

Comparisons of box model calculations and measurements of formaldehyde from the 1997 North Atlantic Regional Experiment

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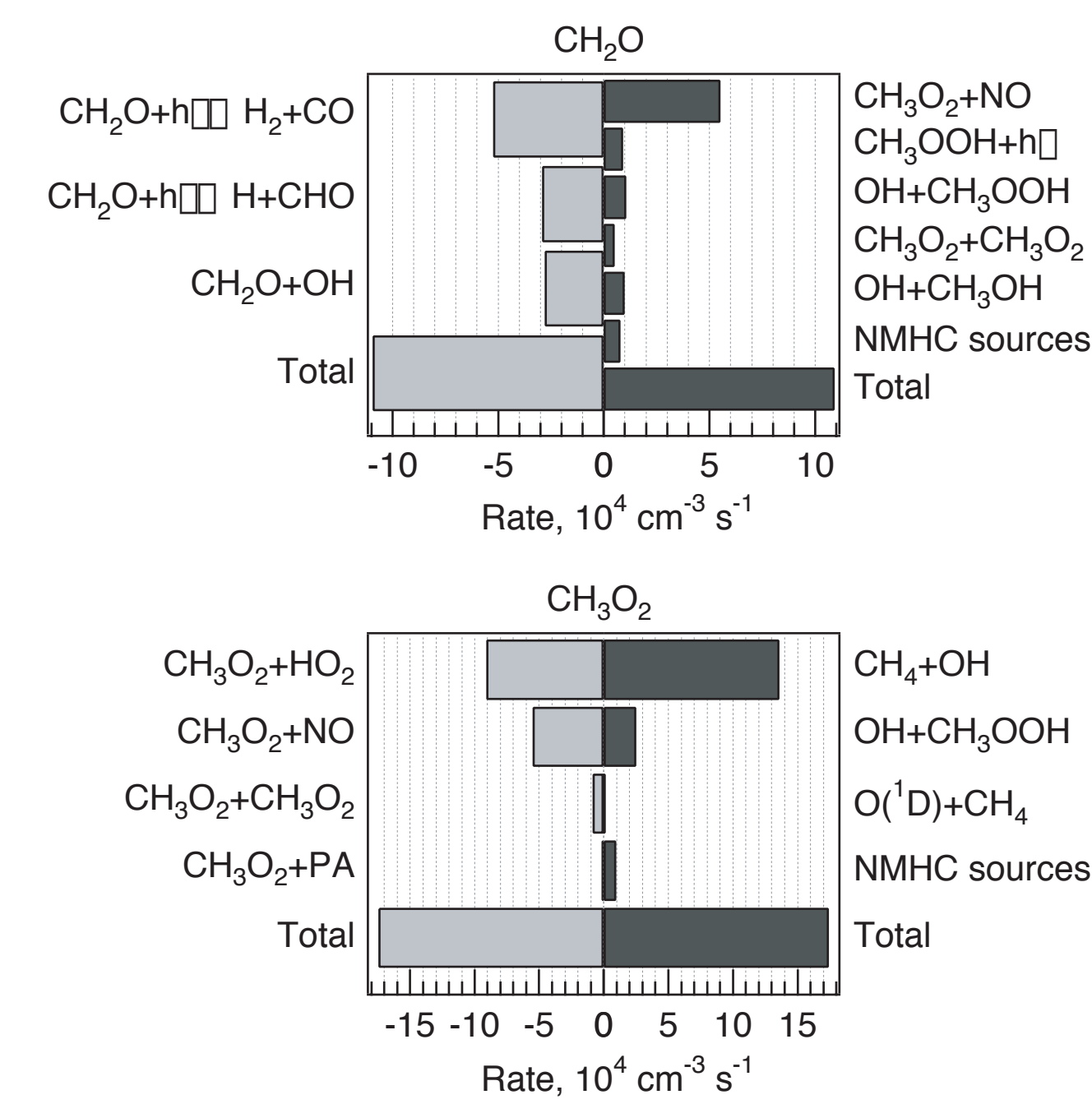
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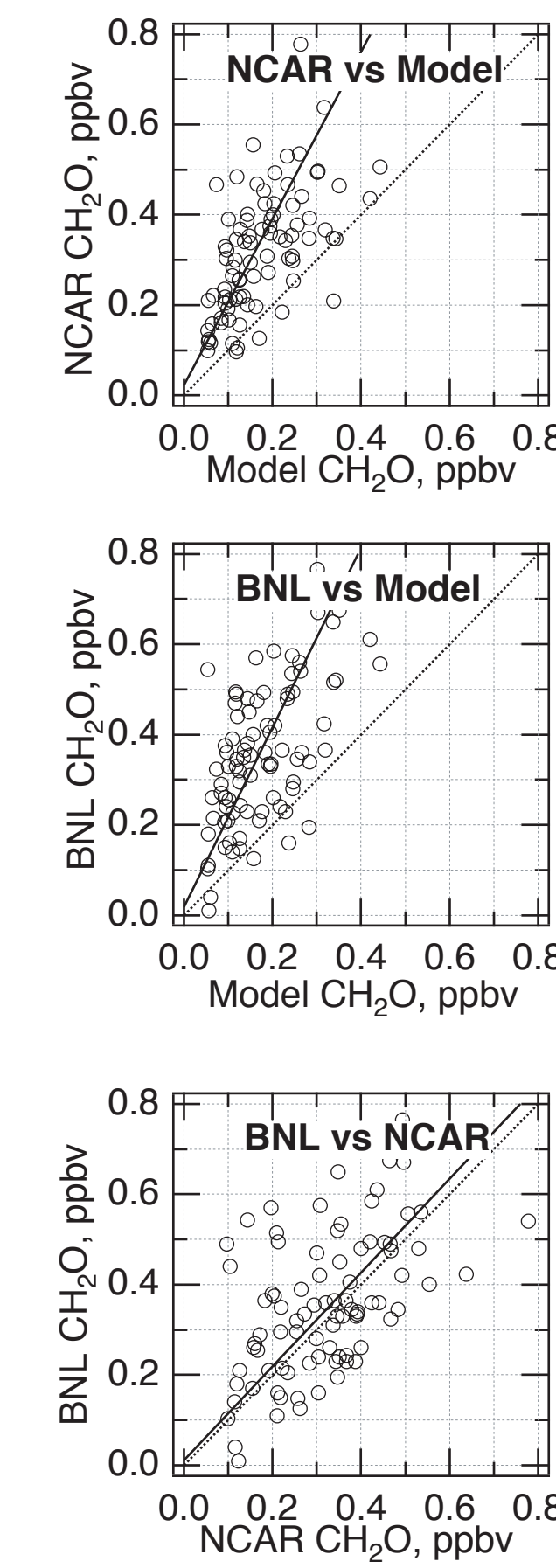
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Abstract

