

Improved Estimation of Vegetation Uptake of Carbonyl Sulfide (COS) in a Biosphere Model (SiB4)

Ara Cho, Linda Kooijmans, and Maarten Krol

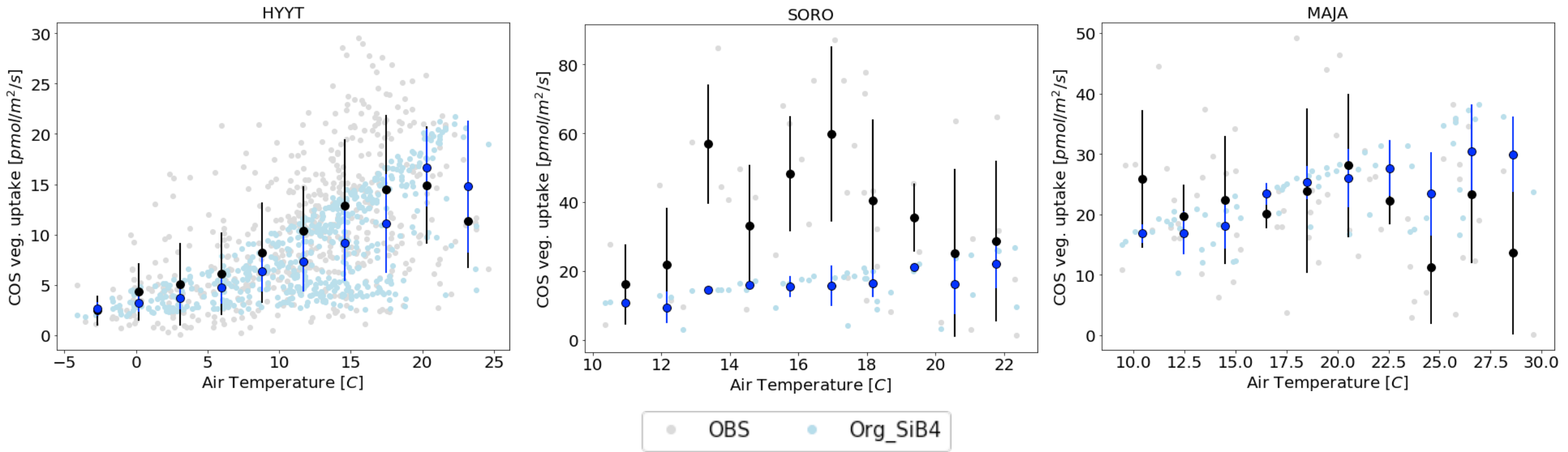
Wageningen University

Why COS?

- Carbonyl Sulphide (COS) is a chemical compound in the atmosphere, and it is predominantly produced in the ocean surface and consumed by plants accompanying photosynthesis
- COS can be a proxy for Gross Primary Production (GPP) because it has a similar pathway into leaves as CO₂, without respiration.
However, the unknown budget of COS is about 36%, that means biosphere uptake is also uncertain (Ma et al. 2020).
- This study aims to better understand COS leaf assimilation and apply it into the Simple Biosphere model (SiB4) to derive more accurate COS biosphere flux.

Limitation of modeled COS vegetation flux

Comparison observed and modeled COS vegetation flux



- The capacity of estimating COS flux in SiB4 differs between stations.
- Especially, it cannot capture the decreasing COS uptake in the range of high temperature
- It is necessary to improve the simulating COS flux in the SiB4 model

Strategy

- SiB4 simulates the COS vegetation flux (COS Assim) as a series of conductances (g_s : stomata, g_b : air boundary, g_{CA} : enzyme activity)

$$COS\ Assim = M_{COS} \left(\frac{1.94}{g_s} + \frac{1.56}{g_b} + \frac{1.0}{g_{CA}} \right)^{-1}$$

- COS assimilation increases with atmospheric COS mole fraction (M_{COS}), and we use optimized M_{COS} from TM5 4D-VAR
- g_s and g_b are used for GPP estimation as well, and it is assumed to be accurate
- g_{CA} impact is more significant than g_s and g_b in COS assimilation,

Problem: g_{CA} is estimated by $1400 \times$ Rubisco's carboxylate rate with Rubisco's temperature function

Remedy : Explore Carbonic Anhydrase's properties and apply its kinetics to g_{CA}

Observations

- Five fluxnet stations are used

- Evergreen Needleleaf :
Hyytiälä (Finland) ⁽¹⁾
- Deciduous Broadleaf :
Harvard Forest (US) ⁽²⁾,
Soro (Denmark) ⁽³⁾
- C3 grass :
Neustift (Austria) ⁽³⁾
Las Majadas (Spain) ⁽³⁾



