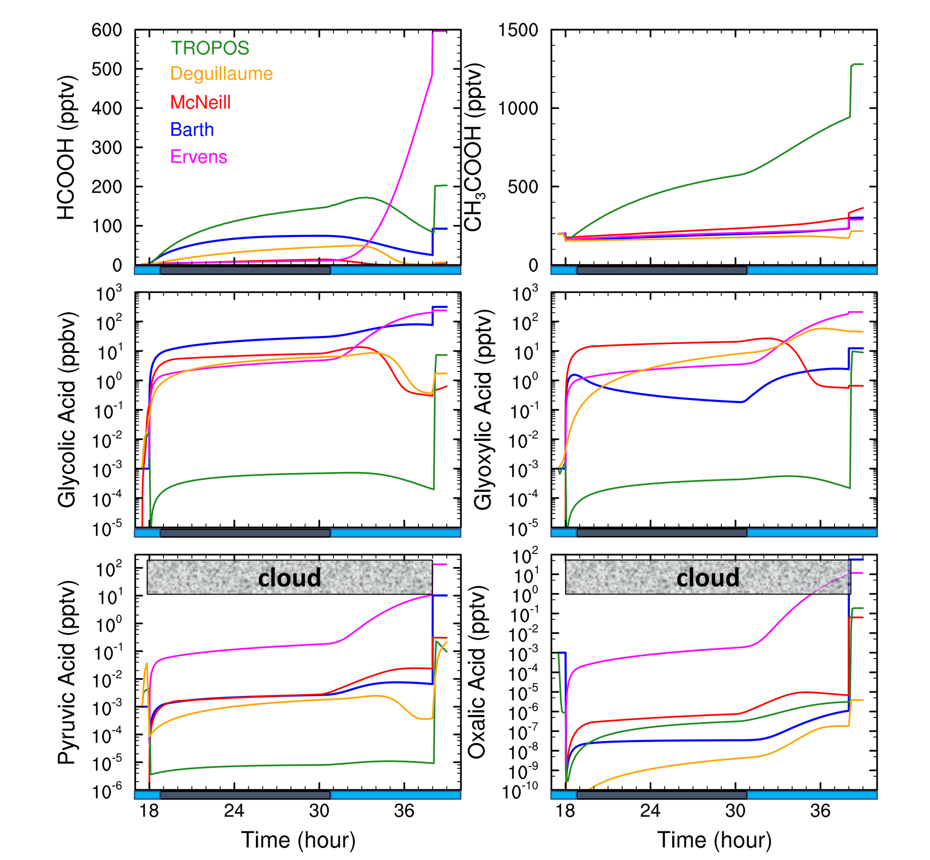
Variation in cloudy results is greater than that found in clear-sky case