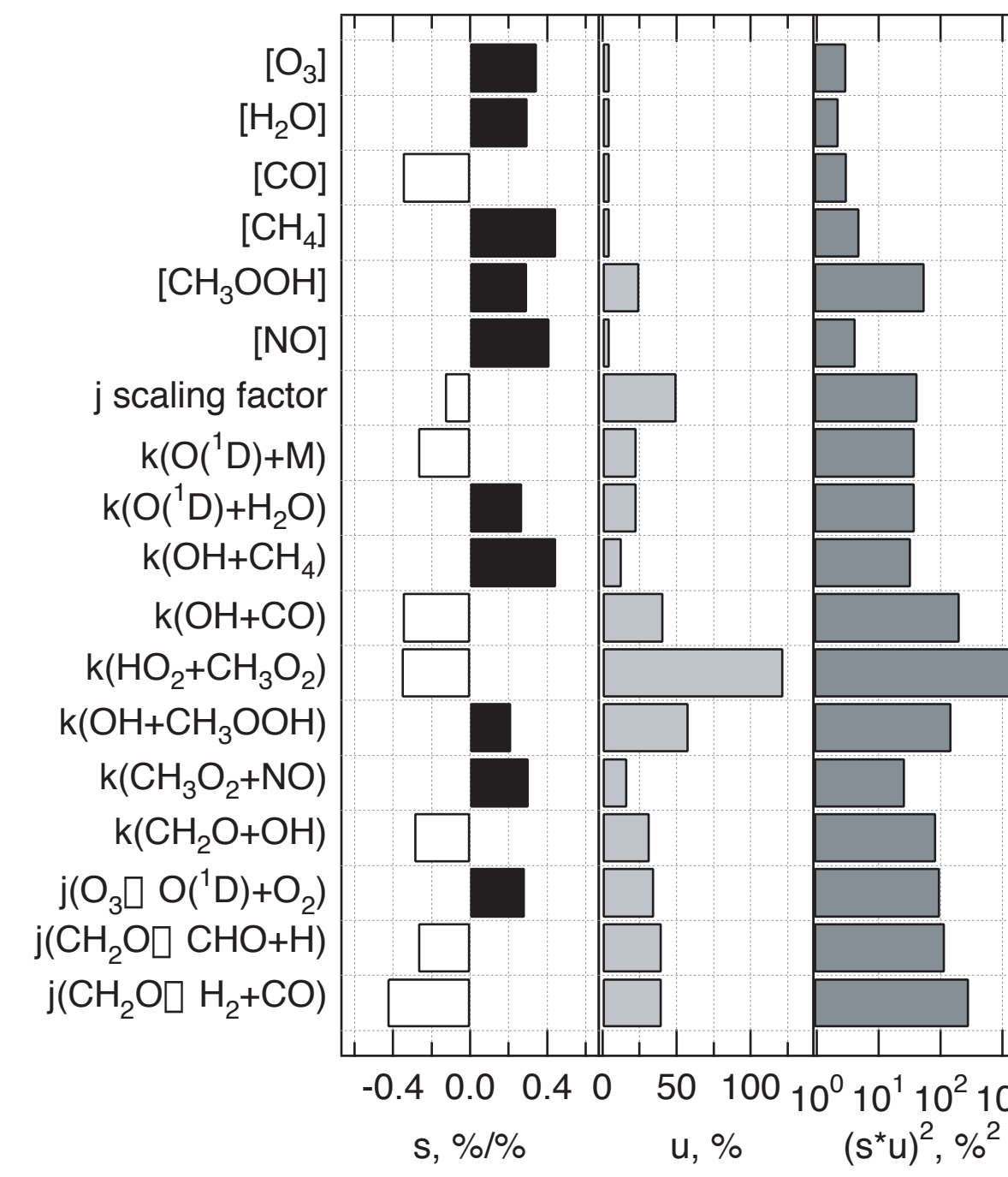
Formaldehyde (CH₂O) measurements from two independent instruments are compared with photochemical box model calculations. The measurements were made on the NOAA P-3 aircraft as part of the 1997 North Atlantic Regional Experiment (NARE 97). The data set considered here consists of air masses sampled between 0 and 8 km over the North Atlantic Ocean which do not show recent influence from emissions or transport. These air masses therefore should be in photochemical steady state with respect to CH₂O when constrained by the other P-3 measurements, with methane oxidation being the predominant source of CH₂O. The two instruments, which agree with each other on average though with relatively low correlation, both show systematically higher CH₂O levels than the model. The median measured - modeled CH₂O difference is 0.13 or 0.18 ppbv (depending on the instrument), or about a factor of two. Such large differences cannot be accounted for by varying model input parameters within their respective uncertainty ranges. After examining the possible reasons for the model - measurement discrepancy, we conclude that there are probably one or more additional unknown sources of CH₂O in the North Atlantic troposphere.



