Stomatal regulation of oxygenated VOC emissions at the eco-system scale

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Motivation

- Bi-directional exchange of many oxygenated VOCs including CH_3OH & CH_3CHO has recently been observed above a number of ecosystems
- CH_3OH & CH_3CHO are ubiquitous in the atmosphere and chemically active contributing to O_3 and PAN formation
- Their foliage emissions are known to be subject to stomatal control

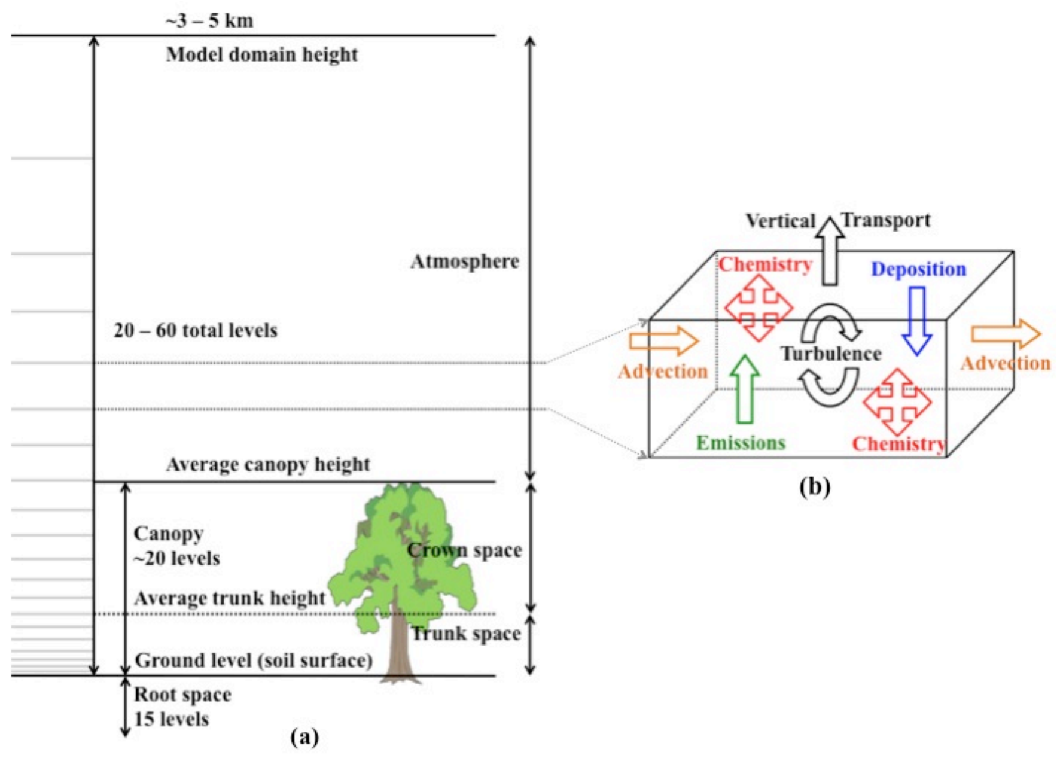
Science Qs

- Can a model of canopy-atmosphere exchange processes reproduce observed bi-directional fluxes of CH_3OH & CH_3CHO?
- Is leaf-level stomatal control of fluxes observable at the canopy scale?
- Can regional models represent canopy processes and adequately capture bi-directional fluxes?

FORCAsT

(FORest Canopy-Atmosphere Transfer)

- single column model
- 40 vertical layers; 18 representing canopy
- incorporates CACM chemistry mechanism
- biogenic emissions calculated on-line
- dry deposition based on resistance model
- in-canopy vertical exchange modified to account for turbulence within canopy



(a) A schematic of the FORCAsT column model. Each level within the column is a box model (b) incorporating all of the processes involved in canopy-atmosphere exchange of energy and mass relevant at that level.