(1) Kooijmans et al. 2017; Sun et al. 2018,

(2) Commane et al. 2015; Wehr et al. 2017, (3) Spielmann et al. 2019

google map

- To remove errors in data,

- only use 1.5 STD of diurnal variation

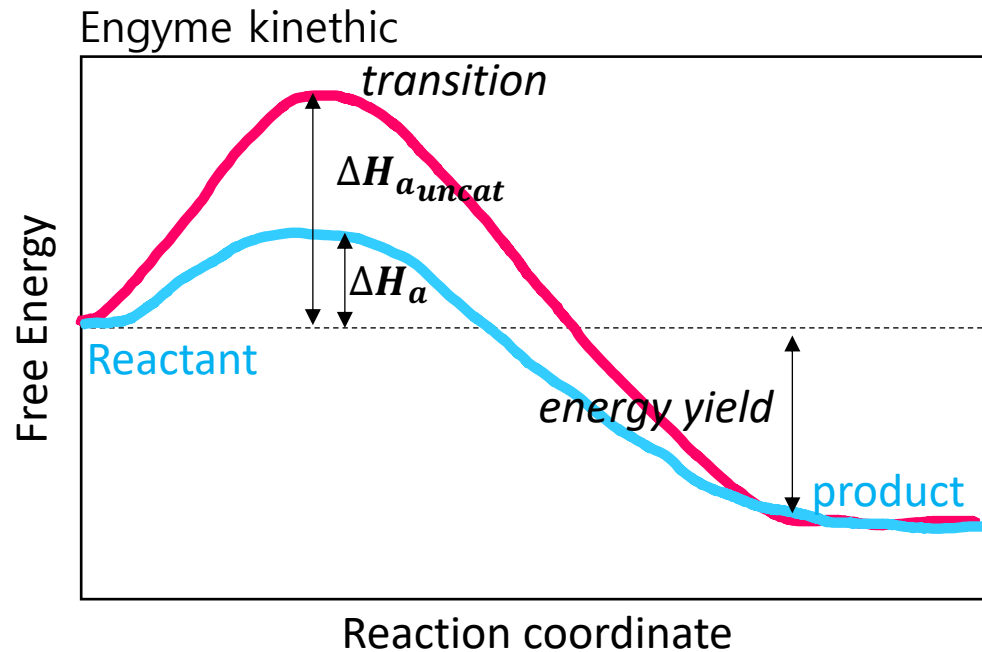
$$COS\ Assim = M_{cos} \left(\frac{1.94}{g_s} + \frac{1.56}{g_b} + \frac{1.0}{g_{CA}} \right)^{-1} \quad \longrightarrow \quad g_{CA} = \frac{1}{\frac{M_{cos}}{COS\ Assim} - \frac{1.94}{g_s} - \frac{1.56}{g_b}}$$

Observed data
Modeled data are used

Equilibrium model

- We adopt the Equilibrium model⁽¹⁾ to find CA's thermal behaviour
- Key factors : k_{cat} , ΔH_a , ΔH_{eq} , T_{eq}

(1) Peterson et al. 2004; Daniel et al. 2010; Sun et al. 2015; Ogee et al. 2016



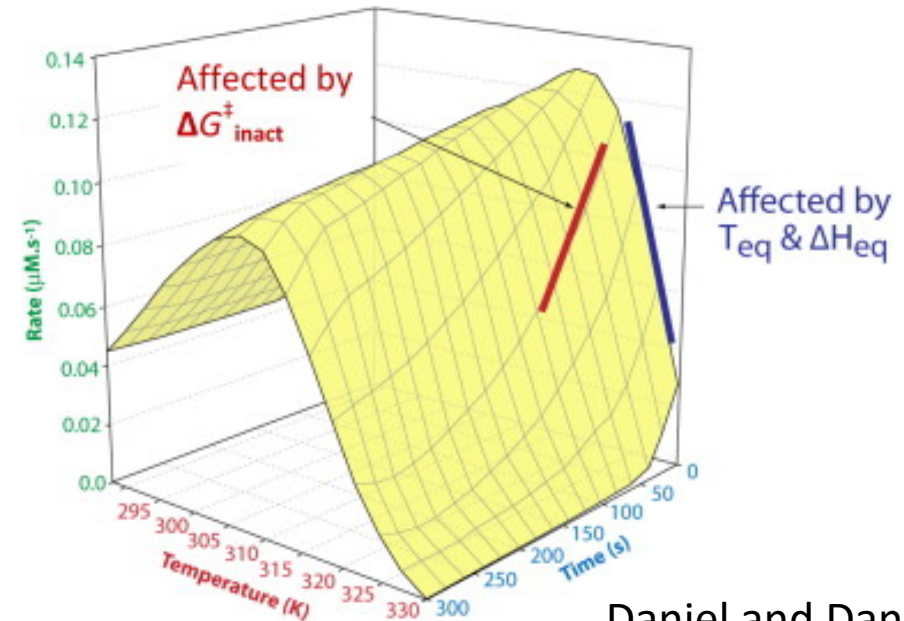
$$g_{CA} = k_{cat} * \frac{1}{f(T_{eq})} * \frac{T \exp\left(-\frac{\Delta H_a}{RT}\right)}{1 + \exp\left[-\frac{\Delta H_{eq}}{R} \left(\frac{1}{T} - \frac{1}{T_{eq}}\right)\right]}$$

k_{cat} : enzyme catalytic rate constant

ΔH_a : activation energy of the catalysed reaction

ΔH_{eq} : enthalpy change

T_{eq} : temperature mid-point of equilibrium



Daniel and Danson, 2013

Hypothesis for optimization

1. Key factors are related to Carbonic Anhydrase's activity

- ➔ Basically, all state vectors are not changed for short-time (target ➔ stationary-base)
- ➔ ΔH_a is the innate property of CA ➔ Same to all locations

2. ΔH_{eq} has the function of catalytic temperature tolerance (sensitivity to temperature)

- ➔ ΔH_{eq} increases proportionally to the variation of temperature at each site.
- ➔ Larger variation = Smaller ΔH_{eq} , Smaller variation = larger ΔH_{eq}

3. T_{eq} related to growth temperature

- ➔ Hypothesis: T_{eq} is larger in the warm habitat, and it is smaller in the cool habitat