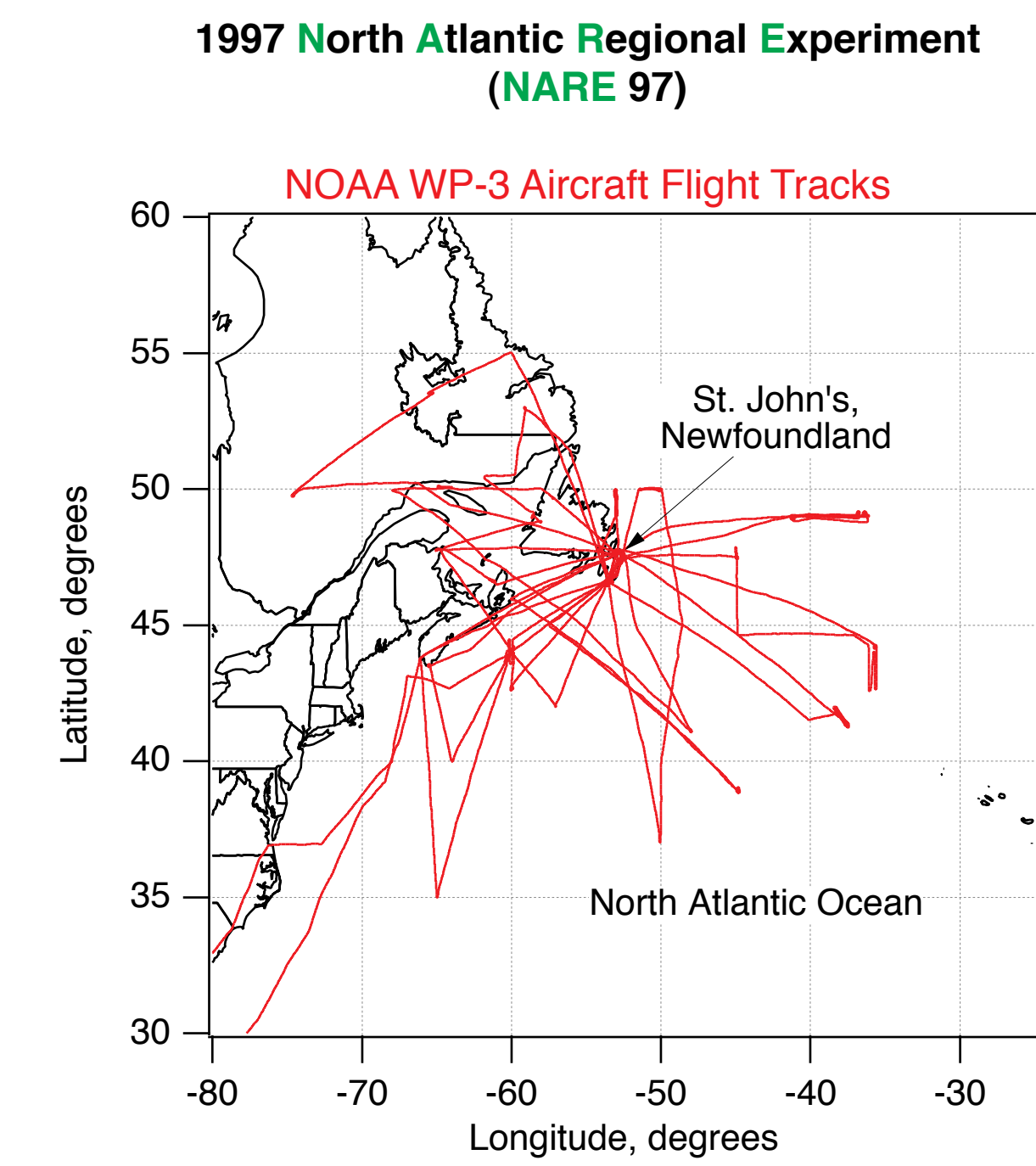
Diurnally averaged loss (left) and production (right) rates for CH₂O (top) and CH₃O₂ (bottom) calculated by the box model. Median values are shown for the full data set of 86 points discussed in this work. PA = peroxy acetyl radical.