Observations

- Harvard Forest summer 2012
- mixed deciduous woodland; N mid-latitudes
- ave. canopy height 23m; measurements 29m
- long-term AmeriFlux measurements of meteorology, trace gases, energy fluxes and ecosystem functioning
- plus PTR-TOF-MS measurements of concentrations of oxygenated VOCs
- fluxes calculated by eddy covariance

Correlations

Canopy-top measurements show that:

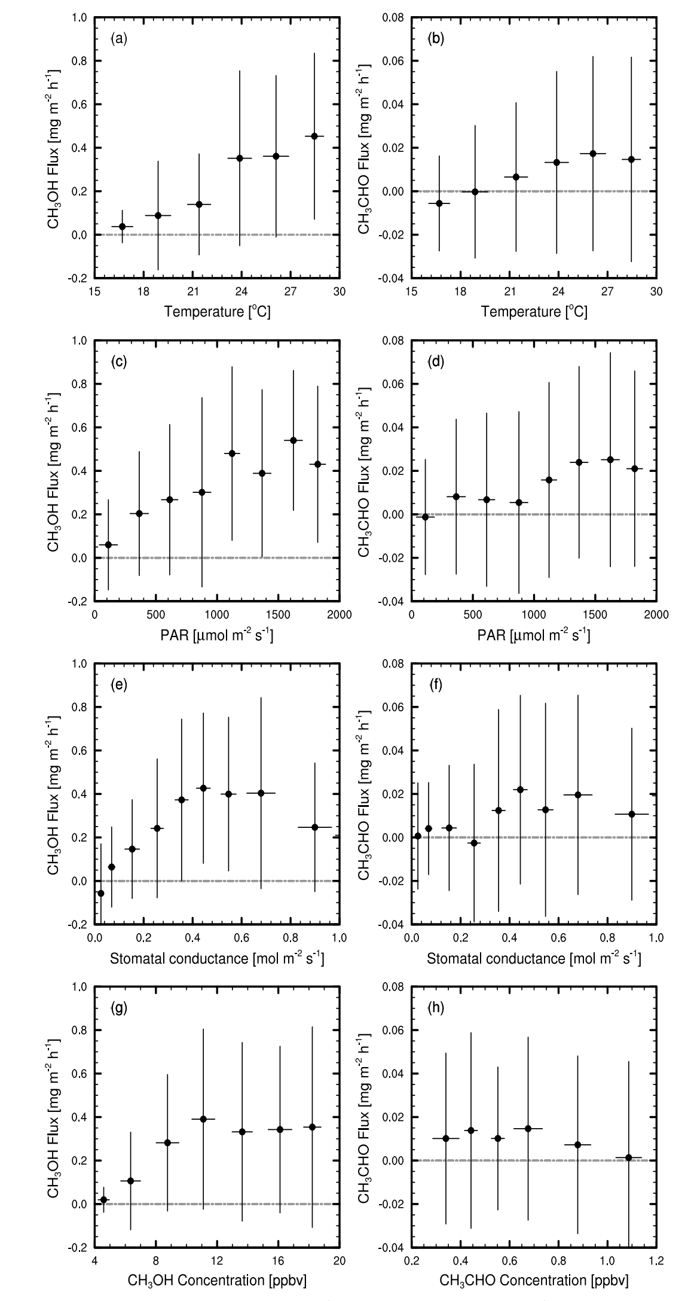
CH_3OH fluxes are positively correlated with

- Air temperature & PAR
- Canopy stomatal conductance & atmospheric concentrations (up to a "threshold" value)

CH_3CHO fluxes are weakly correlated with

- Air temperature (& PAR ?)
- Atmospheric concentrations (negatively)

Note: CH_3CHO has more chemical sources and sinks at canopy-relevant timescales



Observed binned daytime (05:00-19:00 EST) fluxes of CH_3OH (left) vs. (a) air temperature, (c) PAR, (e) canopy stomatal conductance, and (g) CH_3OH concentration (measured at 29 m). Right column (panels b, d, f, h) shows same for CH_3CHO. Circles indicate average values; vertical and horizontal bars ±1s.d.