Optimization of enzyme kinetic variables

- Set the cost function:

$$J(x)_i = (H(x) - y)^T R^{-1} (H(x) - y) \quad (i = 1 \sim 5) \text{ Hyyt, Hvfm, Soro, Neus, Maja}$$

$$x = k_{\text{cat}}, \Delta H_a, \Delta H_{eq}, T_{eq}$$

* Observation error does not correlated each other.

$$\varepsilon_i^{\text{obs}} = \sigma_{i=1 \sim 5} \text{ of observed gCA}$$

STD unit: mol/m²/s

	HYYT	HVFM	SORO	NEUS	MAJA
Error (STD)	0.078	0.174	0.250	0.092	0.081
The number of Datapoints	449	135	28	61	56

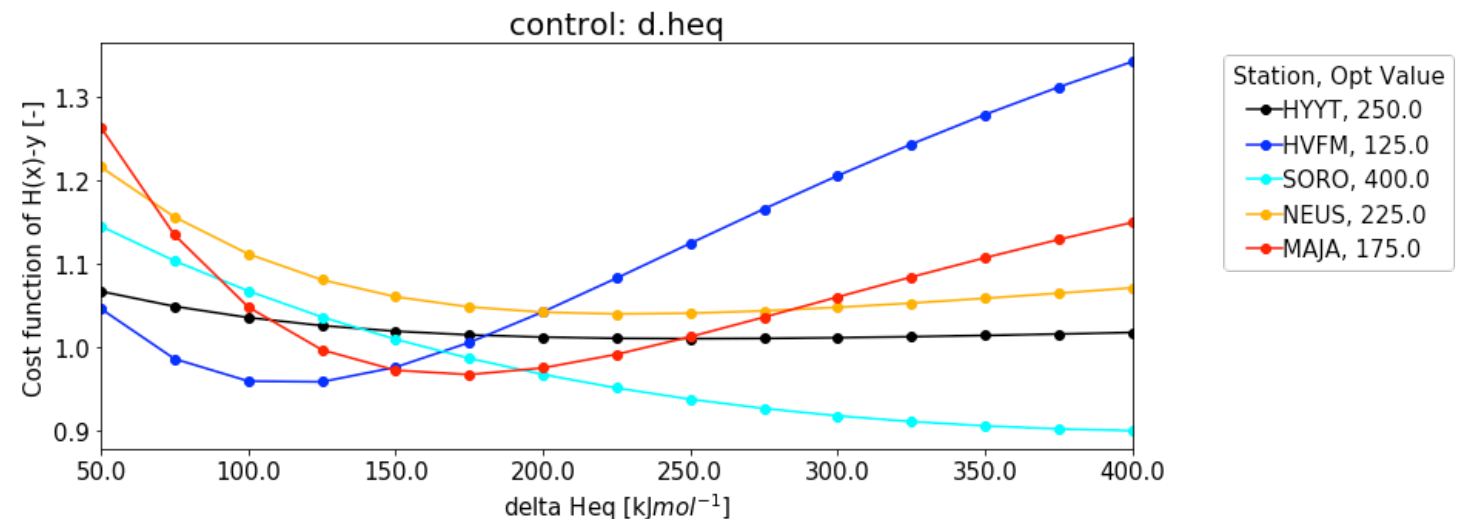
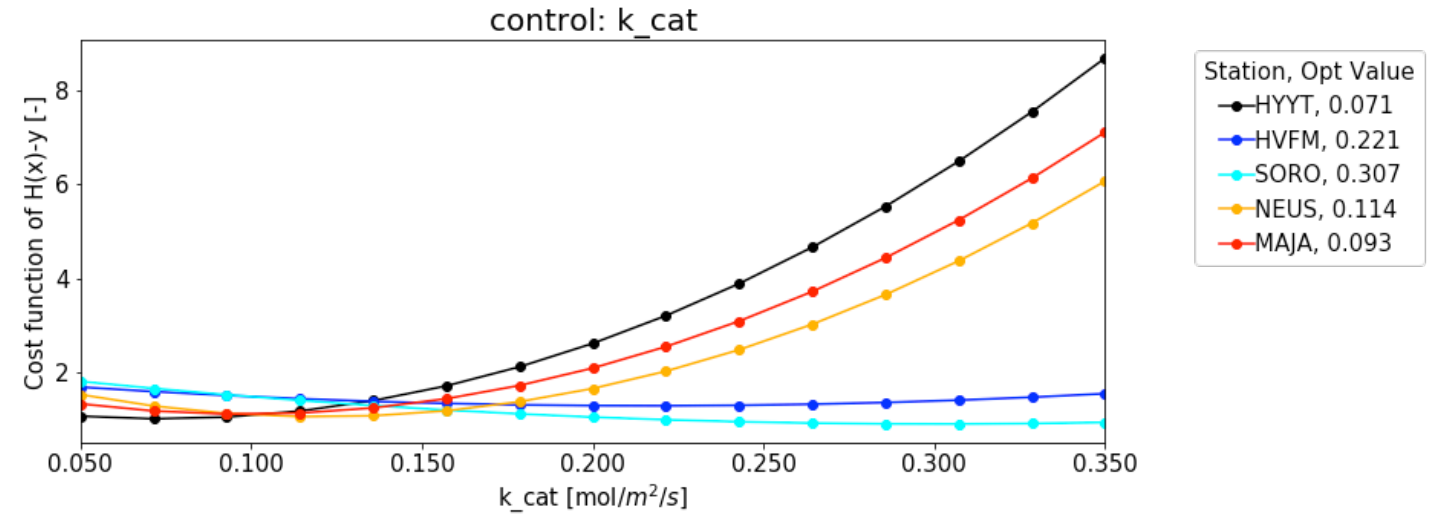
Results