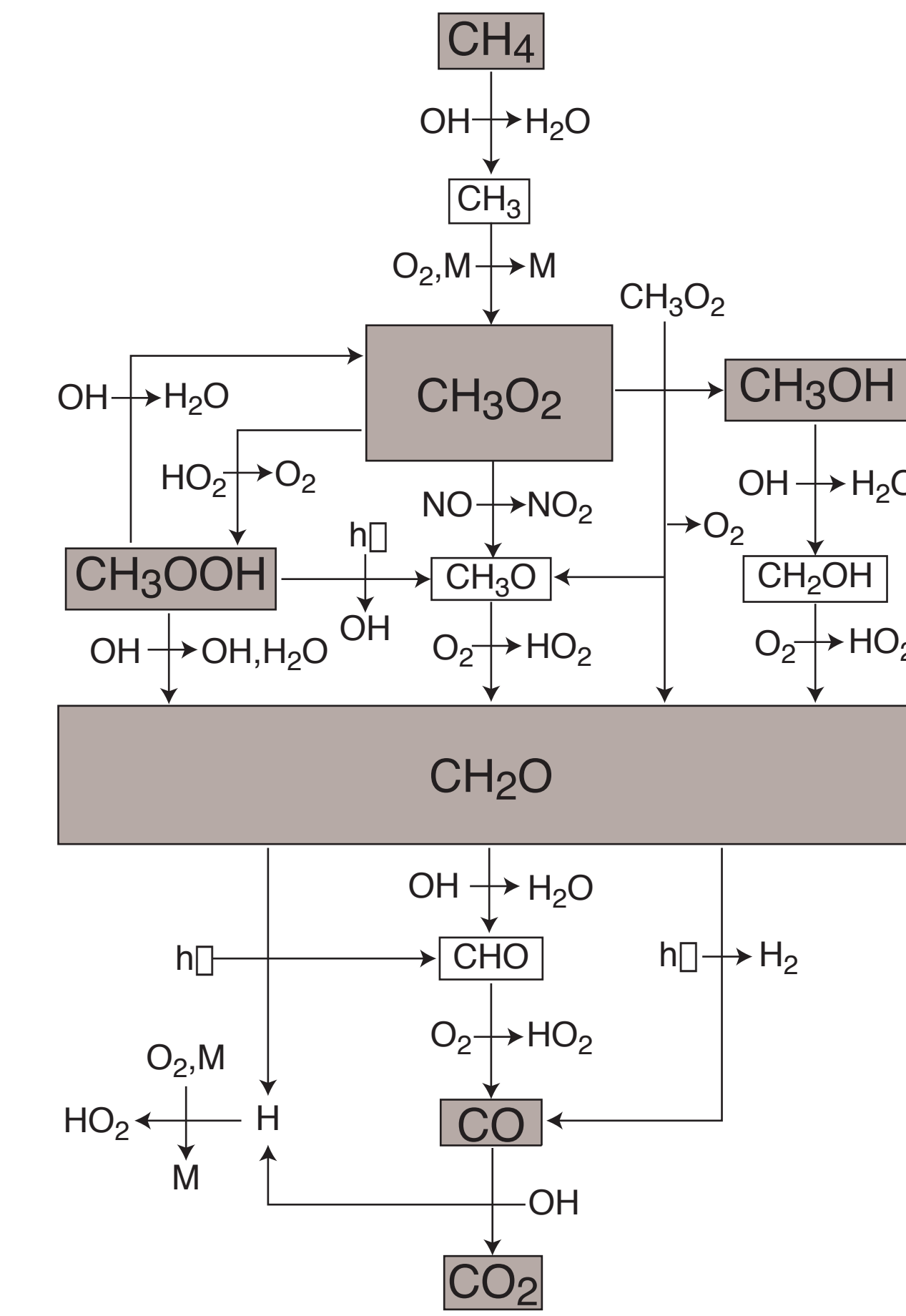
Measured and modeled [CH₂O] comparison scatter plots, showing the 86 data points (circles), the weighted least squares bivariate fit (solid line), and the 1:1 line (dotted line).



Sensitivity in [CH₂O] to (left), 1σ uncertainty in (middle), and contribution to the square of the [CH₂O] uncertainty from (right) the model input parameters, where "s" = sensitivity and "u" = uncertainty. All data are medians for the full data set of 86 points and represent the input parameters to which the modeled [CH₂O] is most sensitive. The contribution of each parameter to the square of the total [CH₂O] uncertainty is the square of the product of the parameter's sensitivity and uncertainty. "j scaling factor" is a constant factor applied to all j values to simulate the effects of clouds.