Simulations

Baseline:

- 2-day simulation; first day discarded as spin-up
- Met conditions for average day in July 2012
- Biogenic emissions of isoprene, α- & β-pinene & *d*-limonene included; emission rates based on those from similar ecosystems
- CH_3OH treated as an individual species in chemistry & dry deposition schemes
- CH_3CHO lumped with short-chain aldehydes

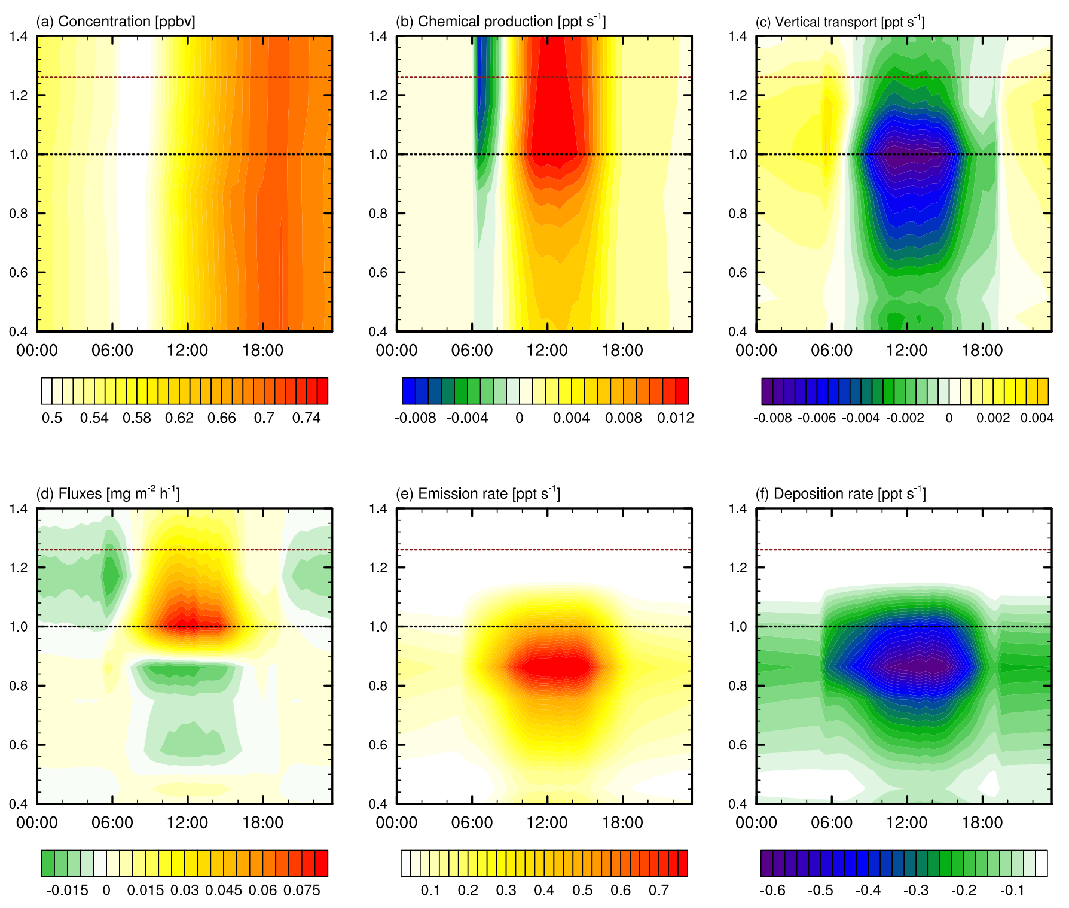
Perturbations from baseline shown in table below:

Simulation	**Changes from baseline**
Emissions (E) of CH_3OH and CH_3CHO included:	
E-direct	100% direct emissions
E-storage	100% storage emissions
E-combo	80% direct; 20% storage
E-combo90	90% direct; 10% storage
Stomatal control (S) of storage emissions included:	
S-storage	Activity factor, γ_T, scaled by stomatal control factor, R_{fct} (*n*=3)
S-combo	As S-storage but 80% direct, 20% storage
Modified stomatal control of storage emissions (R):	
R-storage	Modified R_{fct} (<1.0) used
R-storageN6	Modified R_{fct} (<1.0); *n* =6
R-combo	As R-storage but 80% direct, 20% storage
R-comboN6	As R-combo but *n*=6