First state vector : k_{cat}
enzyme catalytic rate constant

Second state vector : ΔH_{eq}
enthalpy change

Condition: ΔH_{eq} should have a direction
 as following 2nd hypothesis

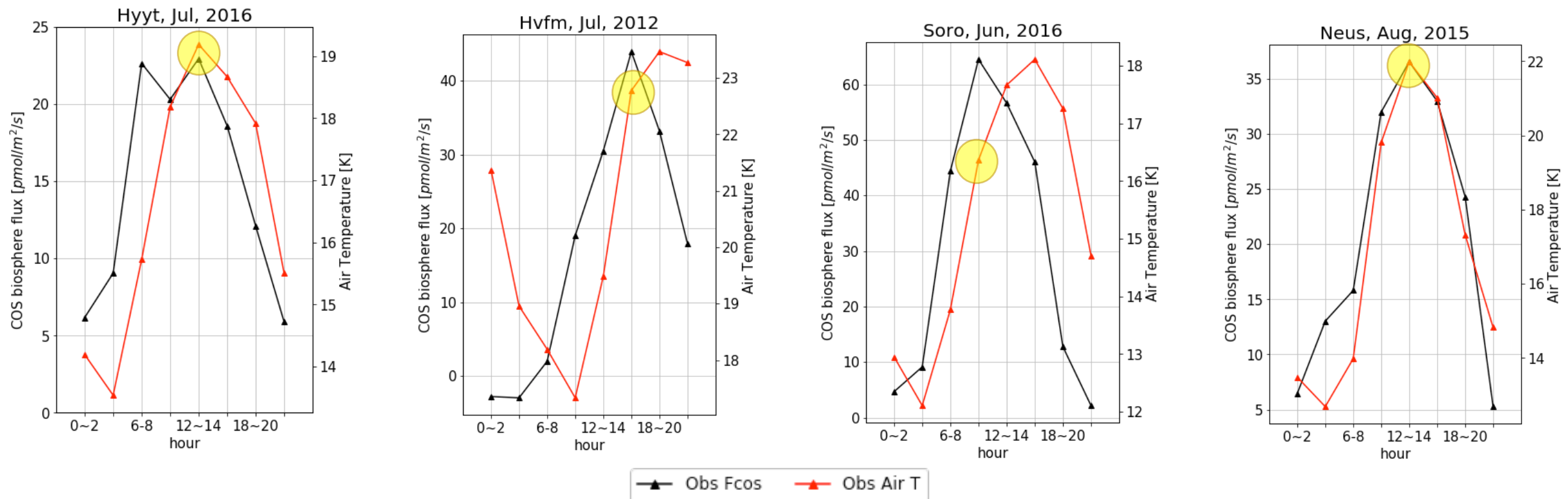
	HYYT	HVFM	SORO	NEUS	MAJA
STD of mod T (°C)	7.59	7.47	3.47	4.85	5.68
Est d.Heq	small	small	large	medium	medium



Results

Third state vector : ΔH_a and T_{eq}
activation energy of the catalysed reaction *temperature mid-point of equilibrium*

- Condition 1. The optimum temperature should be larger than the temperature at the highest COS uptake shown (19C, 23C, 16C, 22C @ Hyyt, Hvfm, Soro, Neus)