Aqueous-phase Oxidants

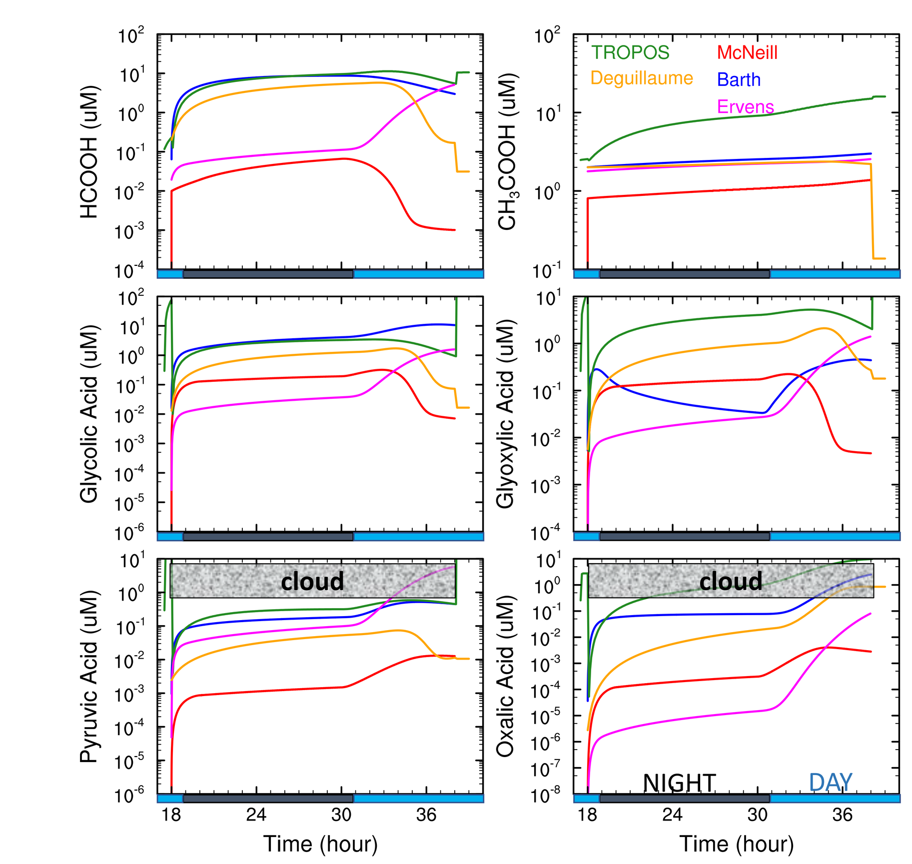


Variation increases during daylight hours

Gas-phase Organic Acids



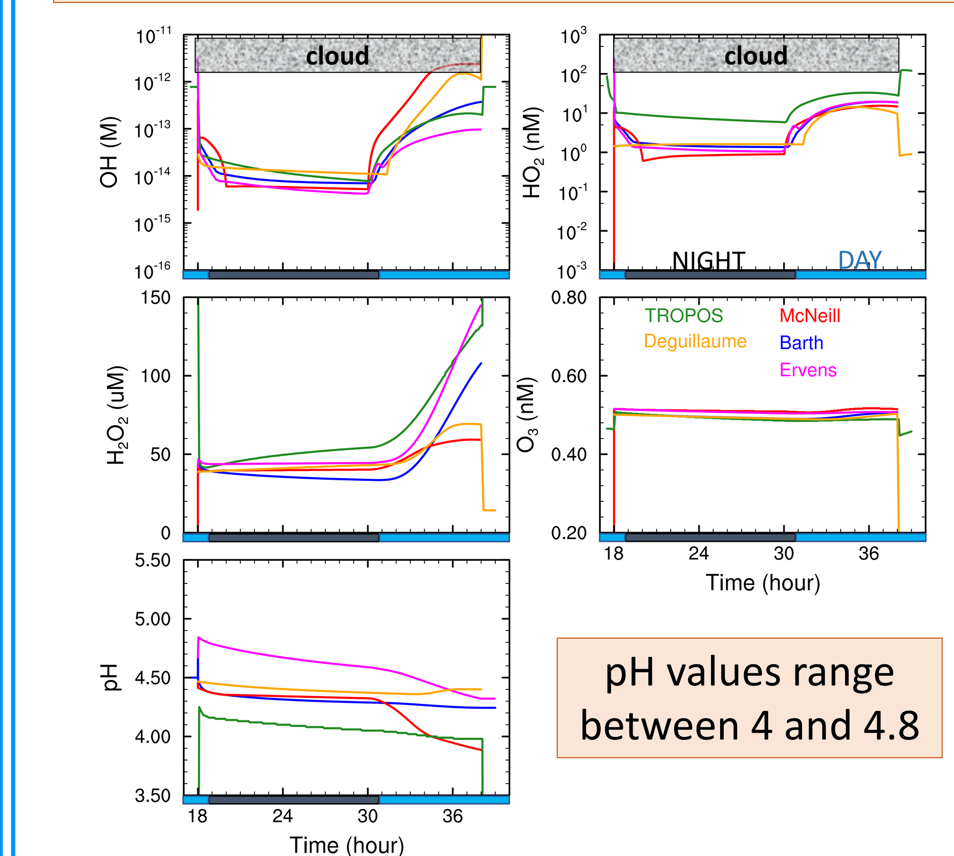
Aqueous-phase Organic Acids



- Wide variety of answers among groups as to how much organic acids are produced, although most groups agree on CH_3COOH production
- Time series of total organic acid (sum of all organic acids) will provide insight of partitioning among acids or simply different oxidation rates

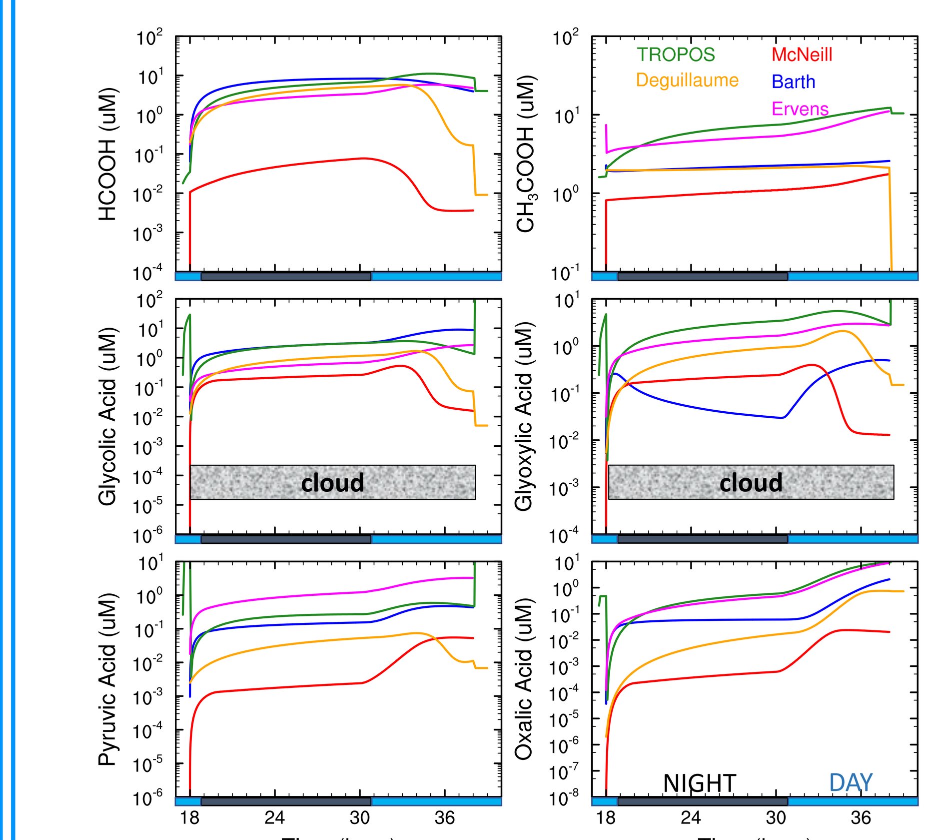
Simulation 3: Set LWC = 0.78 g/kg, pH Varies

Aqueous-phase Oxidants



pH values range between 4 and 4.8

Aqueous-phase Organic Acids



Model results vary by 1-5 orders of magnitude

Conclusions

Goal: Evaluate Current State of Knowledge in Multiphase Chemistry Box Models

- Five groups are conducting simulations in the context of the September 17-19 Whiteface Mountain Cloud Event
- Gas-phase chemistry has some variation among models during daytime that must be accounted for in interpretation of cloud chemistry results
- Cloud chemistry results show wide range of answers, especially for organic acid formation
- More variability found with varying pH simulation
- Understanding these differences is currently underway

https://www2.acom.ucar.edu/cloud-chemistry

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