- emissions modelled with "traditional" algorithms (based on Guenther et al., 1995; 2012)
- "direct" refers to light- & temperature- dependent emissions (released directly on synthesis);
- "storage" refers to temperature-dependent only emissions (released from storage pools)

Key processes

FORCAsT prognostically calculates the potential sources & sinks of CH_3OH & CH_3CHO in and above the canopy at all model timesteps



CH_3CHO production and loss within the canopy space: (a) concentration, (b) chemical production rate (including photolysis), (c) changes in concentration due to vertical mixing, (d) flux, (e) emission rates, and (f) deposition rates for E-combo simulation. Rates are instantaneous in time and space. Vertical axis shows height relative to canopy top height; times on the horizontal axis are EST. Dashed horizontal lines denote canopy top (black) and observation height (red).

- In-canopy production & loss of CH_3OH & CH_3CHO dominated by foliage emissions and dry deposition
- CH_3CHO has a greater number of chemical sources & sinks but they only make a minor contribution
- The top of the canopy is a region of abrupt transition
- The level at which measurements are made and the model evaluated is critical

Stomatal control

Stomatal aperture has been observed to control leaf-level emissions of CH_3OH & CH_3CHO.

We introduce stomatal control by applying a scaling factor, R_{fct}, to "storage" emissions

- standard activity factor: $\gamma_T = e^{-\beta(TL-TS)}$

where TL is leaf T, TS standard T, β is T-response

"S-" and "R-" simulations:

- $\gamma_T = e^{-\beta(TL-TS)}.R_{fct}$

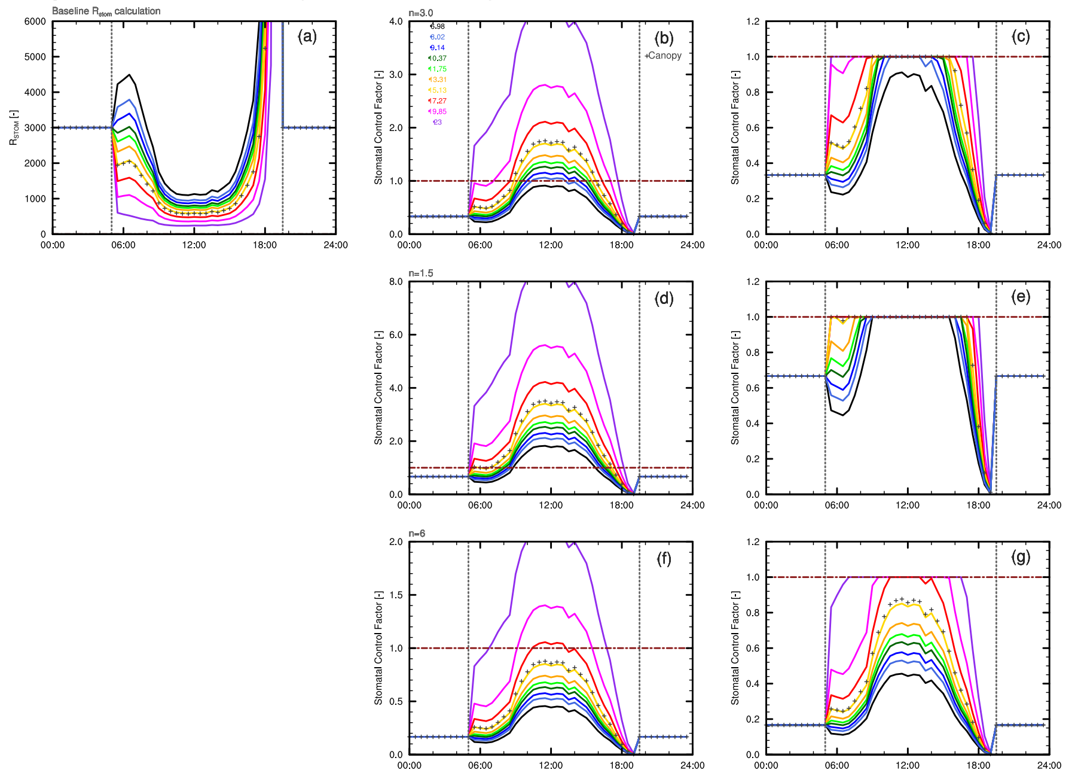
where *R*fct for "S-" simulations is:

- $R_{fct} = \frac{3000.0}{R_{stom}.n}$

where R_{stom} is stomatal resistance, 3000.0 is the default night-time value of R_{stom} and *n*=3 initially and *R*fct for "R-" simulations is:

- max of R_{fct} (as above) or 1.0

"S-" simulations assume stomatal control during transition periods leads to accumulation in storage pools enhancing daytime emissions; "R-" simulations assume traditional emissions algorithms capture daytime emissions well



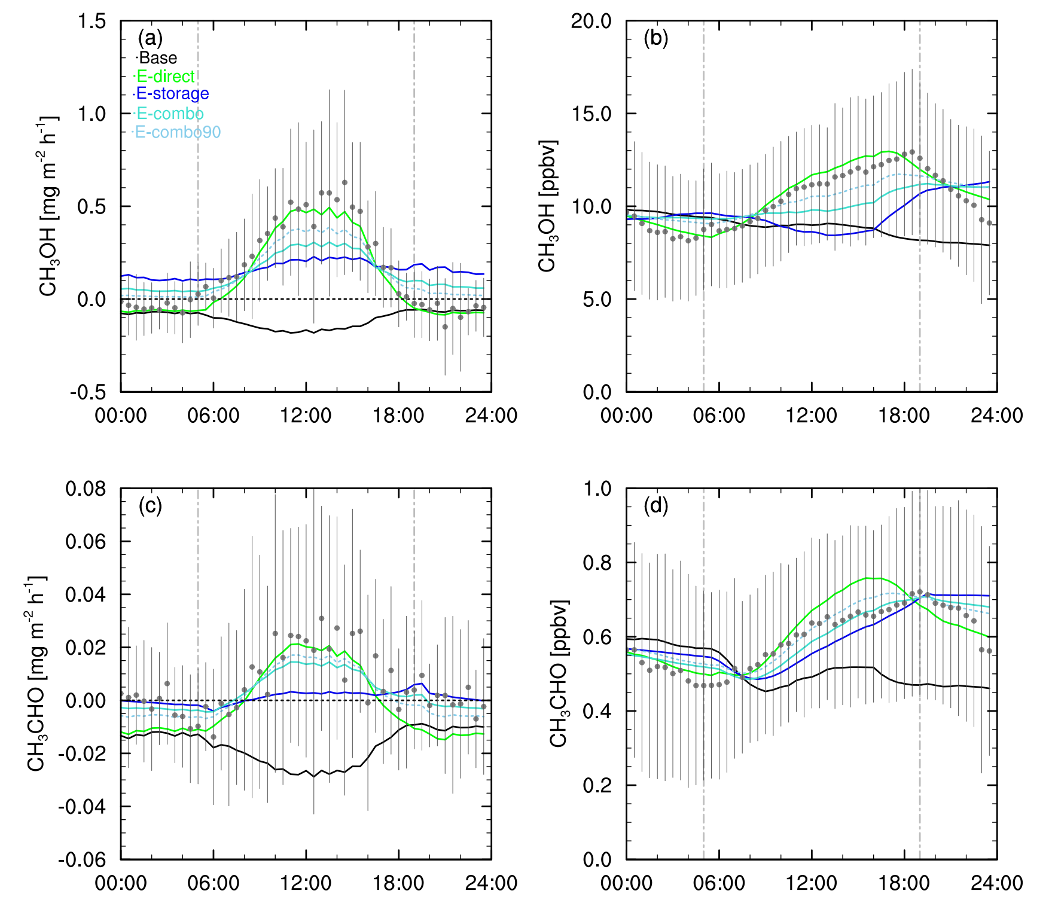
Stomatal control applied to storage emissions. Top row shows baseline(a) stomatal resistance, (b) stomatal control factor, and (c) the modified stomatal control factor (limiting value of 1.0). Coloured lines show resistances and control factors as leaf area-weighted average for each crown space level across all leaf angle classes. Crosses show the canopy average weighted by foliage fraction. Bottom two rows show the effect on R_{fct} of altering the scaling factor, n.