Late summer / early fall frontal passages
 • Transport of boundary layer air to upper troposphere
 • Subsidence of stratospheric air
 • Transport of polluted continental air to free troposphere



Schematic representation of the methane oxidation cycle with carbon-containing species shown in boxes. The shaded boxes indicate those species with tropospheric lifetimes longer than 1 second when [NO] < 1 ppbv. Only photochemical reactions are shown; surface emission and physical removal processes are not included.

CH₂O Measurements

National Center for Atmospheric Research (NCAR):

Tunable IR diode laser absorption

- 100 m path length cell
- 20 s integration, 1 sample/min
- 1σ precision for 5 min average: ±50-80 pptv
- 1σ accuracy: 7%

Brookhaven National Lab (BNL):

DNPH solution collection
 Post-flight separation by HPLC
 Quantitation by UV-VIS absorption

- 5 min integration
- 1σ precision for 5 min sample: ±40-80 pptv
- 1σ accuracy: 9-18%

- Completely independent CH₂O determinations
- First extensive CH₂O aircraft intercomparison

Steady State Box Model

Assumption
 • CH₂O equilibrated with longer lived species (lifetime = 6 - 9 hr under NARE 97 conditions)

Air mass selection

- Average data over 5 - 50 min legs with constant conditions
- Eliminate air with recent emissions
- Total of 86 legs with coincident measurements

Input

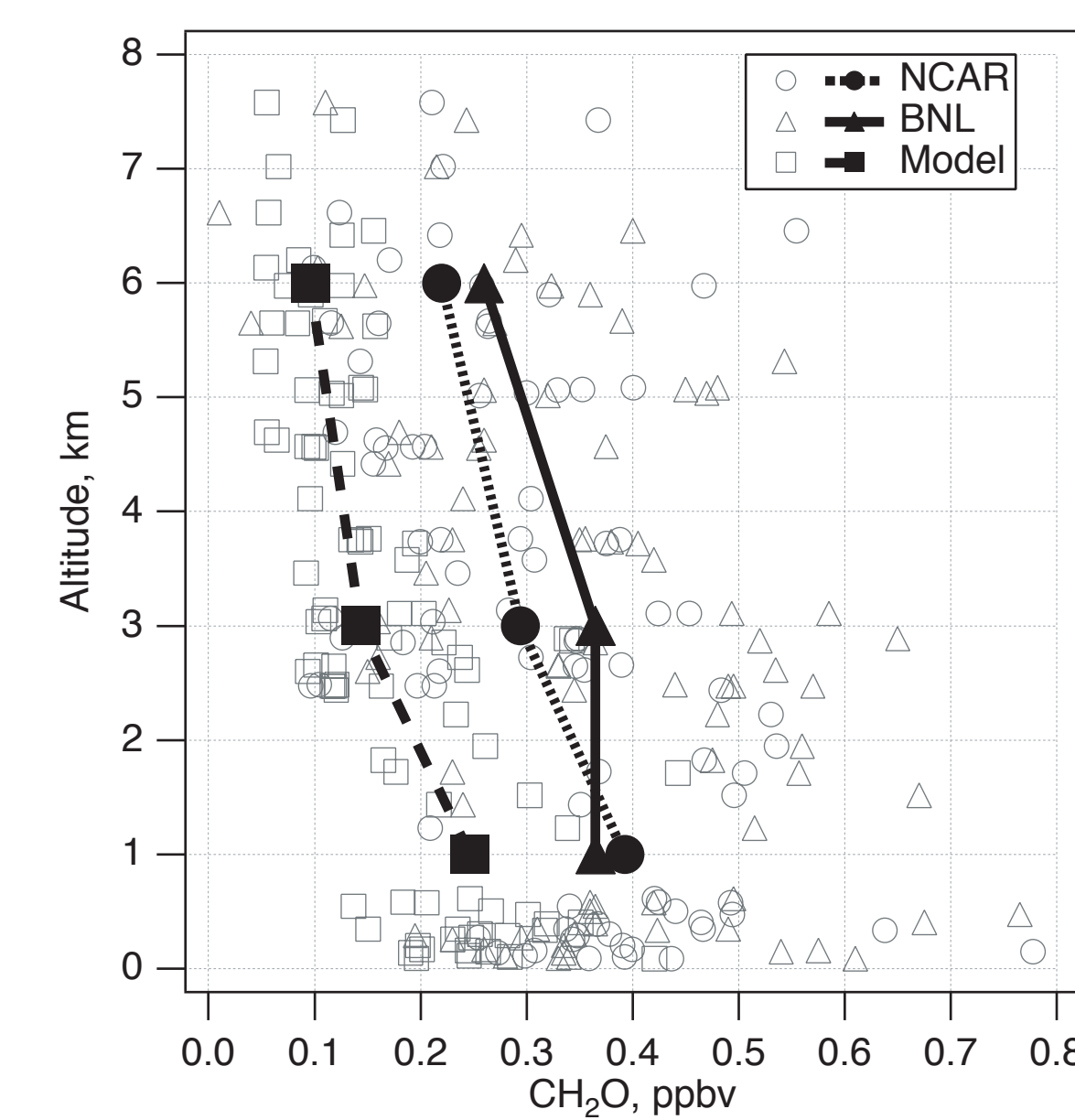
- O₃, NO, NO₂, CO, NMHCs, organic nitrates, H₂O, T, P from NOAA WP-3
- CH₄, H₂, methanol, acetone from other observations
- j values from radiative transfer model (clear sky over full diurnal cycles)