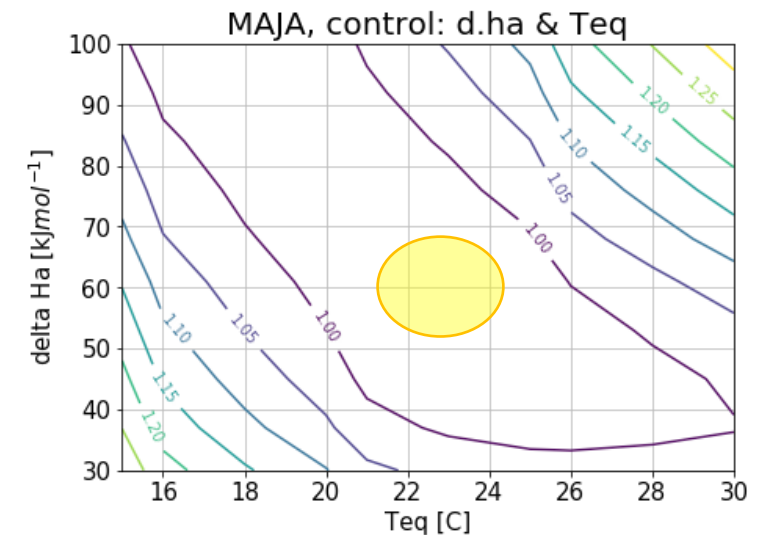
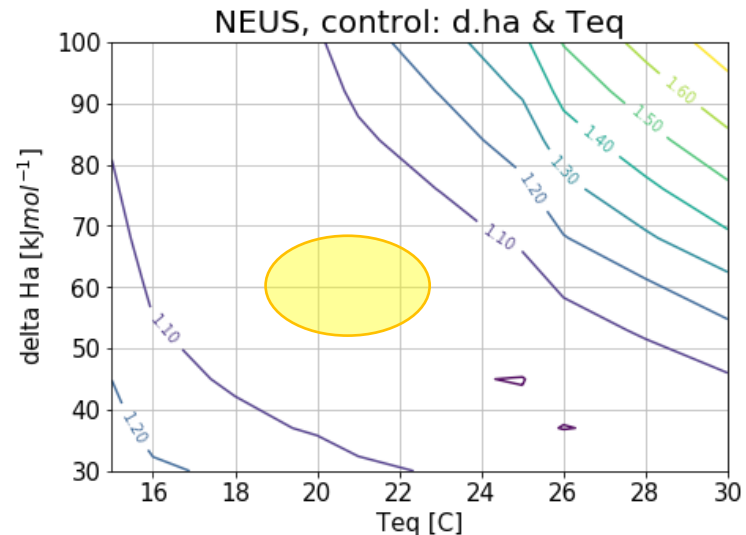
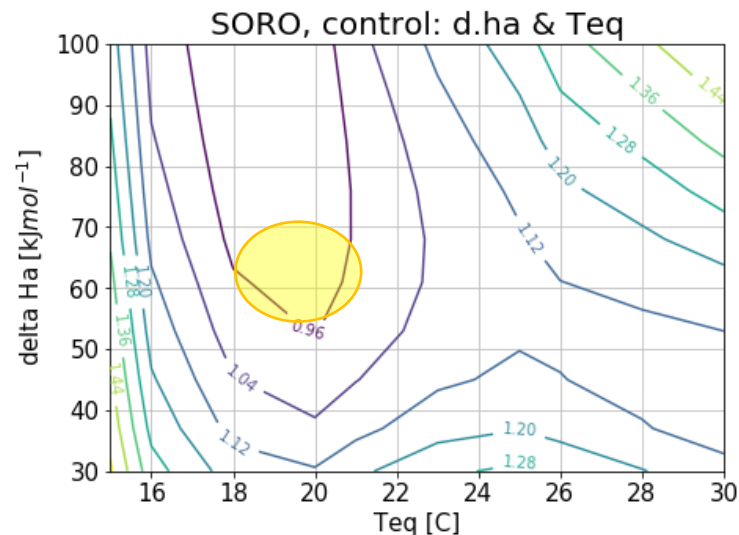
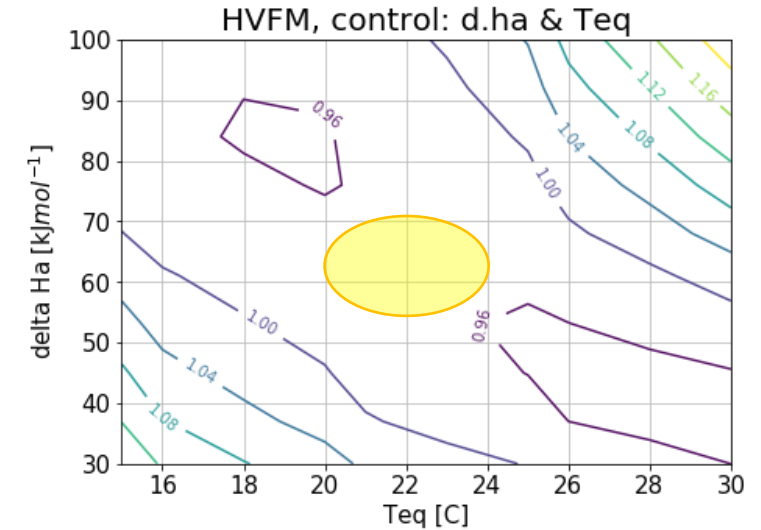
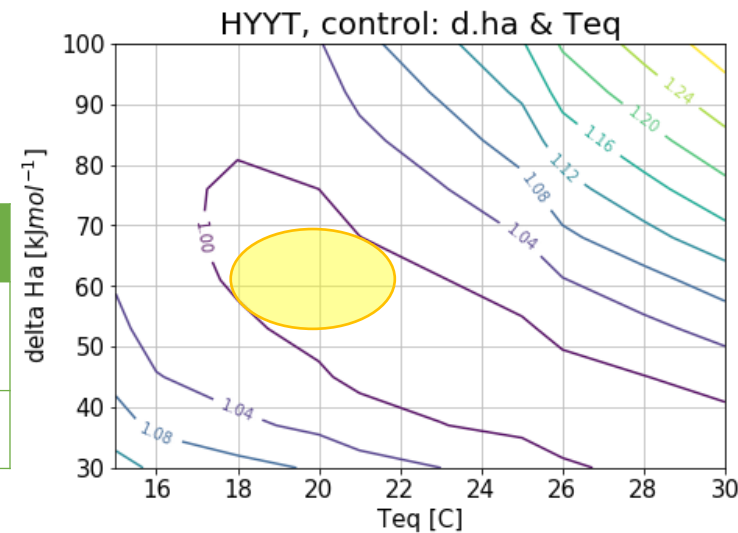


Results

Condition 2. Optimum temperature should have a direction as following 3rd hypothesis :