Results

Baseline case => (a) need to include foliage emissions of both CH_3OH & CH_3CHO
(b) at least a proportion of the emissions are light-dependent

In all figures, measured (grey circles show mean; vertical bars ±1s.d.) and modelled (lines) fluxes (left; mg m^{-2} h^{-1}) and concentrations (right; ppbv) at 29 m for an average day in July 2012 for (a), (b) CH_3OH; (c), (d) CH_3CHO for baseline (black) and perturbation (coloured) model simulations. Dashed grey vertical lines show dawn and dusk. Times are Eastern Standard Time (EST).

"E-" simulations



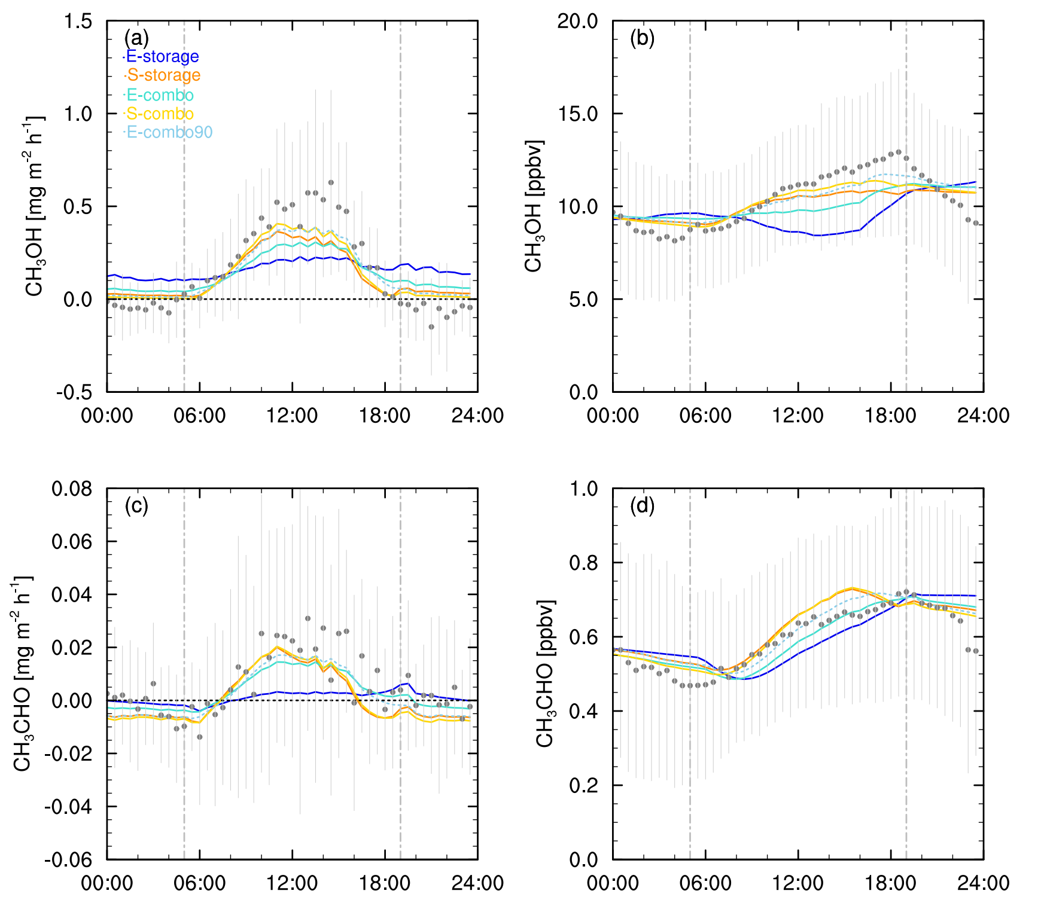
CH_3OH:

- 100% "storage" emissions fail to capture diurnal profile of concentrations
- 100% "direct" emissions give the best fit to night-time fluxes & concentrations

CH_3CHO:

- 100% "direct" emissions underestimate night-time fluxes & overestimate daytime concentrations
- 80% "direct" & 20% "storage" emissions give the best fit to fluxes & concentrations

"S-" simulations



Introducing stomatal control increases daytime and decreases night-time fluxes. Daytime concentrations are increased but there is little change at night.

