Atmospheric OH, HO_2 and OH reactivity Measurements at the Moody Tower

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Objectives

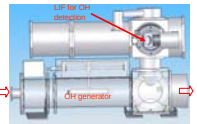
- Measurements of OH, HO_2, and OH reactivity at an urban site to test our understanding of photochemistry
- To compare the observations with model calculations to reveal possible missing radical sources or sinks
- Study of HO_x budget, O_3 production, and oxidation chemistry

Measurements

(1) Site: the roof of the Moody Tower on campus of University of Houston, Houston, TX
Local pollution: from nearby roads and residential areas
Most pollution: Ship Channel
Period: August 11 – September 27, 2006

(2) Penn State laser-induced fluorescence (LIF) for OH, HO_2 and OH reactivity.

OH and HO_2 sampling unit



OH reactivity sampling unit

(3) Other measurements:
Trace gases: O_3, CO, NO, NO_2, HNO2, HNO3, VOCs
Meteorological parameters: T, P, RH, UV-B wind speed, wind direction, photolysis frequencies (J)

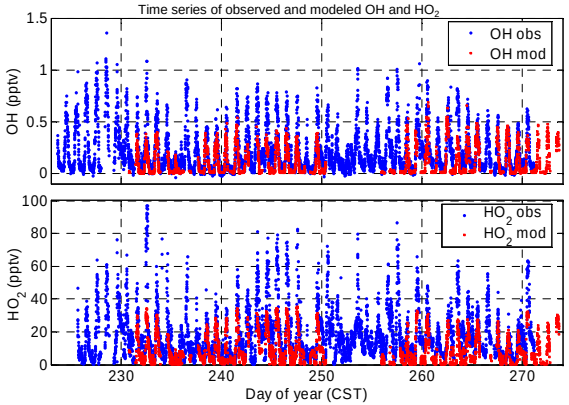
Model Calculation

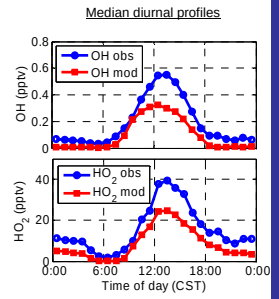
(1) Mechanism: RACM (Regional Atmospheric Chemistry Mechanism) Stockwell et al., JGR, 1997

(2) The model was constrained to observed inorganic gases (O_3, NO_x, CO), VOC species, J values.

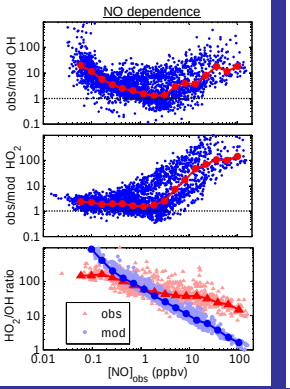
(3) Model output includes steady state OH, HO_2, and organic peroxy radicals as well as other intermediates.

HOx Observations and Model Comparison





- Typical diurnal variations of OH and HO_2 were observed.
- OH: mid-day peak mixing ratios varied from 0.5 to 1.0 pptv.
- HO_2: mid-day peak mixing ratios varied from 40 to 100 pptv.
- On average, both OH and HO_2 are under-predicted, day and night, which may indicate missing OH sources and/or incomplete chemistry in the model.



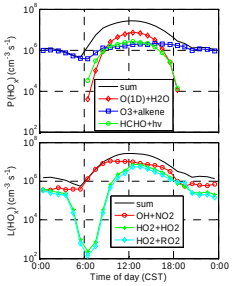
NO dependence

- OH: under-predicted when [NO]<~1 ppb or [NO]> a few ppb
- HO_2: obs/mod ratio increases as [NO] increases when [NO]>2 ppb
  better agreement when [NO] < 2 ppb, although HO_2 is still under-predicted.
- HO_2/OH: over-predicted when [NO] < 1 ppb, under-predicted when [NO] > 1 ppb

HOx budget

$P(HO_x)$:
dominant: $O(^1D) + H_2O$ during daytime
O_3+ alkene reactions at night
others: photolysis of HONO, HNO_3, peroxides, and glyoxal