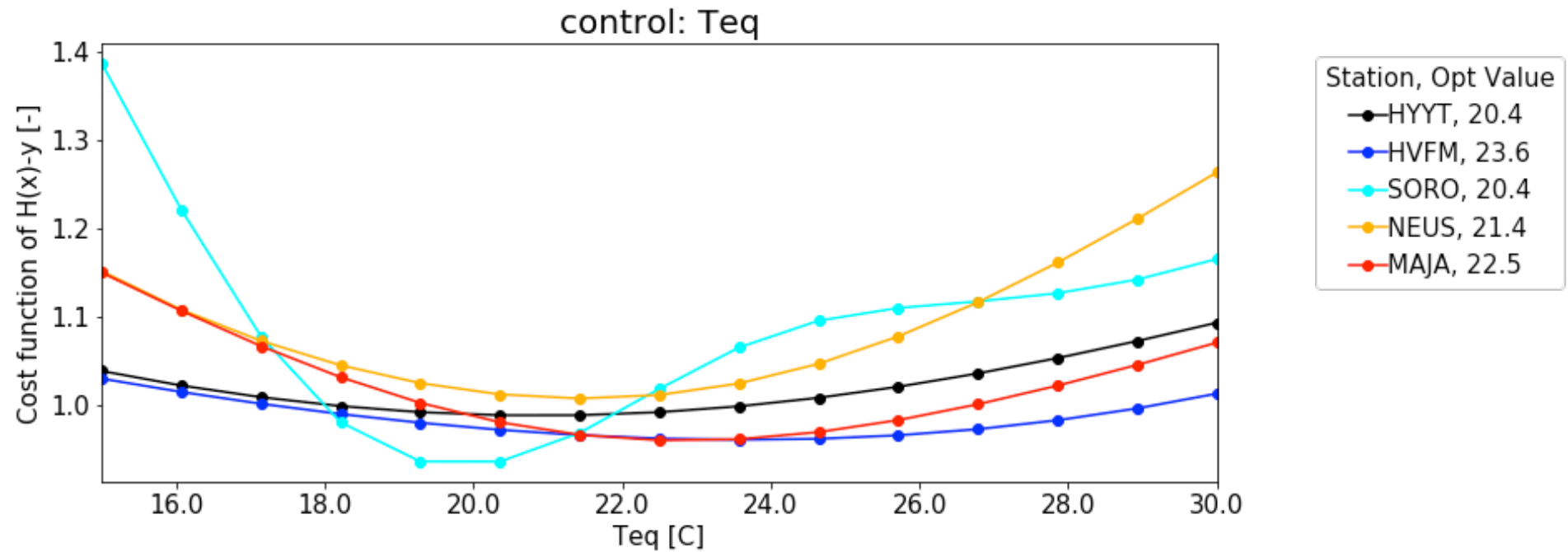
	HYYT	HVFM	SORO	NEUS	MAJA
Mean of T(°C)	12.08	20.77	18.22	16.75	19.48
Teq	small	large	medium	medium	large

The criteria where satisfy two condition: : $\Delta H_a = 60 \text{ kJ mol}^{-1}$



Results

Third state vector : ΔH_a and T_{eq}
activation energy of the catalysed reaction *temperature mid-point of equilibrium*