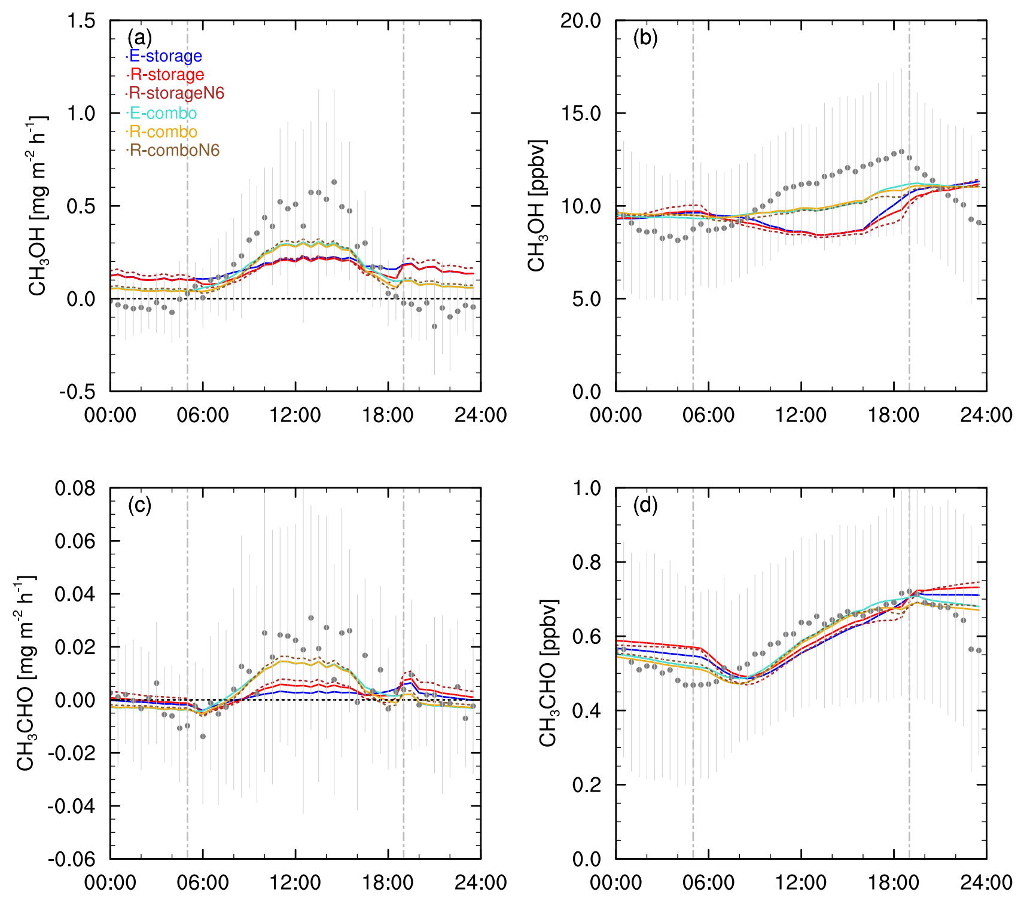
CH_3OH:

- Modelled night-time fluxes are closer to obs
- E-direct is still the best fit overall

CH_3CHO:

- Modelled night-time fluxes are now too low
- E-combo is still the best fit overall

"R-" simulations



Applying modified stomatal control limits the changes to periods of light-dark transition. Fluxes & concentrations are reduced around these times (i.e. dawn and dusk).

CH_3OH:

- Daytime fluxes too high & concentrations too low; night-time fluxes too high
- E-direct is still the best fit overall

CH_3CHO:

- Changes are small
- E-combo is still the best fit overall

Conclusions

- Canopy models can reproduce bi-directional exchange
- "Traditional" emissions models capture canopy-top fluxes & concentrations adequately without incorporating stomatal control
- Foliage emissions & dry deposition dominate CH_3OH & CH_3CHO production & loss and must be treated holistically in regional models

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Acknowledgements

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