$L(HO_x)$:
dominant: $OH+NO_2$
others: HO_2+HO_2, and HO_2+RO_2



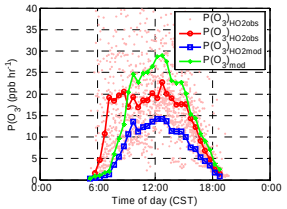
Ozone Production

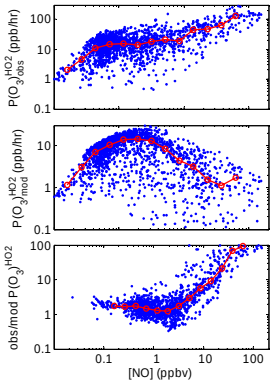
Diurnal $P(O_3)$

- $P(O_3)_{HO2obs} > P(O_3)_{HO2mod}$
- Cumulated $P(O_3)_{mod}$ ~ 210 ppb/day
- Cumulated $P(O_3)_{HO2obs}$ ~ 191 ppb/day

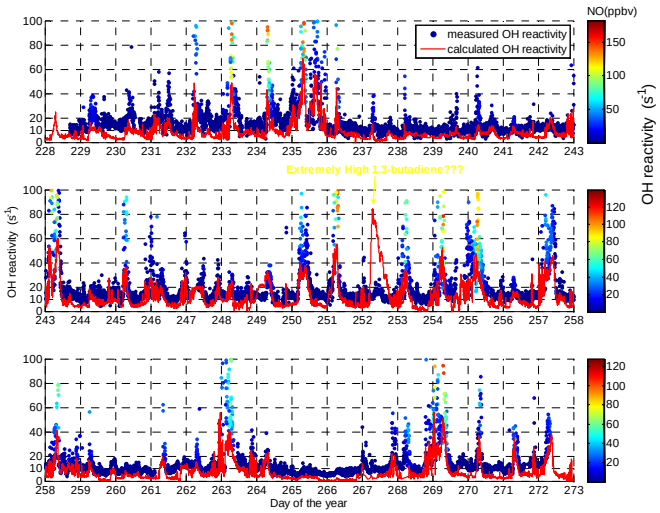
NO dependence

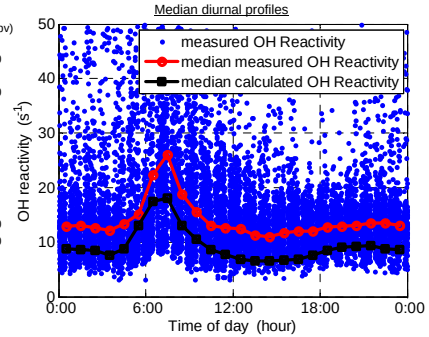
- Higher-than-expected $P(O_3)$ at high [NO]
- Good agreement between obs. and mod. $P(O_3)$ as [NO] < a few ppb.



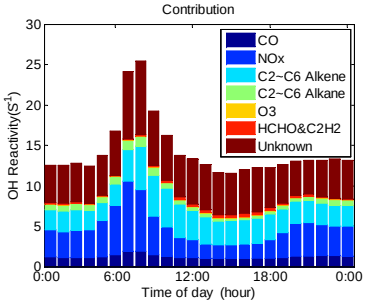


OH Reactivity: Observations and Calculations

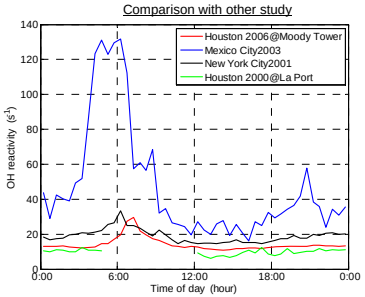




- The variations in measured and calculated OH reactivity are similar.
- Calculated OH reactivity is lower than the measurements because the calculations are only based on limitedly available data:
  (1) NOx,CO,O3
  (2) C2~C6 alkenes
  (3) C2~C6 alkanes
  (4) HCHO
  (5) Acetylene



- NOx is an important contributor to OH loss in big cities.
- Unknown OH reactivity is about 5~8 s^{-1} all day along.
- The unknown is the difference between the measurements and calculations using currently available data. Aromatics and large carbonyls are not included in the calculations yet and should be in the unknown.



- OH reactivity measurements in Houston2000 were limited by NO levels. The measurements need to be corrected at high NO levels. This correction has not been performed for this dataset yet. The green line was the median profile for the data points with [NO] < 1 ppb.

Discussion

In the current calculations, only limited VOC data (currently available) were used. Missing OH reactivity could be due to the measured VOC species currently not available or other unmeasured species. Further calculations and analyses will be performed once all other data become available.