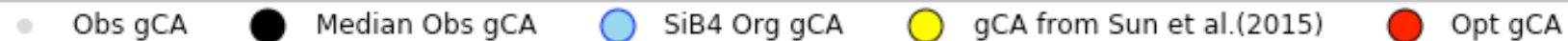
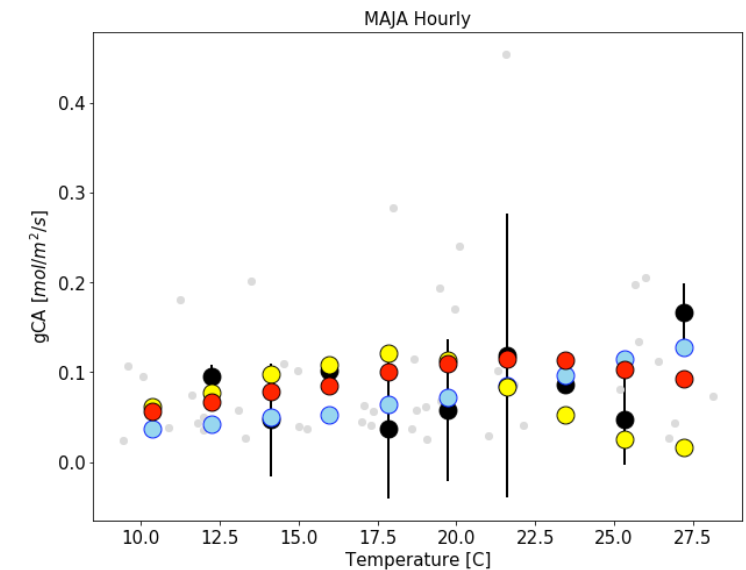
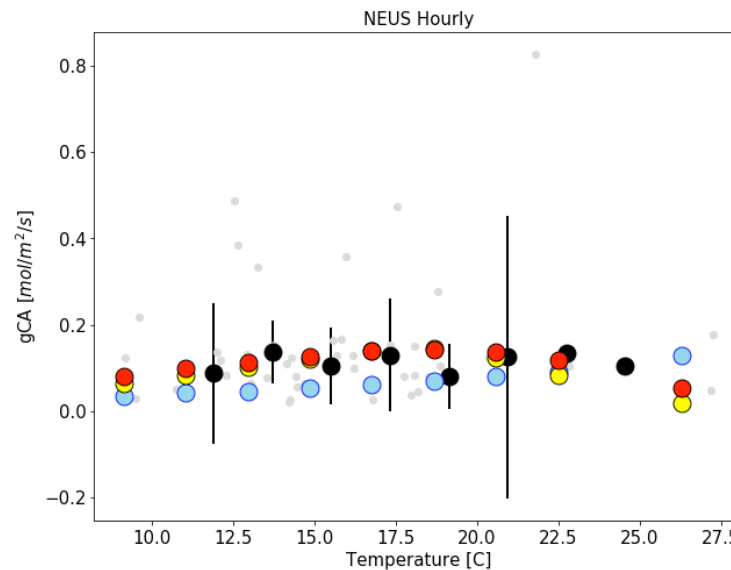
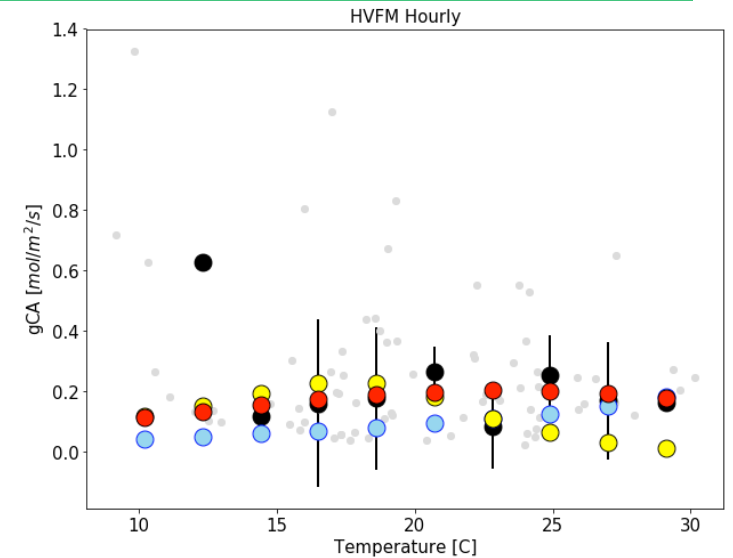
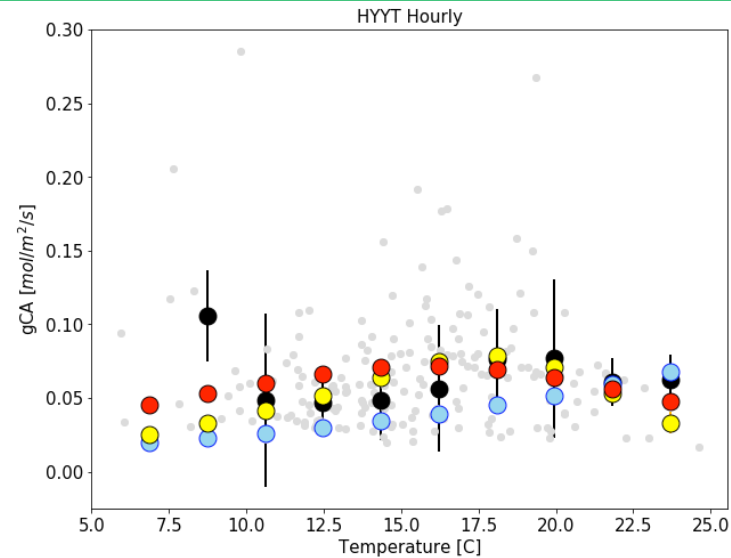
Results

- k_{cat} is classified to the plant functional type (PFT)
 - **ENF**= 0.07 (cool), **DBF**= 0.22 (warm), 0.31 (cool), **C3G**= 0.11 (cool), 0.09 (warm)
- ΔH_{eq} and T_{eq} are explained by the function of STD and average of yearly temperature

	HYYT	HVFM	SORO	NEUS	MAJA
PFT	ENF	DBF	DBF	C3G	C3G
Mean of T (°C)	12.08	20.77	18.22	16.75	19.48
STD of T (°C)	7.59	7.47	3.47	4.85	5.68
k_{cat} (mol/m ² /s)	0.071	0.221	0.307	0.114	0.093
ΔH_a (kJ mol ⁻¹)	60	60	60	60	60
ΔH_{eq} (kJ mol ⁻¹)	250	125	400	225	175
T_{eq} (°C)	20.4	23.6	20.4	21.4	22.5