Output

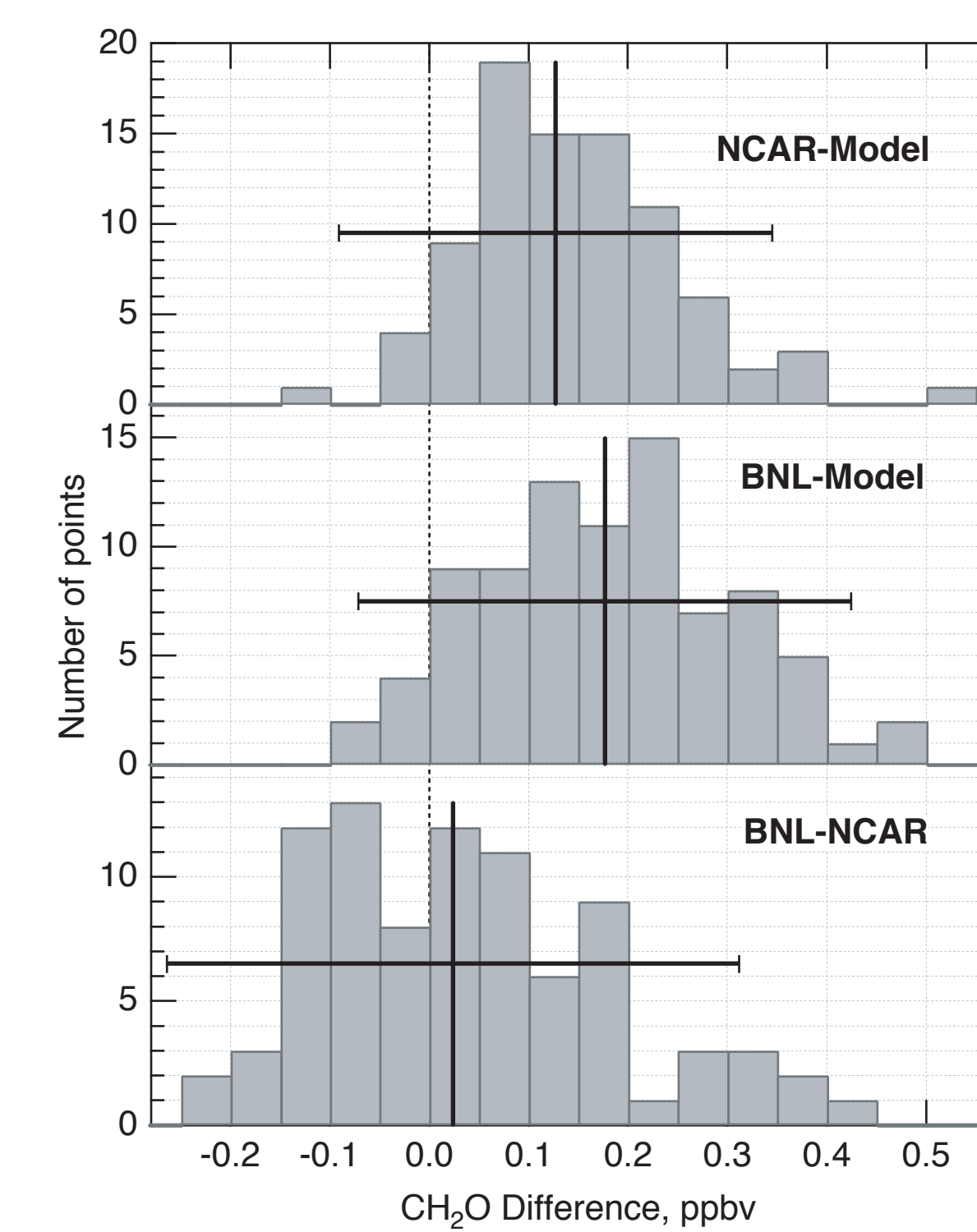
- OH, HO₂, RO₂, NO₂, and CH₂O (diurnal steady state)

Estimated accuracy

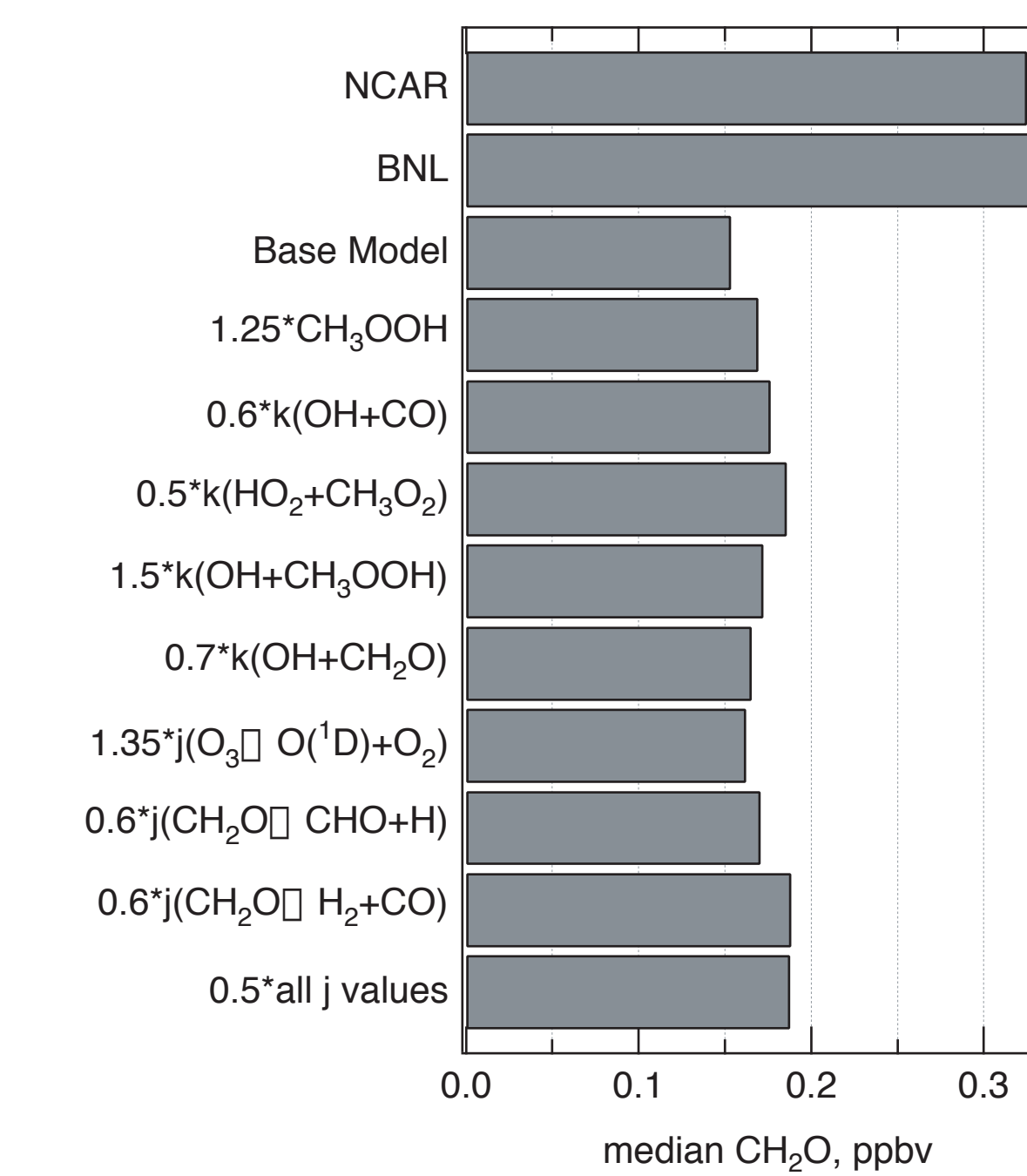
- 50 - 60% (1σ) from rates and concentrations



CH₂O mixing ratios as a function of altitude. Gray open symbols are the individual data points. Black solid symbols joined by lines are the medians for the 0 - 2, 2 - 4, and 4 - 8 km altitude bins.