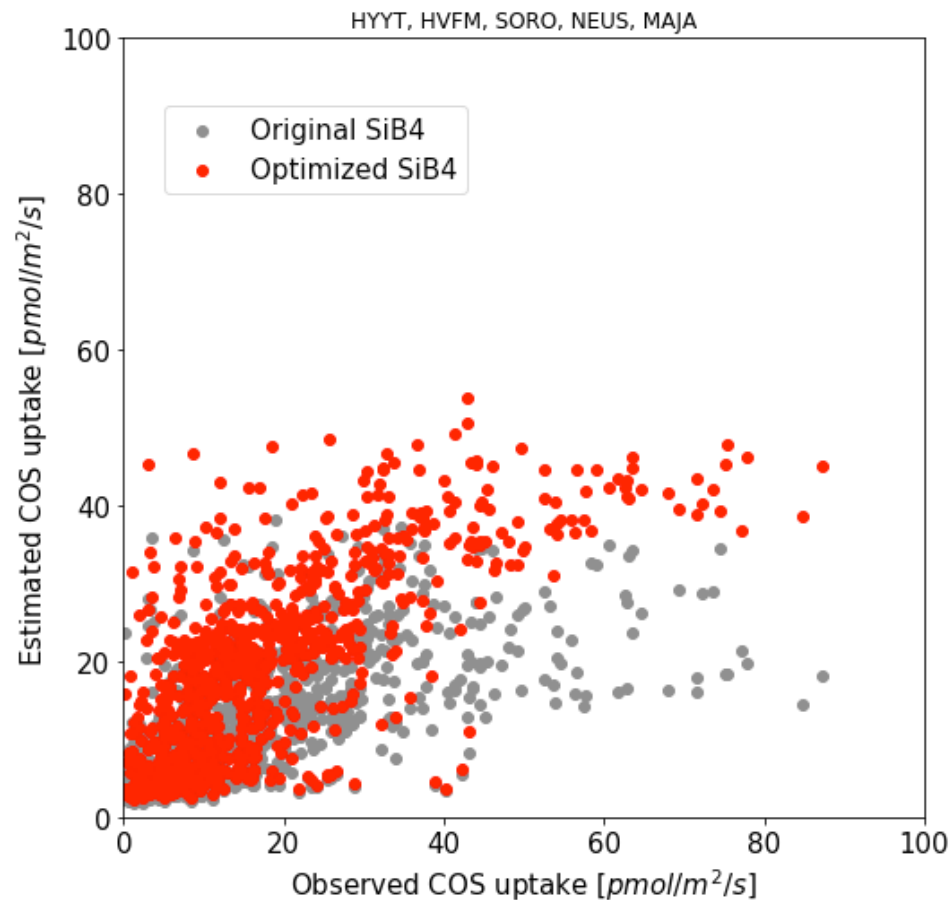
Results

- **Optimized gCA** explains observed gCA better than previous methods (Original SiB4 (1400*Rubisco activity), Equilibrium model in the soil model by Sun et al.2015)



Results

- Optimized g_{CA} shows better results in RMSE and MBE!
- In particular, the underestimate tendency is improved for large COS uptake!



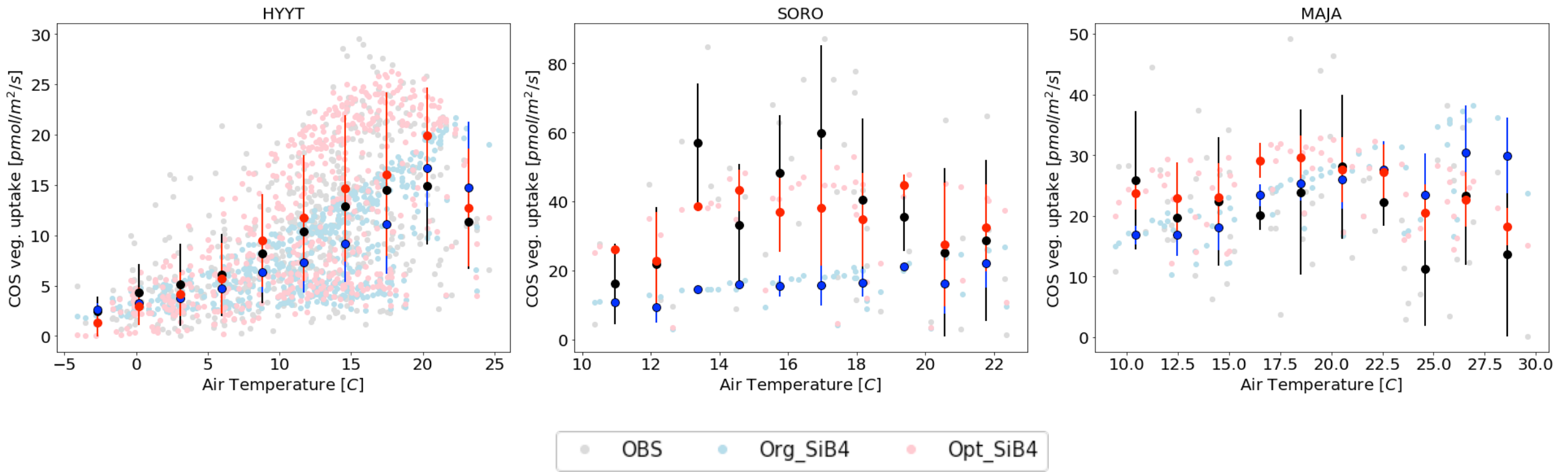
[unit: $\text{pmol/m}^2/\text{s}$]

	RMSE	MBE
Original SiB4	12.54	4.98
Optimized SiB4	10.11	-1.13

-
- Figure 10 displays five line plots showing the COS biosphere flux (pmol/m²/s) versus hour for five stations: HYYT, HVFM, SORO, NEUS, and MAJA. The plots compare observed data (Obs, black dotted line with triangles), a priori estimates (a priori, blue solid line with triangles), and a posteriori estimates (a posteriori, red solid line with triangles). The x-axis represents time in hours, and the y-axis represents the COS biosphere flux in pmol/m²/s.
- The legend indicates:
- Obs: Black dotted line with triangles
 - a priori: Blue solid line with triangles
 - a posteriori: Red solid line with triangles

Results

- Go back to the first figure..



In a nutshell

- To better understand the COS leaf assimilation, we have focused on the **internal conductivity**, which has the largest impact on COS uptake.
- The problem is that **SiB4 uses Rubisco's activity** as a linear function to CA, so that SiB4 has limitation to estimate **denaturing CA's behaviour** at the **high temperature**.
- To find CA's catalysis rate and the response to temperature, we apply the **equilibrium model** and **optimize four critical variables** for each station.
- Simulated COS uptake with optimized equilibrium model **describes observed pattern well** for most stations.
- We expect these results can be used in the **global simulation of COS biosphere flux** and look forward to seeing better **COS budgets** for the next step.