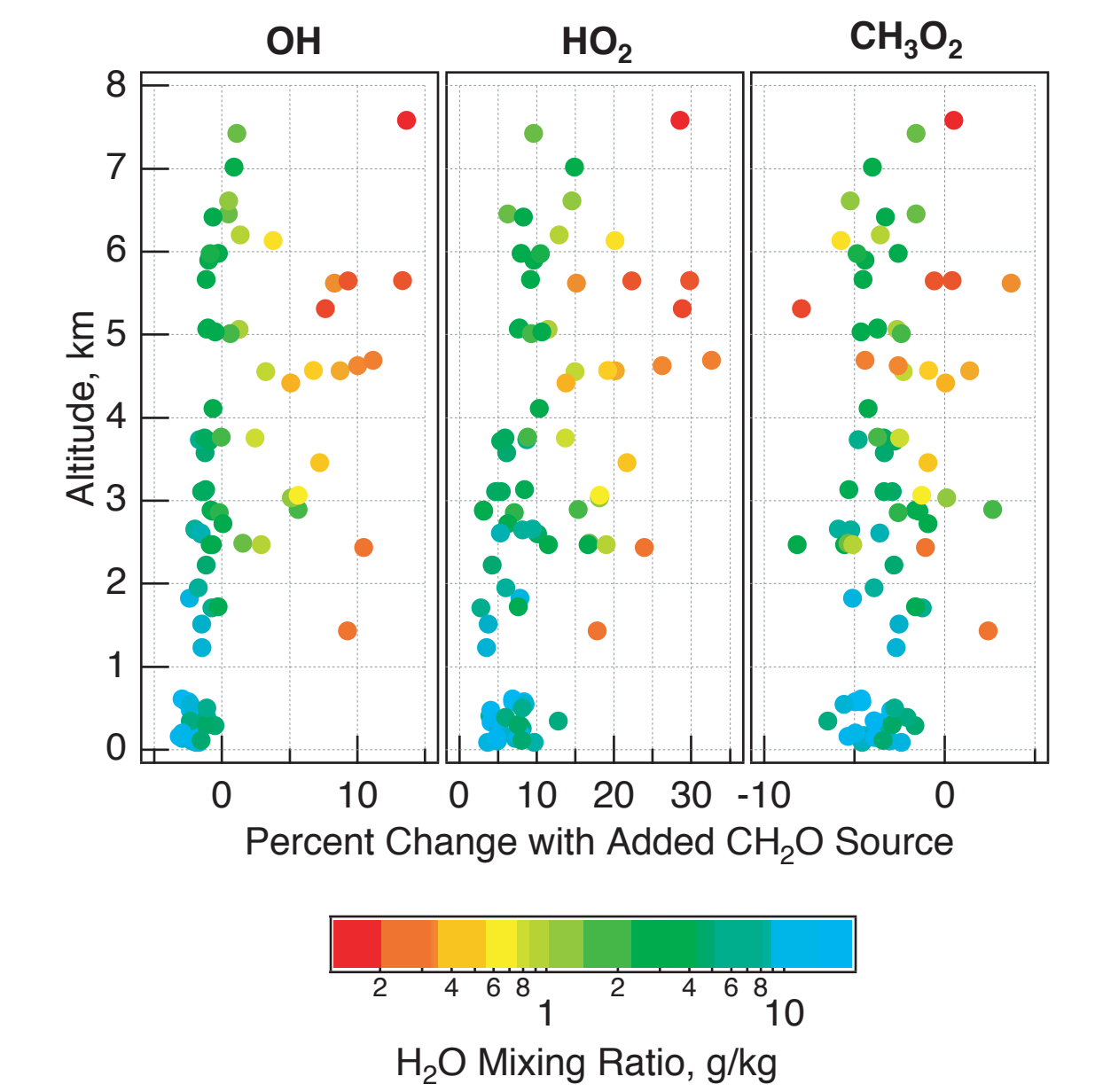
Distribution of absolute differences between measured and modeled [CH₂O] for the full data set of 86 points. The solid black vertical lines are the median differences and the horizontal bars indicate 2 standard deviations.



Median CH₂O mixing ratios for the full data set of 86 points are shown for the two measurements, the base model, and a number of model sensitivity tests. In each test, the indicated parameter was adjusted by the given amount and the model was rerun for all points. These adjustments represent the estimated 1σ uncertainty range for the parameter and were made in the direction which would increase the modeled [CH₂O].

Possible Reasons for Measurement-Model Discrepancies

- Instrument problems:
 - Independent instruments, same trend
 - Similar discrepancies seen at Cape Grim and in SONEX
- Steady state assumption invalid:
 - CH₂O < 1 day
 - Clean air only, no recent emissions
 - No recent vertical transport in most air masses
- Model sinks:
 - Model and measured OH agree in other remote areas
 - Model CH₂O not very sensitive to j values
- Model sources:
 - Need 0.4 ppbv/day extra CH₂O source
 - Fairly constant from 0 - 8 km
 - HO₂ + CH₂O → CH₂O + H₂O + O₂?
 - up to 40% yield at low T and P
 - unlikely for T and P of this data set
 - CH₂OH reaction on aerosols?
 - no aerosol measurements on WP-3
 - constant with altitude?
 - Unmeasured long lived NMHCs or oxygenates?
 - need additional source equivalent to 0.7 - 2 ppmv CH₄ or 5 - 10 ppbv CH₃OH



Effect of adding a 0.4 ppbv day⁻¹ source of CH₂O on the levels of OH, HO₂, and CH₂O as a function of altitude and H₂O mixing ratio, compared with the base model run.

Conclusions

- Steady state point model calculations of CH₂O compared with 2 independent aircraft measurements in 86 air masses from NARE 97.
- Model-measurement discrepancies within uncertainties.
- Measured CH₂O systematically larger than model; median measured/model ratio = 2.
- Model uncertainties could be reduced by
 - more laboratory studies:
 - HO₂ + CH₂O rate and products
 - CH₂O photolysis quantum yields
 - k(OH + CO)
 - k(OH + CH₂OOH)
 - additional aircraft measurements:
 - OH
 - HO₂
 - other VOCs besides C2-C6 hydrocarbons (oxygenates)
- More CH₂O measurements with better precision needed in non-polluted environments.
- Additional sources of CH₂O besides CH₄ oxidation appear to be present in non-polluted troposphere.